## DEVELOPMENT OF NANOCASTING SYNTHESIS ROUTES FOR THERMOELECTRIC EFFICIENCY ENHANCEMENT IN BULK NANOWIRE COMPOSITES

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### Preface

Thermoelectrics could play an important role in waste heat recovery and solid-state cooling as they possess the ability to convert heat directly to electricity and vice versa. They are used in various applications, such as radioisotope thermoelectric generators for space missions, waste heat recovery in cars, cooling devices for sensors, electronics, optics, car seats, portable refrigerators, etc. Over the last decades, progress in nanotechnology and resonant level doping have led to the development of thermoelectric materials with an efficiency double that of the best Bi<sub>2</sub>Te<sub>3</sub> based commercial thermoelectrics. The aim of this research is to develop new synthesis routes to transfer the enhanced performances observed in nanosized thermoelectrics into a bulk material through the fabrication of bulk nanowire composites to improve the materials' heat to electricity conversion efficiency.

This work consists of the development of new synthesis methods and material designs to enhance the thermoelectric efficiency of nanocomposite thermoelectrics. More specifically,  $SrTiO_3$  and  $Bi_{1-x}Sb_x$  nanowire composite thermoelectrics were studied for their use as high temperature thermoelectric for heat to electricity energy conversion and low temperature thermoelectric for solid state cooling applications, respectively. Nanowire composites were synthesized via the nanocasting methodology, which has led to the synthesis of bulk nanowire composites, showing an enhanced thermopower as a result of size quantization. This research demonstrates the potential of this new nanostructuring approach to enhance the efficiency of thermoelectric bismuth alloys.

This doctoral research was carried out in the Sol-gel Centre for Research on Inorganic Powders and Thin films Synthesis (SCRIPTS) and the Centre for Ordered Materials, Organometallics and Catalysis (COMOC) at the Department of Inorganic and Physical Chemistry at Ghent University, and the Thermal Materials Lab at the Department of Mechanical and Aerospace Engineering at The Ohio State University.

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# Symbols and Abbreviations

$\dot{Q}_1$	heat exchanged per unit of volume per second
ħ	Planck constant
μ	Thompson heat
η	efficiency
П	Peltier heat
τ	relaxation time
κ	thermal conductivity
<i>α</i> , S	Seebeck coefficient
$\sigma \alpha^2$ or $\sigma S^2$	thermoelectric power factor
K <sub>e</sub>	electronic thermal conductivity
$arphi_{e}$	tilt angle of electron ellipsoids in Brillouin zone
E <sub>Fe</sub>	Fermi energy of electrons
8 <sub>Fh</sub>	Fermi energy of heavy holes
ε <sub>Fl</sub>	Fermi energy of light holes
Eg	Fermi energy of direct band gap
$arphi_h$	tilt angle of hole ellipsoids in Brillouin zone
κ <sub>L</sub>	lattice thermal conductivity
Lo	Lorentz number
ΔT	temperature difference
ΔV	potential difference
$\nabla_{\mathbf{x}}T$	temperature gradient along the x-axis
A	cross section area
Å	Angstrom
a, b, c	lattice constants
a.u.	arbitrary units or relative unit of measurement
a <sub>H</sub> , c <sub>H</sub>	lattice parameters for hexagonal structure
APTES	(3-aminopropyl)triethoxysilane
В	magnetic flux density (Tesla, T)

Bi <sub>1-x</sub> Sb <sub>x</sub>	bismuth antimony alloy with composition Bi <sub>1-x</sub> Sb <sub>x</sub>
Bz	magnetic flux density along the z axis
с	concentration
CA	citric acid
cm⁻¹	wavenumber
CMK-3	carbons mesostructured from Korea (type 3: replicated from SBA-15 silica)
CMK-5	carbons mesostructured from Korea (type 5: hollow rods replicated from SBA- 15 silica)
COP	coefficient of performance
CVD	Chemical Vapor Deposition
DRIFTS	Diffuse reflectance infrared fourier transform spectroscopy
DTA	Differential Thermal Analysis
е	electron charge
E	energy
EA	ethanolamine
E <sub>F</sub>	Fermi energy
$E_g$	energy gap
EtOH	ethanol
eV	electronvolt
$E_y$	electrical field along the y-axis
f(E)	Fermi distribution function
FDU	Fudan University type mesoporous silica
FT-IR	Fourier Transform Infrared
g(E)	density of states
IDA	iminoiacetic acid
IUPAC	International Union of Pure and Applied Chemistry
<i>I</i> <sub>x</sub>	electrical current along the x-axis
$J_x$	current density along the x-axis
k <sub>B</sub>	Boltzmann constant
KIT	Korea Advanced Institute of Science and Technology type mesoporous silica
L	length

$L_{z,y}$	length along z-axis at height y
<i>m</i> *	effective mass
МСМ	Mobil Crystalline Materials or Mobil Composition of Matter
MeOH	methanol
MPTES	(3-mercaptopropyl)trimethoxysilane
n	carrier density
Ν	Nernst coefficient
n,p	induces indicate n-type and p-type semiconductors respectively
<b>n</b> <sub>OPT</sub>	optimal carrier concentration
Р	Ettingshausen coefficient
PEO	poly(ethylene oxide) propylene
PPO	poly(propylene oxide) propylene
PFA	Perfluoroalkoxy alkanes are fluoropolymers, similar to PTFE or polytetrafluoroethylene
q	charge
q	rate of heat flow
R	electrical resistance ( $\Omega$ )
R <sub>H</sub>	Hall coefficient
S	entropy
${f S}_\perp$	Seebeck coefficient along the axis perpendicular to the trigonal axis of a single crystal
S//	Seebeck coefficient along the axis parallel to the trigonal axis of a single crystal
SAED	selected Area Electron Diffraction
SBA	Santa Barbara amorphous type material
λ	scattering parameter
SEM	scanning Electron Microscopy
SPS	Spark Plasma Sintering
SSE	spin Seebeck effect
STO	strontium titanate or SrTiO <sub>3</sub>
t	time
Т	temperature

T <sub>c</sub>	cold temperature
TE	thermoelectric
TEA	triethanolamine
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
T <sub>h</sub>	hot temperature
THF	tetrahydrofuran is a cyclic ether used as solvent
T <sub>m</sub>	average temperature
TTiP	Titanium tetra-isopropoxide
V	velocity
<i>x,y,z</i>	indices indicate the orientation along the x, y and z axis, respectively
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
Ζ	figure of merit of couple (p,n junction)
Z	figure of merit of individual material
Z <sub>NE</sub>	thermomagnetic or Nernst-Ettingshausen figure of merit
zT	dimensionless figure of merit of couple
zT⊥	Thermoelectric figure of merit along axis perpendicular with trigonal axis
zT <sub>//</sub>	thermoelectric figure of merit along axis parallel with trigonal axis
ρ	electrical resistivity (= 1 / $\sigma$ )
σ	electrical conductivity

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# Introduction

### 1.1. Thermoelectric energy conversion

The growing global demand for energy production and our reliance on fossil fuels is a serious threat to the sustainability of our planet in the long term. Studies have already shown the correlation between the combustion of fossil fuels and global warming, which may have unprecedented consequences on the environment and our society. [1-4] Therefore, the search for alternative energy sources is of major importance to address these issues. [5-7] As the conversion of fossil fuels to useful energy is accompanied with the production of a vast amount of waste heat, technologies which could harvest the lost energy and produce electricity that can be returned to the system as usable energy have a similar effect as a new alternative energy source. [8] Herefore, thermoelectrics could play an important role, as they possess the ability to convert heat directly to electricity through a solid-state process. This involves that thermoelectric devices have no moving parts, are extremely reliable, guiet and have a long lifetime. [9] In a reverse manner, thermoelectrics can act as a heat pump when current is passed through the material, causing one side of the material to cool while the opposite side heats up. They are mainly used as solid-state cooling devices, better known as a Peltier coolers. [10, 11] An additional advantage of solid-state coolers is the fact that they do not require fluorocarbons, which are used in compressor based refrigerators and known to deplete the ozone layer and contribute to the greenhouse effect. [12-14]

Despite the advantages of thermoelectrics, the limiting factor preventing their large-scale production for both power production and solid-state cooling is their relatively low efficiency. The commercially available thermoelectrics currently used are  $(Bi_xSb_{1-x})Te_3$  based and were developed already in the 60's. [9, 15-18] The material's efficiency, described as the figure of merit or denoted *zT*, was limited for a long time to *zT* = 1 at 300 K [17, 19], which corresponds with an efficiency of 6% in power generation mode when a temperature gradient of 150 °C is applied between the hot and the cold side of the material. That efficiency increases to 10 % when a material with a *zT* = 2 is used for the same temperature gradient. It can be understood from this example that materials with a high *zT* are desired to maximize the heat-to-electricity conversion efficiency. The *zT* of 1 in Bi<sub>2</sub>Te<sub>3</sub> alloys is seen as a benchmark for the development of new thermoelectrics. In other words, anything above *zT* one is considered good, whereas materials with a lower *zT* are regarded as poor thermoelectrics. In 1993, Hicks and Dresselhaus theoretically predicted that nanostructured thermoelectrics, possessing

dimensions lower than 10 nanometer (nm), could have an enhanced zT value compared to their bulk counterparts. [20, 21]. The experimental evidence of enhanced TE performances in low dimensional TEs, such as in Bi<sub>2</sub>Te<sub>3</sub>/Sb<sub>2</sub>Te<sub>3</sub> superlattices [22] and in PbTe/PbSeTe and PbTe/PbSnSeTe quantum dot superlattices with zT = 2 at 300 K [23], had led to a resurgence of interest for thermoelectric materials. Although those initially studied nm thin layered TEs or superlattices exhibited superior TE performances, materials fabricated by atomic layer deposition techniques are difficult to incorporate into commercial devices and at high temperatures the nanostructures spontaneously dissolve during the course of operation as they are thermodynamically unstable. [24] Consequently, the research area has now evolved into studies on bulk samples containing nanostructured constituents and band structure engineering of bulk thermoelectrics, which are easier and cheaper to fabricate. [25-27] Typically, bulk materials containing nano-sized features scatter phonons more than electrons, causing an overall enhancement of the material's zT if the ratio of electrical conductivity to the thermal conductivity is enhanced. [28, 29] Recent developments using these technologies have led to bulk nanocomposite materials with a zT reaching 1.5 - 1.8 at 750 - 900 K for PbTe with SrTe nano inclusions. [30] Parallel with the development of nanomaterials, continuous progress in the efficiency of bulk  $CoSb_3$  based skutterudites has resulted in zT's reaching 1.7 at 850 K using Ba, La, and Yb fillers to reduce the thermal conductivity of the material. [31]

In refrigeration mode, the efficiency is denoted as the coefficient of performance or COP, which is defined as the amount of heat pumped from the cold side of the thermoelectric refrigerator to the hot side where it is rejected, divided by the amount of input electrical power. An evaluation of thermoelectric coolers compared to mechanical vapour-compression refrigerators was made by Heremans et *al.* [32] It was shown that for a temperature gradient of 40 °C, a classic thermoelectric cooler with a device zT = 1 has a COP of only 25 % of that of a vapour-compressor based refrigerator, making them inferior to conventional technologies. However, advancements in material efficiency (zT = 2) and heat exchangers have led to COP's for TE coolers comparable with that of vapour-compression coolers.

### 1.2. State of the art thermoelectrics

The thermoelectric effect itself was discovered by Seebeck in 19<sup>th</sup> century [33], but it took till the 1950's, until it was observed that doped semiconductors were good thermoelectrics. [15] The semiconducting materials bismuth antimony alloys ( $Bi_{1-x}Sb_x$ ), bismuth telluride ( $Bi_2Te_3$ ) and lead telluride (PbTe) were found to be among the best thermoelectric materials, each in their specific temperature range (see Figure 1.1 and Figure 1.2). [34, 35] However, these thermoelectric materials were unable to compete with other power production devices or compressor refrigerators due to their low performance, which limited their applications to niches where their reliability, compactness and long lifetime outweigh the poor efficiency. As mentioned earlier, advances in material synthesis of bulk nanostructured thermoelectrics and band structure engineering have led to the development of bulk thermoelectrics with zTs as high as 2.2 at 850 K in MgTe doped PbTe<sub>0.8</sub>Se<sub>0.2</sub> [36], which is among the highest reported for bulk materials.

An overview of state of the art of metal based thermoelectric materials is given in Figure 1.1 and Figure 1.2.



Figure 1.1. State of the art p-type bulk thermoelectric efficiencies. Image replotted from [37].



Figure 1.2. State of the art n-type bulk thermoelectric efficiencies. Image replotted from [37].

Parallel with the study on nanostructured metallic TEs, much effort has been devoted to seeking ceramics exhibiting good TE properties since they are thermally and chemically more stable than their metallic counterparts. [38] Furthermore, they contain no toxic heavy metal elements, consist of cheaper materials and they can operate at high temperature which is beneficial to achieve a high TE conversion efficiency. Promising ceramic TE materials are Na<sub>x</sub>CoO<sub>2</sub> and Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> as p-type TE material and SrTiO<sub>3</sub>, CaMnO<sub>3</sub> and ZnO as n-type TE material. [39-45] However, they are inferior in terms of efficiency compared to metallic thermoelectric, mainly because of their poor electrical conductivity. Note the difference in the units on the vertical axis between the oxide thermoelectrics in Figure 1.3 and Figure 1.4, compared to those of the metallic thermoelectrics shown above.



Figure 1.3. State of the art bulk thermoelectric efficiencies of p-type oxide materials. [38, 46, 47]



Figure 1.4. State of the art bulk thermoelectric efficiencies of n-type oxide materials. [38, 48-50]



Figure 1.5. Overview of well-studied thermoelectric materials and their application areas.

Figure 1.5 shows the most studied classes of thermoelectric materials, each with their own temperature range. Since most thermoelectric materials achieve their maximum zT at high temperatures, the main application envisaged has been the heat recovery in the automotive

industry to produce electricity from waste heat from exhaust fumes in an attempt to improve fuel efficiencies. [51-53] Although a lot of advancement has been booked in terms of obtaining high *zT* materials for high temperature applications, hardly any improvements have been realised for thermoelectrics for room temperature and cryogenic refrigerators. As for the last 50 years, the highest *zT* is still obtained in  $Bi_2Te_3$  and  $Bi_{1-x}Sb_x$  based alloys, respectively for room temperature and cryogenic cooling applications.

### 1.3. Limitations in thermoelectric materials development

Although high zT's have been obtained in PbTe based alloys, the presence of Pb in commercial devices is often restricted and depends on governmental regulations. In addition, the best thermoelectrics contain Te, which is a scarce metal with an availability similar to that of Pt. Although its price is relatively low (about  $\in 240$  /Kg compared to  $\in 32$  000 /Kg for Pt), the material cost would skyrocket if a technology based on the material would expand significantly. As a comparison, the price of Te was only about  $\in 29$  /Kg in 2000, but has become more expensive due to rising demand, mainly for the production of thin film CdTe solar cells. [54, 55] Therefore, high zT thermoelectric materials which do not contain either of the aforementioned materials are desired. Although much progress has been booked in the development of alternative high zT materials for power generation applications (such as CoSb<sub>3</sub> based skutterudites), there is a lack of efficient materials for thermoelectric temperature control and cooling applications, which is to date the largest market for thermoelectrics. Consequently, enhancement of the efficiency of Bi<sub>1-x</sub>Sb<sub>x</sub> based thermoelectrics would be highly valued.

In addition, the vapour deposition fabrication processes of low dimensional thermoelectrics are too costly to be competitive with conventional power generation and refrigeration technologies, even when high efficiencies could be achieved.

### 1.4. Objectives and methods

The predictions made by Hicks and Dresselhaus that low dimensional thermoelectrics could have superior efficiencies compared to their bulk counterparts inspired us to develop new synthesis methods to fabricate nanostructured thermoelectrics and find pathways to transfer those nanostructures into a bulk material, an approach that had been hardly explored and consequently the goal of this research.

It was demonstrated by Ohta et *al.* that nm thin layered SrTiO<sub>3</sub> low dimensional structures of SrTiO<sub>3</sub> can lead to a drastic enhancement of the Seebeck coefficient. [56] Therefore, we studied whether quantization effects would take place in nanocasted SrTiO<sub>3</sub> and lead to better thermoelectrics. The envisaged transfer of nanowire structures into a bulk material was tested by compressing nanowire composite powder into pellets, while maintaining the nanostructured architecture (see Figure 1.6). It was expected that the nanostructures would lead to a drastic decrease of the lattice thermal conductivity and an increase of the Seebeck coefficient  $\alpha$  due to confinement effects [56, 57], resulting in an improvement of the thermoelectric figure of merit *zT*. Firstly, since the thermal conductivity  $\kappa$  of undoped bulk SrTiO<sub>3</sub> is relatively high, approximately 10 W/mK at room temperature, we believed that the phonon transport could be effectively reduced since scattering centres were created from atomic level through doping to nm level (diameter of the nanowires), up to  $\mu$ m level due to the many interfaces of the template. Secondly, we strived to create SrTiO<sub>3</sub> nanowires of such small diameters that an enhancement of the Seebeck coefficient  $\alpha$  would occur as was observed by Ohta et *al.* [58]

Bismuth, on the other hand, has a very small band overlap energy and can transform from a semi metal to a semiconductor by preparing Bi as nanowires with a diameter below approximately 50 nm or by doping Bi with about 5 - 15 at % Sb. Heremans et *al.* demonstrated a drastic enhancement of the Seebeck coefficient in Bi nanowires grown in porous alumina. However, the high thermal conductivity of the alumina template is detrimental for the thermoelectric efficiency as it causes parasitic heat loss through the matrix. In addition, the vapour deposition technique used to grow the nanowires, does not allow the synthesis of  $Bi_{1-x}Sb_x$  nanowires, which is supposed to have superior thermoelectric properties over Bi. [59] The alloying of Bi with Sb has been shown to drastically enhance the thermoelectric properties of bulk  $Bi_{1-x}Sb_x$ . [60]

The main objective of this research is to develop thermoelectric nanowires embedded in a mesoporous matrix to enhance the thermoelectric properties and render the materials practical applicability through the fabrication of bulk nanowire composites as schematically depicted in Figure 1.6. Herefore, a highly porous mesoporous silica template was impregnated with a metal precursor solution, reduced and finally sintered into pellets. This new conceptual synthesis pathway is described for SrTiO<sub>3</sub> and bismuth and was validated for bismuth based bulk nanowire composites.





### 1.5. Outline

Chapter 2 provides a theoretical understanding of thermoelectricity and explains how better materials could be obtained based on an analysis of the different material properties determining the material's zT and how their interdependence makes it difficult to enlarge the material's figure of merit. Next, several device configurations for power generation and cooling are discussed, with the calculation of their efficiencies. A summary is given of some typical applications.

In Chapter 3, the structural and electronic properties of Bi are discussed, which provided a fundamental basis for the thermoelectric efficiency enhancement in  $Bi_{1-x}Sb_x$ . Further, pioneering work on Bi nanowires and the motivation of this research is discussed.

Chapter 4 gives an overview of the different mesoporous silica materials that are of interest as template material for the synthesis of nanowire networks in their pore channels. Particularly mesoporous silica materials with a 3D interconnected pore network are desired as they give rise to longer percolation paths than 2D pore channels. We are interested in how to engineer the pore structure and pore dimensions to meet the requirements of their applications, such as high pore volume (>  $0.8 \text{ m}^2/\text{g}$ ), large pores (10 - 30 nm) and an interconnected pore structure (3D pore network). The synthesis mechanism of mesoporous silica materials via soft-templating and different strategies to tailor the pore diameter and pore structure are discussed, as well as their thermal stability.

Chapter 5 describes the nanocasting method, which is a versatile technique for the synthesis of nanostructured and mesoporous materials, typically using the pores of mesoporous silica as nano-reactor. The silica materials discussed in Chapter 4 were used as hard template. The principles, advantages, limitations and the comparison of state of the art nanocasting techniques with the synthesis process developed throughout this research are discussed. It is shown how the impregnation of the template is affected by its surface chemistry, precursor composition and how these could be optimized to improve the nanocasting process and the pore loading.

Chapter 6 is dedicated to the development of a sol gel based nanocasting synthesis route of  $SrTiO_3$ . Different strategies to adapt the impregnation rate of a mixed precursor solution are discussed to control the stoichiometry of the impregnated material. The impregnation of a double salt precursor, which provides greater control of the stoichiometry and pore loading is discussed.

Chapter 7 is dedicated to the synthesis of several mesoporous materials made via the nanocasting procedure introduced in Chapter 5. In order to study the applicability of the new nanocasting process, several classes of materials were synthesized. Namely, mesoporous oxides, such as  $TiO_2$ , mesoporous chalcogenides, for example  $TiS_2$  and mesoporous metals, such as silver. It is shown which parameters during the synthesis affect the replication process and how it could be improved.

Chapter 8 focusses on the synthesis and optimization of Bi nanowire composites for their use as thermoelectric material. The objective of this work is to transfer the advantages of  $Bi_{1-x}Sb_x$ nanowires into a bulk material and enhance the thermoelectric efficiency. The implementation of this plan involved two approaches to improve the thermoelectric performance of Bi alloys. Firstly, Bi nanowire arrays confined within the pores of a mesoporous silica template were synthesized and tested as bulk nanocomposite material. These bismuth based nanowires embedded in a mesoporous silica matrix were synthesized through the impregnation of a bismuth precursor solution in the template as introduced in Chapter 5. The use of post treatments with reactive gasses Me<sub>3</sub>Sb and H<sub>2</sub>Se were performed to synthesize Bi<sub>1-x</sub>Sb<sub>x</sub> and Bi<sub>2</sub>Se<sub>3</sub> respectively. Secondly, Sb doped Bi nanowires were synthesized using a mixed precursor solution and utilized in the same manner as for bismuth nanowire arrays, with the purpose to get a greater enhancement of the thermoelectric properties of the material than possible with Bi nanowires alone or in bulk  $Bi_{1-x}Sb_x$  alloys. Transport property measurements were performed on sintered samples with different  $Bi_{1-x}Sb_x$  compositions. It is shown for the first time that an enhancement of the Seebeck coefficient could be achieved in Bi<sub>1-x</sub>Sb<sub>x</sub> bulk nanowire composites. Several suggestions are discussed how further improvements could be achieved.

Chapter 9 describes a new direction in the field of thermoelectrics, namely the contribution of spin Seebeck effect to the transverse Nernst thermopower in bulk nanocomposite materials. The physics of spin transport through interfaces of a normal metal and a ferromagnet have been intensively studied in thin films [61, 62], but the work described here is the first experimental confirmation that the spin Seebeck effect can lead to an enhancement of the transverse thermopower in bulk nanocomposite samples consisting of Ni nanoparticles coated with Pt nanoparticle. The experiments were performed in collaboration with S. Boona and published in Nature Communications [63]. Although this is solely a demonstration of the concept, the use of nanowires composites, synthesized as described in Chapter 5, can be used to further exploit this effect, which is the focus of ongoing research.

Prospects for future work are addressed in the "Conclusion remarks and future prospects" section.

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# 2

# Thermoelectric energy conversion

In this chapter, we discuss the basic thermoelectric and thermomagnetic properties of materials, the figure of merit and its relation to the materials energy conversion efficiency. Further, the efficiency of a typical thermoelectric and thermomagnetic module is calculated.

### 2.1. Thermoelectric effect

### 2.1.1. Seebeck and Peltier

Thermoelectricity was discovered by T. Seebeck in the 19th century. He observed that an electromotive force could be produced when a junction of two dissimilar electrical conductors, forming a closed circuit, was heated as shown in Figure 2.1a.



Figure 2.1. Basic thermoelectric circuits. (a) If 1 and 2 are dissimilar conducting materials, generally, a thermoelectric current will flow in a closed circuit when one junction is heated while the other is cold. (b) A thermoelectric potential difference,  $\Delta V_{12}$ , is generated in an open circuit when one junction is heated while the other is cold.  $\Delta V_{12}$  will be proportional to  $\Delta T$  if  $\Delta T/T << 1$ . The indicated polarity  $\Delta V_{12}$  is positive for  $\Delta T > 0$  and  $\alpha_1 > \alpha_2$ , with  $\alpha$  the Seebeck coefficient or also called the thermopower, expressed in  $\mu V/K$ .

In addition to the heat flowing from the hot side to the cold side, also a current referred to as thermoelectric current was produced. Specifically, Seebeck observed the deflection of a magnet compass in proximity of the conductor due to the interaction with the induced magnetic field caused by the motion of electrons in the conductor. Intuitively, the origin of the Seebeck voltage in a single conductor can be understood as the diffusion of the charge

carriers from the hot side to the cold side, causing an accumulation at the cold side what leads to a potential difference between both ends. [1] When the charge carriers are electrons, we have an n-type material, which has a negative Seebeck coefficient. In the case of conduction through holes is, the material is p-type, which results in a positive Seebeck coefficient.

In Figure 2.1b, when one junction is heated, while the other junction is cold, a small voltage,  $\Delta V_{12}$ , is generated. The magnitude of the thermoelectric voltage is proportional with temperature difference  $\Delta T$  between the hot and cold junctions. The junction of the two wires are also a thermocouple. If, as in Figure 2.1b, a small temperature difference, dT, is applied to the thermocouples, the Seebeck coefficient is defined as the derivative of the observed potential difference, dV, to the temperature difference as:

$$\alpha = \frac{dV}{dT}$$
 Eq. 2.1

The sign of the derived Seebeck coefficient depends on the absolute Seebeck coefficient  $\alpha_1$  and  $\alpha_2$  of both conductors, which are temperature dependent. The net thermoelectric power as observed in Figure 2.1b is given by  $\alpha_{12} = \alpha_1 - \alpha_2$  and is a relative value and is considered positive when the electromotive force induces a current through conductor 2 from the hot junction to the cold junction. The absolute Seebeck coefficient can be measured in case one of the conductors is a superconductor below its critical temperature. [2-5] Since superconductors possess no resistivity, they do not exhibit a thermoelectric effect. Consequently, the measured Seebeck coefficient becomes an absolute value.



Figure 2.2. Peltier heat is defined as the heat absorbed or evolved when an electrical current, *I*, is passed through the junction between two materials, 1 and 2. The direction of I and its value affect the rate of heat adsorbed or evolved, as well does the temperature of the junction. The Peltier heat,  $\Pi_{12}$ , is positive if heat is evolved at the junction when the current flows from material 1 to 2.

It was discovered by J. Peltier that heat may either be absorbed or generated in the junction area two materials if an electrical current is passed through it (Figure 2.2). The absorption or rejection of heat depends on the direction of the current flow and is different from the Joule heating, which solely depends on the resistivity of the conductor. Also, Joule heating is irreversible and is always dissipated from the conductor, regardless of the direction of the current flow. On the other hand, the Peltier heat is a reversible phenomenon as it is linearly dependent on the sign and magnitude of the current. The Peltier coefficient  $\Pi_{12}$  is defined as the amount of heat Q developed in a reversible manner at the junction per unit time per unit electric current along the x-axis,  $I_x$ , flowing in the direction  $1 \rightarrow 2$ .

$$\Pi_{12} = \frac{Q}{I_x}$$
 Eq. 2.2

The Peltier heat  $\Pi_{12}$  also depends on the common temperature of the two conductors forming the junction. The net Peltier heat at a junction between two conductors is given by  $\Pi_{12} = \Pi_1 - \Pi_2$ .

#### 2.1.2. The Kelvin (Thomson) relations

W. Thompson postulated that if an electrical current with current density  $j_x$  along the x-axis is passing through an individual conductor, and a temperature gradient  $\nabla_x T$  in the same direction is present, that the net heat produced in the conductor per unit of volume per second  $(\dot{Q}_1)$  follows the relationship:

The first term in Equation 2.3 is the irreversible Joule heat and depends on the electrical conductivity ( $\sigma$ ) and the square of the current density. The second term is the thermoelectric heat and is linearly dependent on the current density and the temperature gradient. The sign of  $\dot{Q}_1$ , (+) for heat emitted and (-) for heat absorbed, depends on the directions of the current and the temperature gradient relative to each other. The coefficient  $\mu$  is defined as the Thompson heat of the material and also depends on the temperature of the conductor.



Figure 2.3. When an electrical current, with current density  $j_x$ , flows in a conductor subjected to a temperature gradient, in addition to the Joule heat generated, Thomson heat is dissipated or absorbed throughout the conductor depending on the relative direction of  $j_x$  and  $\nabla_x T$ . The magnitude of the Thomson heat is directly proportional to the product  $j_x \nabla_x T$ , and dependent in magnitude on the temperature of the conductor. For the given direction of the thermal gradient and current flow,  $\mu$  is positive.

Based on Equation 2.3, Thomson derived the following relations between the Thomson heat ( $\mu$ ), the absolute thermoelectric power ( $\alpha$ ) and the Peltier heat ( $\Pi$ ) of a conductor:

$$\mu = \frac{T d\alpha}{dT}$$

$$\Pi = T \alpha$$
Eq. 2.4
Eq. 2.5

Equation 2.4 and 2.5 are usually referred to as the Kelvin relations. The absolute thermoelectric power,  $\alpha$ , of a conductor can be determined by integrating the first Kelvin relation and calorimetric measurements of the Thomson heat,  $\mu$ , as:

$$\alpha(T) - \alpha(0) = \int_0^T \frac{\mu}{T} dT \qquad \qquad \text{Eq. 2.6}$$

Based on the third law of thermodynamics it can be said that the thermoelectric effect disappears for  $T \rightarrow 0$  as the entropy at absolute zero is 0, hence Equation 2.6 can be written as:

$$\alpha(T) = \int_0^T \frac{\mu}{T} dT \qquad \qquad \text{Eq. 2.7}$$

The Kelvin relations show us how to derive all thermoelectric properties of a conductor based on the knowledge of the Seebeck coefficient, which can be easily measured.

### 2.1.3. Thomson heat and thermoelectric power

If we rewrite Equation 2.3 in terms of the charge q, transported in a time, t, through a section of the conductor with resistance R under a small temperature difference, then we may write:

$$Q = \frac{q^2 R}{t} - \mu q \Delta T \qquad \qquad \text{Eq. 2.8}$$

Q is now the heat evolved or absorbed in a section of the conductor in a time t. Eq. 2.8 shows that the heat exchanged is proportional on the rate at which the electric charge is transported. In the case the time is made sufficiently long, the first (Joule) term becomes insignificant compared to the (Thomson) second term and the amount of heat involved is then directly proportional to the electric charge transported. Hence, the Thomson heat can be referred to as the heat absorbed or evolved per unit charge and unit temperature difference, when the charge is transported sufficiently slowly in the direction of increasing temperature.

### 2.2. Thermomagnetic effect

While the Seebeck, Peltier and Thomson effect described the absorption or dissipation of heat in a conductor, new interactions occur in the presence of an external magnetic field. Namely, electric charges are subject to transverse Lorentz forces when they travel in a magnetic field. Hence, the thermoelectric effect is affected by an external applied field and gives rise to new phenomena, such as the Hall effect and the thermomagnetic Nernst-Ettingshausen effect which could lead to new methods of energy conversion. [6, 7]

### 2.2.1. Hall effect

The Seebeck and Peltier effects are particularly affected in an external magnetic field when the material's carrier mobility is high and a strong magnetic field is applied. In a magnetic field, the Kelvin relation in Equation 2.5 becomes:

$$\Pi(B) = T\alpha(-B)$$
 Eq. 2.9

Electrons traveling in a magnetic field will experience the Lorentz force in a direction perpendicular to both the current and  $\vec{B}$ , which is proportional to the cross product of the velocity of the electrons and the magnetic field strength and the charge:  $(\vec{v} \times \vec{B})e$ . In a conductor, the deflection of the charges creates an electric field counteracting the Lorentz force:  $(\vec{v} \times \vec{B_z})e = e\vec{E_y}$  as shown in Figure 2.4, with the magnetic field  $\vec{B_z}$  coming out of the



Figure 2.4. Hall effect. Deflection of charge carriers under influence of an applied field  $B_z$ , creating an electric field opposite the Lorentz force.

plane, the velocity of the charge carriers  $\vec{v}$  and the  $\vec{E_v}$  the transverse electric field.

Since the current density  $j_x$  (in scalar form) along the x-axis is defined by the product of the charge carrier density *n*, the electrical charge e and the velocity as:  $j_x = n e v$ , with  $R_H$ :

$$R_{H} = -\frac{1}{ne} = -\frac{E_{y}}{B_{z} j_{x}}$$
 Eq. 2.10

The Hall coefficient,  $R_H$ , given Equation 2.10, is inversely proportional to the number density of conduction electrons. Consequently, the carrier density is defined as  $1/R_H$ . Although the Hall effect is not directly relevant to energy conversion, it is important to understand better the behaviour of the charge carriers. The sign of the Hall coefficient depends upon the sign of the charge carriers, electrons or holes.

In semiconductors with both electrons and holes as charge carriers, the Hall resistance  $R_H$  becomes more complex and is determined now by the hole concentration p, the hall mobility  $\mu_h$ , the electron concentration n, the electron mobility  $\mu_e$ , and the elementary charge e, and can be written as:

$$R_{H} = \frac{p\mu_{h}^{2} - n\mu_{e}^{2}}{e(p\mu_{h} + n\mu_{e})^{2}}$$
 Eq. 2.11

### 2.2.2. Nernst and Ettingshausen effects

More interesting for energy conversion are the transverse Nernst and Ettingshausen effects. The Nernst effect is observed as the transverse voltage generated when a sample is subjected to a thermal gradient and a perpendicular magnetic field. When a temperature gradient  $\nabla_x T$  along the x-axis is applied between the two ends of a material, the charge carriers diffuse from the hot side of the sample to the cold side. As the charge carriers move in the presence of a transvers magnetic field, they are deflected as a result the Lorentz force acting on them, causing a potential difference  $E_{\gamma}$  as shown in Figure 2.5.



Figure 2.5. Nernst effect. Net diffusion of charge carriers from the hot side to the cold side are subjected to Lorentz forces under influence of the magnetic field  $B_z$ , causing a deflection of the charge carriers and the buildup of a potential  $E_y$ , perpendicular to both  $B_z$  and the direction of the net charge current.

A transverse electric field is generated to balance the Lorentz force. The induced electric field is normal to both the temperature gradient and the magnetic field. The Nernst coefficient, N, is defined by:

$$N = \frac{E_y}{B_z \nabla_x T}$$
 Eq. 2.12

With  $E_y$  the transverse electric field,  $B_z$  the magnetic flux coming outside the plane and  $\nabla_x T$  the longitudinal temperature gradient. In contrast from the Hall effect, the sign of the Nernst effect is independent of the type of charge carriers. The Ettingshausen and Nernst effects are related to each other in a similar manner as the Seebeck and Peltier effects. The Ettingshausen effect is a transverse temperature gradient,  $\nabla_y T$  caused by the effect of a transverse magnetic field,  $B_z$ , and a longitudinal flow of electric charge,  $I_x$ , as shown in Figure 2.6.



Figure 2.6. Ettingshausen effect. Slow electrons are deflected in a greater extent than fast electrons, causing a cooling at the side where the low energetic electrons are deflected towards.

Slow electrons tend to be deflected more than fast electrons under influence of an external field  $B_z$ . As the energy of the slow electrons is lower, the side to which they are deflected becomes colder than the opposite side. The Ettingshausen coefficient, *P*, can be defined as:

$$P = \frac{\nabla_y T}{I_x B_z},$$
 Eq. 2.13

with  $\nabla_y T$  the transverse temperature gradient,  $B_z$  the transverse magnetic field and  $I_x$  he longitudinal current. In contrast from the Hall effect, the sign of the Nernst effect is independent of the type of charge carriers. The thermodynamic relationship between the Nernst and Ettingshausen coefficients is given by:

$$P \kappa = N T \qquad \qquad \text{Eq. 2.14}$$

In Equation 2.14,  $\kappa$  is the thermal conductivity, which is included here since the Ettingshausen coefficient is defined by the induced temperature gradient in the material.

### 2.3. Thermoelectric figure of merit

As mentioned earlier, the material properties defining the efficiency of a thermoelectric material are the Seebeck coefficient  $\alpha$  or also denoted as *S*, the electrical conductivity  $\sigma$ , and the thermal conductivity  $\kappa$ . The dimensionless figure of merit for a material is denoted as *zT* and is defined as:

$$zT = \frac{\sigma \alpha^2 T}{\kappa}$$
 Eq. 2.15

Intuitively, we want a high Seebeck potential for a certain applied temperature gradient over the material, while a low thermal conductivity is desired to maintain the temperature difference. A high conductivity, on the other hand, reduces the resistive losses in the material.

### 2.3.1. Thermoelectric power factor

In bulk materials, the three properties  $\alpha$ ,  $\sigma$  and  $\kappa$  determining the zT are interdependent, making it difficult to improve one of them without sacrificing the others. For example, by increasing the carrier density, n, the electrical conductivity increases, whereas the Seebeck coefficient reduces (based on the Pisarenko relation for semiconductors [8]:  $\alpha \propto -\ln(n)$ ), leading to a deterioration of zT. Intuitively, the Seebeck effect can be understood as the diffusion of the charge carriers from the hot side of a conductor to the cold side. Consequently, a potential difference is generated due to a difference in charge carrier concentration at both ends of the conductor. In a semiconductor, there is approximately 1 electron for every 100 to 1000 atoms, which leads to a larger potential gradient than in metals, which have approximately 1 electron for every atom. The interrelations between them are given in Figure 2.7. Generally, the product  $\sigma \alpha^2$ , denoted as the power factor, should be maximized to obtain the material's highest zT and depends on the optimum carrier concentration for the material. In semiconductors, the total thermal conductivity  $\kappa$ , is dominated by the lattice component  $\kappa_L$ , whereas the electronic thermal conductivity  $\kappa_e$  is low. Consequently, any effort to reduce  $\kappa_L$  may enhance zT provided that the electrical conductivity does not reduce too much.



Figure 2.7. Influence of carrier concentration on thermoelectric properties, with  $\alpha$  the Seebeck coefficient,  $\sigma$  the electrical conductivity or  $\rho = 1 / \sigma$  the electrical resistivity,  $\kappa$  the thermal conductivity,  $\sigma \alpha^2$  the power factor and *z*T the thermoelectric figure of merit.

The Seebeck coefficient in a degenerated system, such as in metals or degenerately doped semiconductors, can be approximated by the Mott relation and is generally valid regardless of the conduction mechanism:

$$\alpha = \frac{\pi^2}{3} \frac{k_B}{e} k_B T \left\{ \frac{d[ln(\sigma(E))]}{dE} \right\}_{E=E_F}$$
 Eq. 2.16

Here  $k_B$  is the Botlzmann constant, *e* the electric charge, and  $E_F$  the Fermi energy. The Mott relation shows that any enhancement in the energy dependence of the electrical conductivity  $d\sigma(E)/dE$  enhances the Seebeck coefficient. Hence, if we substitute the electrical conductivity by the carrier density *n*, the electron charge *e*, and the carrier mobility  $\mu$ , we obtain:

$$\sigma(E) = n(E)e\mu(E)$$
, with Eq. 2.17

$$\mu(E) = e \frac{\tau(E)}{m^*}$$
 Eq. 2.18

In the latter,  $\tau$  is the relaxation time, and  $m^* = m(E)$  the effective mass of the electron in solids with non-parabolic bands. In the case of metals or degenerately doped semiconductors the energy distribution of the electrons can be described by Fermi statistics. Consequently, n(E) can be written as the product of, the density of states g(E) and the Fermi distribution function f(E):

(-)

$$n(E) = g(E) f(E).$$
 Eq. 2.19

It can be seen from Eq. 2.17 and Eq. 2.19 that the energy dependence of the electrical conductivity  $d\sigma(E)/dE$  is influenced by dg(E)/dE and  $d\mu(E)/dE$ . The former can be increased in low dimensional structures as shown in Figure 2.8. Specifically, when the dimensionality is reduced from 3D (bulk), to 2D (quantum well), to 1D (quantum wire), to 0D (quantum dot), the occurrence of sharp features in the density of states lead to a large dg(E)/dE, which subsequently yields an enhancement of the Seebeck coefficient  $\alpha$ .



Figure 2.8. Density of states of bulk, quantum well, quantum wire and quantum well. Image reprinted from [9].

On the other hand, increasing the energy dependence of the mobility  $d\mu(E)/dE$  to enlarge  $\alpha$  can be achieved if the energy dependence of the relaxation time  $\tau d(E)/dE$  increases. This means that electrons are scattered depending on their energy, which is described as electron energy filtering. In conventional semiconductors with parabolic bands, the relaxation time  $\tau$ , is written as:

$$\tau = \tau_0 E^{\lambda - \frac{1}{2}}$$
 Eq. 2.20

If we consider the relaxation time as the inverse of the scattering probability, we can say that the latter depends on two factors: (1) the density of initial and final states, which in bulk materials results in the factor  $E^{1/2}$ , and (2) the probability component yielding the factor  $E^{\lambda}$ , with  $\lambda$  the scattering exponent. Its value for various scattering mechanism is approximated as:  $\lambda = 0$  for scattering of electrons on acoustic phonons,  $\lambda = 1/2$  for scattering of electrons on neutral impurities and  $\lambda = 2$  for scattering of electrons on ionized impurities. [10] It was realized in the early years of semiconductors that  $\lambda$  could be increased by ionized impurities and correcting the carrier concentration by counter doping. [3] However, this also
affects the carrier mobility and does not always results in an enhancement of zT. Other mechanisms to achieve electron filtering are discussed more detailed in Ref. [9].

#### 2.3.2. Thermal conductivity

It can be seen from the formula of zT in Equation 2.15 that a low thermal conductivity is desirable to obtain a higher figure of merit, since a high thermal conductivity would prevent the build-up of a large temperature gradient in the material. The main contributions to heat transport through a conductor is by the movement of charge carriers and by the lattice. Specifically, the electronic contribution  $\kappa_e$  and a lattice contribution via the phonons  $\kappa_L$ , with the total thermal conductivity:

The electronic part of the thermal conductivity is related to the electrical conductivity by the Wiedemann-Franz law:

$$\kappa_e = L_0 T \sigma , \qquad \qquad \text{Eq. 2.22}$$

with  $L_o$  the Lorentz factor. In metals, the Lorentz number:  $L_0 = \frac{\pi^2}{3} \left(\frac{k_B}{e}\right) = 2.45 \ 10^{-8} V^2 / K^2$ , which is generally used as an approximation in degenerated semiconductors too. However, the Lorentz number can vary depending on the material and the temperature and it is strongly dependent on but not limited to the dimensionality in nanostructured materials, the electronic density of states and the doping level. [11, 12] Upon replacing the thermal conductivity in Eq. 2.15, it can be seen that an optimization of zT implies minimizing  $\kappa_L$ :

$$zT = \frac{\sigma \alpha^2 T}{\kappa} = \frac{\sigma \alpha^2 T}{L_0 T \sigma + \kappa_L} = \frac{\alpha^2}{L_0} \cdot \frac{\kappa_e}{\kappa_e + \kappa_L}.$$
 Eq. 2.23

The third term in Eq. 2.23 shows that only the lattice contribution to the thermal conductivity reduces zT and not the electronic contribution. Consequently, the zT in metals is low due to their low Seebeck coefficient and not because of their high thermal conductivity (which is dominated by the electronic contribution). Slack *et al.* suggested that materials with a "phonon-glass electron-crystal" behaviour could be good thermoelectrics. [13, 14] This had led to various mechanisms to reduce the lattice thermal conductivity, such as:

- complex crystalline structures with a large unit cell. While the conduction of heat occurs predominantly by acoustic phonons, complex structures increase in the number of optical phonon modes, what reduced the thermal conductivity. [15]
- the insertion of heavy atoms in empty cages of crystalline structures causing rattling centers introduces independent phonon modes from the lattice, for example CoSb<sub>3</sub> based skutterudites; [16, 17]
- solid solutions cause phonon diffusion due to mass fluctuations, as in ZrNiSn-based half-Heusler compounds; [18]
- by forming nanograins, the phonon mean free path becomes of the same length scale as the grains, causing effective scattering at the grain boundaries, while electrons are less affected. [19, 20]

#### 2.4. The efficiency of thermoelectric generators and refrigerators



Figure 2.9. (Left) Thermoelectric generator consisting of a p-type and n-type TE leg, electrically coupled in series to a load and thermally in parallel. (Right) A thermoelectric cooler or also called a Peltier cooler is obtained when a current is passed through a thermoelectric module, pumping heat from one side to the other.

A thermoelectric module is constructed using a p-type and an n-type thermoelectric semiconducting material electrically connected in series and thermally in parallel as shown in Figure 2.9. In the p-type leg, the charge carriers are holes and result in  $\alpha > 0$ , while conduction in the n-type leg occurs through electrons, with  $\alpha < 0$ . The figure of merit of a device is denoted as *ZT*, with *Z* a capital letter, while *zT* is used for the material's figure of merit. The figure of merit *Z* of a module is given by:

$$Z = \frac{\left(S_p - S_n\right)^2}{\left(\left(\kappa_p \rho_p\right)^{1/2} + (\kappa_n \rho_n)^{1/2}\right)^2},$$
 Eq. 2.24

in which the indices p and n refer to the p-type and n-type legs of the module, respectively.

In order to derive the device efficiency, the following assumptions are made:

- It is assumed that the electrical contacts connecting both legs have no Seebeck coefficient;
- the contact resistance is assumed negligible;
- the temperature gradient  $T_h T_c$  between the junctions are considered constant;
- all heat transfers through the legs;
- the cross section of the leg is constant;
- the material properties are considered temperature independent.

For thermoelectric heat to electricity conversion, the efficiency of the module is given by Eq. 2.25, with  $T_m$  the average temperature between the cold and hot side.

$$\eta_{max} = \frac{T_h - T_e}{T_h} \cdot \frac{\sqrt{1 + ZT_m} - 1}{\sqrt{1 + ZT_m} + \frac{T_c}{T_h}}$$
 Eq. 2.25

For cooling applications, the efficiency of the system is given by the coefficient of performance (COP), which is defined as the amount of heat absorbed or removed from a reservoir divided by the amount of work consumed by the heat pump. In an optimized system, it can be written as:

$$COP = \frac{T_c}{T_c - T_h} \cdot \frac{\sqrt{1 + ZT_m} - \frac{T_h}{T_c}}{\sqrt{1 + ZT_m} + 1}$$
 Eq. 2.26

It can be seen from the efficiency calculations in Eq. 2.25 and 2.26 that the second term becomes 1 when  $ZT_m$  becomes infinity and the Carnot efficiency is reached. The calculation of the efficiency based on Eq. 2.25 as a function of the temperature difference between the hot and cold side for different  $ZT_m$  values is shown in Figure 2.10a. It can be seen from the graph that a sufficiently high thermal gradient is required to get an acceptable efficiency. Note that the assumption that the material properties are temperature independent is not correct, as it be seen in Figures 1.1 to 1.4 that the material's zT's are strongly temperature dependent. In order to obtain a more realistic ZT value, the average  $ZT_m$  between the cold and hot side is used. It can be understood from this that it is desirable to have a high ZT over a large temperature range.



Figure 2.10. (a) Calculation of maximum TE efficiency as a function  $\Delta T$  for different  $ZT_m$  values. The maximum thermodynamic efficiency or Carnot efficiency for any given temperature difference is shown in bold. (b) Optimum Coefficient of Performance (COP) as a function of  $ZT_m$  for temperature differences between the cold side and the heat sink at 300 K

It can be seen from Figure 2.10b that it becomes increasingly difficult to maintain a large temperate difference using a Peltier cooling device. In practice, the devices operate in a region between their maximum cooling power and optimum COP.

Compared to compressor based refrigerators TEs are inferior. While a COP of approximately 2 is reached for a TE material with zT = 1,  $\Delta T = 20 K$  and the hot side at 300 K, commercial refrigerators operate at a COP of approximately 2 - 4.

An important parameter that characterizes Peltier coolers is the maximum temperature difference that can be generated using a single stage, which is given by:

In order to enhance the temperature difference in a Peltier cooler beyond the limit set in Equation 27, multi stage devices are used. However, it is important to mention that each

stage needs to have a greater cooling capacity than the than its successor. This is because every stage does not only reject the heat from the previous one, but also Joule heat that is generated.



Figure 2.11. Multistage arrangement TE cascades.

In contrast to Peltier refrigerators, thermomagnetic coolers based on the Ettingshausen effect do not require a p and n-type of material, what simplifies the material optimization. Because of the separation of the heat and current flow, a single bar is sufficient to obtain a reasonable temperature difference. For a given current I, the cooling power is inversely proportional to the thickness in the direction y.



Figure 2.12. Schematic of an Ettingshausen refrigerator. Note that the heat is pumped along the y direction, normal to the current flows in the x-direction and the magnetic field in the z-direction.

Their efficiency can be calculated in a similar manner as for Peltier coolers. The efficiency, denoted  $Z_{NE}$  can be written as:

With *N* the Nernst coefficient,  $B_z$  the magnetic field,  $\kappa$  the thermal conductivity and  $\rho$  the electrical resistivity.



Figure 2.13. Exponentially shaped Ettingshausen cascade cooler.

In order to enhance the cooling capacity of Peltier devises, a multi stage geometry consisting of different layers of thermoelectric material is used. On the other hand, in the case of Ettingshausen coolers, it is possible to make an infinite stage device by shaping one element in a trapezoid. The sample is shaped in a way that the cross section,  $L_x$ , by  $L_z$  at height y or  $L_{z,y}$  is much larger at the bottom than that at the top.

#### 2.5. Applications

In recent years, a lot of effort has been devoted to the development of thermoelectric materials for energy recovery in the automotive industry. Considering the large amount of waste heat that is lost through the exhaust, thermoelectrics are used to partially convert the waste heat to electricity by wrapping the exhaust pipe in thermoelectric modules. Other applications in the automotive industry involve seat heating/cooling. [21] Thermoelectrics have also been used for remote power generation applications, such as space missions. Namely, when a radioactive isotope is used as heat source, it could provide energy for the thermoelectrics in waste heat recovery applications, the largest market in thermoelectrics remains refrigeration. Solid state heat pumps are particularly interesting where active cooling of small areas, such as electronics, sensors, optics, etc. is required. Also, thermoelectrics are very reliable, are small in size, do not require any maintenance, and operate silent.

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## 3

### Thermoelectric properties of Bi<sub>1-x</sub>Sb<sub>x</sub>

This chapter gives an overview on the crystal structural, electronic and thermoelectric properties of  $Bi_{1-x}Sb_x$ . It is shown how the band structure of Bi could be altered by alloying with Sb to enhance the material's thermoelectric properties. Further, an introduction to Hicks and Dresselhaus' work is given, which predicted an enhancement of the thermoelectric properties in Bi nanowires compared to their bulk counterparts, which is the motivation of our work. Finally, the experimental works on Bi nanowires by Heremans et al. are discussed, which provided the first confirmation of Hicks and Dresselhaus' theory.

#### 3.1 Introduction

In the 1820's, Thomas Seebeck [1] reported that the material with the highest negative Seebeck coefficient was elemental bismuth, while the one with the highest positive Seebeck coefficient was elemental antimony. Both Bi and Sb are group V elements and behave as semimetals, which means that they have an equal number of electrons and holes at the Fermi surface. Consequently, electrical conduction occurs through both charge carriers. The comparison of the band structures of metals, semimetals and insulators are depicted in Figure 3.1. Due to the approximate cancellation of the partial contributions of the electrons (negative S) and holes (positive S) to the Seebeck coefficient, the total thermopower of bismuth is rather low. Namely,  $S_{\perp} \approx -50 \ \mu V \ K^{-1}$  at 300 K in the direction perpendicular to the trigonal axis, and  $S_{\parallel} \approx -105 \ \mu V \ K^{-1}$  parallel to the trigonal axis. [2] The Seebeck coefficient of bulk Bi can be calculated based on  $S_{\perp}$  and  $S_{\parallel}$  for single crystals:  $S_{bulk} = \frac{S_{\perp} + 2 \times S_{//}}{3} = -68 \ \mu V \ K^{-1}$ <sup>1</sup>. In the experimental section is  $S_{bulk}$  referred to as S. The relatively low Seebeck coefficient limits its zT value. Namely, the thermoelectric figure of merit of elemental Bi at 300 K is  $zT_{\perp}$ = 0.07 perpendicularly to the trigonal axis and  $zT_{//}$  = 0.38 from 250 to 300 K along the trigonal axis. Again,  $zT_{bulk} = zT = \frac{zT_{\perp} + 2 \times zT_{//}}{3} = 0.17$  at approximately 300 K. In order to be industrially viable a zT of minimum one is required, which makes Bi unusable. In the case of antimony, the band overlap energy is larger than in bismuth. Consequently, Sb has many more charge carriers than elemental Bi (respectively, 3.74 x 10<sup>19</sup> and 2.7 x 10<sup>17</sup> cm<sup>-3</sup>, with an equal number of electrons and holes), what makes its thermoelectric performance very poor.

At the first glance, the thermoelectric properties of Bi and Sb seem too low to be useful, however, theory predicted that better performance could be obtained. Namely, Gallo *et al.* proposed that if somehow the compensation of electrons by holes could be eliminated, then zT of Bi could reach 1.3. The optimum carrier concentration to obtain these numbers were calculated by Heremans *et al.* to be of the order of  $n_{OPT} = 1 \times 10^{18} \text{ cm}^{-3}$ , which is about one third of the carrier concentration in elemental Bi. Although the aforementioned results have never been achieved so far, two approaches that have been investigated to lift the band overlap in Bi are alloying with Sb and using nanowires, which are both the subjects of this work.



Figure 3.1. (a) Comparison of band structure of metals, semimetal, zero-gap material, semiconductor and insulator at 0 K. The bold solid line indicates the fermi level. (b) The band structure of bismuth at 0 K, with  $\varepsilon_{Fe}$ ,  $\varepsilon_{Fh,}$ ,  $\varepsilon_{Fl,}$  and  $\varepsilon_g$  the Fermi energies of electrons, heavy holes, light holes and the direct band gap respectively. Image reprinted from [3].

Generally, the highest zT achieved in Bi-Sb alloys at zero magnetic field was obtained in a single crystal Bi<sub>94.5</sub>Sb<sub>5.5</sub> doped with potassium, forming a resonant level in the density of states (DOS). [4] The alloy has a maximum n-type  $zT_{//} = 0.7$  between 100 and 150 K, and  $zT_{//} = 0.5$  from 50 to 300 K. Although the materials synthesized during this research are polycrystalline samples, they can be compared to single crystal data provided that the conversion  $zT_{bulk} = zT = \frac{zT_{\perp}+2\times zT_{//}}{3}$  is used.

#### 3.2 Crystal structure

As with all group V semimetals, bismuth and antimony crystallize in the rhombohedral structure  $(R\overline{3}m)$  as shown in Figure 3.2, with a trigonal axis (denoted 3), the binary axis (denoted 1) normal to the trigonal axis, a mirror plane ("binary plane") and a centre of inversion. The bisectrix axis (denoted 2) completes an orthonormal axis set.



Figure 3.2. Hexagonal representation of the crystal structure. Image reprinted from [5].

The hexagonal representation of the crystal structure of Bi and Sb is depicted in Figure 3.2, which consists of stacked double layers. Since the lattice parameters, electronegativity and valence configuration of bismuth and antimony are similar, Bi-Sb alloys form a solid solution over the entire composition range. The lattice constants of pure Bi and Sb, and of Bi<sub>1-x</sub>Sb<sub>x</sub> alloys in the range x = 0 to 30 at. % are given in Table 1 at various temperatures. The lattice constants  $a_H$  and  $c_H$  of single crystal Bi<sub>1-x</sub>Sb<sub>x</sub> solid solutions vary linearly with the Sb content following Vegard's law. [6]

Table 3.1. Lattice parameters for B	, Sb and Bi <sub>1-x</sub> Sb <sub>x</sub> alloys (x is in at	omic %). Data reproduced from [7].
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	Т (К)	а <sub>н</sub> (Å)	с <sub>н</sub> (Å)
Bi	$298\pm3$	4.5460	11.862
Sb	$298\pm3$	4.3084	11.2740
Bi <sub>1-x</sub> Sb <sub>x</sub>	$298\pm3$	4.546 -23.84·10 <sup>-6</sup> x	11.863 -51.66 10⁻ <sup>6</sup> x

#### 3.3 Electronic structure



Figure 3.3. Fermi surfaces of bismuth in the first Brillouin zone. The electrons in bismuth are at the L-points while the holes are at the T-points. The axes denoted 1,2,3 are parallel with the binary, bisectrix and trigonal axes and the angles  $\varphi_e$  and  $\varphi_h$  are the tilt angels of the electron and hole ellipsoids, respectively. Images reprinted from [3].

The semimetal behaviour of bismuth originates from the small band overlap of its conduction and valence band. Figure 3.3 displays the location of the Fermi surfaces of bismuth within the first Brillouin zone. The two half-ellipsoidal hole pockets of bismuth are located at the Tpoints along the trigonal axis. The electrons are located in six half-quasi-ellipsoidal pockets centred at the L-points of the Brillouin zone. Bismuth has a direct bandgap of  $E_g$  = 13.6 meV at 0 K between the conduction band and the "light" hole band at the L-point.



Figure 3.4. Schematic band diagram of  $Bi_{1-x}Sb_x$  as a function of the antimony content x, at 0 K.  $L_s$  represents the bonding band and  $L_a$  the antibonding band. Figure reprinted from [6].

Since the energy of the conduction and valence band are temperature dependent, the value of  $E_g$  is too. [8] Above approximately liquid nitrogen temperature, the effective masses of the electrons at the L-point of Bi become temperature-dependent, as is the case for the direct energy gap  $E_g$ . Consequently, the band structure of Bi at 300 K looks quite different from that at 4 K. [9] Particularly, the energy overlap increases to such an extent that the electron and hole concentrations increase by an order of magnitude from ~  $3 \times 10^{17}$  cm<sup>-3</sup> at T  $\leq$  77 K to ~  $3 \times 10^{18}$  cm<sup>-3</sup> at 300 K.

Antimony has a higher degree of overlap between the valence and conduction bands ( $E_a \approx$ 180 meV, an order of magnitude larger than in Bi) and a carrier density in antimony about two orders of magnitude larger than in Bi. [10] Solid solutions of Bi and Sb are formed throughout the entire composition range. The surprising emergence of semiconducting behaviour in an alloy of two semimetals can be understood from the fact that the hole bands in Bi and Sb are at different points in the Brillouin zone and move differently with x. The direct bandgap at the L-point decreases in the range 0 < x < 4 %, until the bonding band L<sub>s</sub> and antibonding band L<sub>a</sub> cross and a zero-gap state occurs. The occurrence of a Dirac point in Figure 3.4 can be seen when both bands cross at approximately  $x \approx 4$ . Beyond the composition of the Dirac point, the bands invert and the bandgap opens with increasing antimony content, but remains semi metallic. [11] When the antimony concentration exceeds  $x \approx 7$  %, the overlap between the valence band at the T-point and the conduction band at the L-point vanishes and the semimetal to semiconductor transition occurs. For x > 9 %, the alloys have a Bi-like valence band, while for for  $\sim 9$  at.% < x <  $\sim 15$  % they are direct-gap semiconductors with symmetric electron and hole bands located at the L-points of the Brillouin zone. A maximum band gap of approximately 30 meV is reached around  $x \approx 15$  to 17 %. For ~ 15 at.% < x < ~22 %, the valence band becomes Sb-like, and above x = 22%, the alloys are Sb-like semimetals. The alloy with the record zT is K-doped Bi<sub>94.5</sub>Sb<sub>5.5</sub> at the composition of the Dirac point where the electrical conductivity is optimal. Solids with the Fermi energy exactly at the Dirac point would have zero thermopower, but this sample was doped with the resonant impurity K and maintains a high thermopower.

Both Bi and the BiSb alloys can be doped n- or p-type at low temperatures. Examples of donors are Se [12] and Te [13], while Pb [12] and Sn [12, 14] are acceptors. While potassium forms a resonant level, Li is an interstitial Li [15] donor.



#### 3.4 Bi<sub>1-x</sub>Sb<sub>x</sub> thermoelectrics

Figure 3.5. Thermoelectric figure of merit of  $Bi_{1-x}Sb_x$  measured along the direction parallel (z33) and perpendicular (z11) to the trigonal axes. Image reproduced from [17].

While  $Bi_2Te_3$  was for a long time the best thermoelectric material around room temperature,  $Bi_{1-x}Sb_x$  alloys possess better thermoelectric properties than  $Bi_2Te_3$  below 250 K, [16] particularly in the composition range 5 % < x < 22 %. Consequently, they are the most

suitable alloys for cryogenic Peltier [17] or Nernst-Ettingshausen cooling (see Chapter 2). [18] In conventional Peltier modules, one needs both n-type and p-type material to construct a module, while only n-type BiSb show good zT values. A possible Peltier cooler geometry that would not require a p-type element can use a very thin layer or wire of a high-temperature superconductor to close the electrical circuit without conducting too much. In this way only an n-type Bi<sub>1-x</sub>Sb<sub>x</sub> alloy could be used. The thermoelectric performance of Bi<sub>1-x</sub>Sb<sub>x</sub> alloys with varying Sb content is depicted in Figure 3.5. [17] Another alternative p-type material is CsBi<sub>4</sub>Te<sub>6</sub>, discovered in 2000 by Chung *et al.* and reaches a *zT* of 0.8 at 225 K. [19]

Jandl and Birkholtz [20] reported that in single crystals of Sn doped  $Bi_{95}Sb_{5}$ , which corresponds with the Dirac point, a doping level of 145 ppm Sn could lead to  $zT_{\parallel} \approx 1.4$  at 280 K in an external magnetic field H=1.2 T along the bisectrix axis. They reported that  $zT_{\parallel} \approx 1.2$  (280 K) in a moderate field of 0.3 T was achievable with a permanent magnet. However, those results have not yet been reproduced.

The maximum temperature difference  $\Delta T_{max}$  that can be obtained with Peltier coolers is approximately:  $\Delta T_{max} = \frac{1}{2}zT_c^2$ , with  $T_c$  (K) the temperature of the cold side of the module. Considering the relatively low zT values available in commercial thermoelectric materials, which might be  $zT_{//} \approx 1$  in the best case, multiple stages are required to obtain cryogenic Peltier coolers capable of producing any significant  $\Delta T$ . This limitation can be circumvented in Nernst-Ettingshausen coolers, for which Bi<sub>1-x</sub>Sb<sub>x</sub> alloys are extremely suitable. [17] As the electrical conduction in Bi<sub>1-x</sub>Sb<sub>x</sub> alloys with low values of x occurs though bipolar conduction, the Nernst and Ettingshausen effects are high in the material. In an Ettingshausen cooling device, the current is passed along the trigonal axis of the  $Bi_{1-x}Sb_x$  single crystal, while the external magnetic field is applied along a bisectrix axis. The performance of an Ettingshausen refrigerator is characterized by the product of the Nernst coefficient and the applied magnetic field, also called the isothermal thermomagnetic power, and the thermal and electrical conductivities. The isothermal thermomagnetic figure of merit, for the current along the trigonal axis, the heat flow along the binary axis, and the magnetic field along the bisectrix axis (B<sub>2</sub>) are:  $z_{31} = \frac{(N_{31} \cdot B_2)^2}{\kappa_{11} \cdot \rho_{33}} z$ , where N<sub>31</sub> is the Nernst coefficient, in a direction perpendicular to the heat flow along the binary axis (11) and the current along the trigonal axis (33). The thermal conductivity and electrical resistivity along those directions are denoted  $\kappa_{11}$  and  $\rho_{33}$ , respectively. [20] Optimal values for  $z_{31}T$  obtained in Bi<sub>95</sub>Sb<sub>5</sub> doped with 145 ppm Sn are  $z_{31}T \approx 0.36$  (180 K, 145 ppm Sn, 1.2 T) and  $z_{31}T \approx 0.32$  (180 K, 145 ppm Sn, 0.3 T). An Ettingshausen cooler based on Bi<sub>97</sub> Sb<sub>3</sub> was able to reach a  $\Delta T \approx 42$  K starting from 160 K, at 0.75 T, proving that all-solid-state cooling to 118 K is possible using Bi<sub>1-x</sub>Sb<sub>x</sub> alloys. [21]

#### 3.5 Bi<sub>1-x</sub>Sb<sub>x</sub> nanowires

An alternative way to make bismuth semiconducting is via size quantization. Hicks and Dresselhaus predicted that low dimensional structures could lead to an enhancement of the thermoelectric properties through a reduction of the thermal conductivity and an enhancement of the Seebeck coefficient. [22, 23] Firstly, if the phonon mean free path is of the same length scale or longer than the diameter of the wire, while the electron mean free

path is much smaller, the lattice thermal conductivity can be reduced without too much loss in carrier mobility. Secondly, the Seebeck coefficient in a low dimensional system can be enhanced through size effects and electron filtering as discussed in Chapter 2. [5]



Figure 3.6. (a) Normalized resistance in function of the temperature. (b) Thermopower of bismuth nanowires with different diameters. Image reprinted from [24].

Intensive experimental work on Bi nanowires was performed by Dresselhaus and Heremans et al., where a strong enhancement of the thermopower in Bi nanowire composites was identified that correspond well with the prediction of size quantization effects. [23, 24] A review of that body of work is given in Heremans, J. P., "Low-Dimensional Thermoelectricity", Acta Physica Polonica. [5] The temperature dependence of the resistivity of bismuth nanowires with different diameters are shown in Figure 3.6. In order to eliminate the influence of the cross section of the nanowire arrays, the resistivity was normalized by its value at 300 K. Although the electron and hole density of semimetallic Bi decreases with about one order of magnitude upon reducing the temperature from 300 to 70 K, bulk Bi exhibits a positive value for dR/dT over the entire temperature range. This is because the phonon-limited mobility decreases with temperature as almost a T<sup>-4</sup> law. [5] The 70 nm diameter wires have a dR/dT > 0 below 100 K, which indicates they still behave as semimetals in that region. Bismuth nanowires with a diameter below 49 nm have a negative temperature dependence for dR/dT over the entire range, indicating that the carrier density has become temperature dependent at all temperatures. This proves the existence of the size-effect-induced metal-to-semiconductor transition for nanowires with a diameter below about 50 nm. The thermopower, on the other hand, increases drastically as the wire diameter drops from 200 nm to 9 nm and decreases again for 4 nm wires. 200 nm wires exhibit a similar behavior as bulk bismuth, namely, a linear relationship between the temperature and Seebeck coefficient below about 90 K and then flattens as in bulk bismuth. The temperature dependence of the 9 nm wires shows a  $T^1$  relationship at high temperatures, which is typical for nearly intrinsic semiconductors, but the Seebeck coefficient drops at low temperatures. A similar trend is observed for 4 nm nanowires. The behavior of the very narrow wires, with a diameter below 10 nm, is characteristic of weak localization, not of classical band transport in a semiconductor.

A similar study was undertaken with antimony nanowires. [25] Although the effective masses for the holes of Sb are of the same magnitude as for bismuth, the electron effective masses are much higher. Note that also the energy overlap and carrier concentrations are several orders of magnitude larger. Consequently, the temperature dependence of the resistivity of Sb behaves completely different compared to Bi. Moreover, band structure calculations on Sb nanowires predict a semimetal-to-semiconductor transition to occur below 10 nm.



Figure 3.7. (a) Calculated zT 1D for n-type Bi nanowires oriented along the trigonal axis at 77 K as a function of donor concentration for three different wire diameters. (b) Carrier density of bismuth nanowires as a function of the wire diameter. Image reprinted from [26].

Lin *et al.* calculated that the optimal carrier concentration for n-type doped bismuth nanowires oriented along the trigonal axis would be around  $10^{18}$  cm<sup>-1</sup> as shown in Figure 3.7a. Tellurium could be used as dopant to control the carrier density.

However, a consequence of size quantization is the fact that the carrier density plummets as the wire diameter is reduced as shown in Figure 3.7b. Consequently, in order to keep the carrier concentration at  $10^{18}$  cm<sup>-1</sup> for an optimal *zT* value, doping of the nanowires is required to compensate for the reduced carrier density in the nanowires due to quantization effects.

#### 3.6 Conclusion

Since the pioneering paper of Hicks and Dresselhaus, attempts at making Bi nanowire thermoelectrics have resulted in large thermopowers but not large ZT's. One issue has been that no  $Bi_{1-x}Sb_x$  nanowires could be prepared by conventional methods, whereas theory predicted superior performance in these alloy wires. In summary, the thermoelectric properties of Bi can be enhanced both by doping with Sb and due to size quantization effects, which are the main focus of this work. However, it has been reported that the carrier concentration should drop drastically due to size quantization. Therefore, optimization of the doping level is required to compensate for the freeze out of charge carriers and maximize the thermoelectric performances.

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# 4

### Soft-templating synthesis of mesoporous silica materials

This chapter gives a literature overview of the different soft templating synthesis routes of mesoporous silica and the characterization of mesoporous materials. Further, the synthesis of different mesoporous silica materials which are of interest as hard template material for the synthesis of nanowire networks in their pore channels are discussed. We are interested in how to engineer the pore structure and pore dimensions to meet the requirements of their applications, such as high a pore volume (>  $0.8 \text{ m}^2/\text{g}$ ), large pores (10 - 20 nm) and an interconnected pore structure (3D pore network). Consequently, strategies to tailor the pore diameter and pore discussed.

#### 4.1 Introduction

Porous materials can be ordered or disordered and are usually classified by their pore size. According to the IUPAC definitions, microporous materials have pore diameters of less than 2 nm, mesoporous materials have pore diameters between 2 nm and 50 nm, while macroporous materials have pore diameters which are larger than 50 nm. [1] However, these definitions are somewhat in contrast with the terminology used to classify nanoscale objects. Often, they are referred to as nanoporous materials, exhibiting pore diameters between 1 and 100 nm and a density of the material lower than 60 % of the theoretical density, or in other words a porosity above 40 %. [1]

The first ordered mesoporous material, MCM-41, was discovered by researchers at Mobil Company in 1992. [2] They reported a family of mesoporous silicate molecular sieves (M41S) exhibiting a high surface area (up to 1400 m<sup>2</sup>/g) and narrow pore-size distribution (approximately 1.5 - 10 nm). The MCM-41 materials possess a 2D hexagonal ordered pore structure with uniform pore sizes and amorphous pore walls. MCM-41 could be easily synthesized under hydrothermal conditions using the cationic surfactant family alkyltrimethylammonium with an alkyl chain length from 8 to 22 carbons. As a consequence of this discovery, numerous other ordered mesoporous siliceous materials were developed using

the same "surfactant templating" method, such as SBA-n [3], KIT-n [4], FDU-n [5, 6], etc. The latter were obtained by using various new structural directing surfactants, such as the non-ionic block copolymers consisting of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) chains, known under the trade name Pluronics.

Mesoporous silica materials have become an extremely important class of materials since they can be synthesized in a variety of structures with highly ordered pores, high surface area, high pore volumes and good thermal stability without crystallization and significant loss of porosity up to approximately 550 °C. In addition, the surface can be grafted easily extending its applications to adsorption, catalysis, sensing, etc. However, we are primarily interested in the use of mesoporous silica materials as a template for the synthesis of new materials in their pores, which in principle leads to a negative replica of the template's pore structure. This involves that the structure of the replica depends on the pore structure of the template material. Therefore, the control of the pore structure, the pore diameter and the pore wall thickness are important characteristics of the template, as they determine all the structural properties of the obtained replicated structures. Since the impregnated templates are also subjected to a thermal treatment to convert the precursor salt into the desired product, thermal stability tests are discussed too.

#### 4.2 Soft-templating synthesis of ordered mesoporous silica

#### 4.2.1 Soft templating vs. hard templating

Soft-templating is a process in which an ordered structure of organic molecules is used as "mould" around which a rigid framework of the precursor is build. The term soft refers to the fact the organic molecules do not provide any mechanical strength. Hard templating, on the other hand, makes use of a rigid template which is sufficiently strong to withstand crystal growth within the pores of the template without collapsing.

Typically, the 'soft' templates are a liquid state of cationic, anionic or non-ionic surfactants or a mixture of any of these. Two synthesis mechanisms during the soft-templating process are sol-gel or evaporation induced self-assembly processes. These routes are particularly suitable for the synthesis of mesoporous silica since the hydrolysis and condensation rate of silicates can be easily controlled by altering the pH or temperature while the silica remains amorphous above 550 °C. Consequently, the structural directing agent can be removed by calcination while the ordered pore structure is preserved. In general it is very difficult to synthesize crystalline mesoporous materials in that way, due to the fact that their crystallization forces destroy the 'soft' liquid crystal lattice leading to structural collapse. [7] The latter is the case for most metal oxides, but SiO<sub>2</sub> is an exception since it remains amorphous at relatively high temperatures.

Mesoporous silica or mesoporous carbon are typically used when rigid template material is required [8], such as for the nanocasting of typically metal oxide, which is discussed in detail in Chapter 5. In brief, a metal nitrate solution is impregnated into the pores of the "hard" template material, while the solvent is allowed to evaporate. Subsequently, the impregnated template is subjected to a calcination treatment, causing the decomposition of the precursor and formation of a metal oxide inside the template's pores. An ordered replicated structure can only be obtained provided that the template can withstand the crystallization forces, which is generally the case for silica and carbon materials, but not for organic surfactants. Since the

materials of interest during this research cannot be made via soft-templating methods, silica is chosen here as hard template for the nanocasting procedure.

The mechanism in which the surfactant forms a soft template, for example during the synthesis of mesoporous silica, occurs through two main pathways, namely, cooperative self-assembly and the 'true' liquid-crystal templating process.

#### 4.2.2 Cooperative surfactant-templating assembly with inorganic oligomers

This synthesis mechanism is based on the electrostatic interaction between the inorganic precursor, such as silicates, and the surfactants, forming inorganic - organic or hybrid mesostructured composites in solution. The silicate species on the precursor - template interface cooperatively polymerize and cross-link, influencing the charge density between the inorganic and organic species. During the reaction, the cooperative ordering of surfactants and the charge density between the inorganic and organic species influence each other causing the mesophase to order into a 3D ordered arrangement with the lowest energy. A schematic representation of the cooperative surfactant templating assembly is depicted in Figure 4.1. Stucky and co-workers proposed the surfactant precursor interactions S<sup>+</sup>I<sup>-</sup>, S<sup>-</sup>I<sup>+</sup>, S<sup>+</sup>X<sup>-</sup>I<sup>+</sup>, S<sup>-</sup>X<sup>+</sup>I<sup>-</sup>, and S<sup>0</sup>H<sup>+</sup>XI<sup>+</sup> with S<sup>-</sup> surfactant anions, S<sup>+</sup> surfactant cations, S<sup>0</sup> neutral surfactants, I<sup>+</sup> inorganic precursor cations, I<sup>-</sup> inorganic precursor anions, X<sup>+</sup> cationic counter ions, H<sup>+</sup> hydroxonium cations and X<sup>-</sup> anionic counter ions. [6] In order to synthesize mesoporous materials, it is important to adjust the surfactant chemistry head according to the inorganic precursor. For example, the synthesis of mesoporous silica under basic conditions yields silicate anions ( $\Gamma$ ), which requires a cationic surfactant head ( $S^+$ ), forming the double layer  $S^+I^-$ . However, the organic – inorganic assembly is also possible when the surfactant ( $S^+$ ) and the inorganic precursor ( $I^+$ ) possess the same charge, provided that a counter ion X<sup>-</sup> acts as bridge, forming the interaction  $S^{+}X^{-}I^{+}$  under acidic conditions.



Figure 4.1. Schematic representation of cooperative assembly mechanism of mesoporous materials. Image modified from [9].

A milestone in the field of mesoporous material synthesis was the development of a synthesis route of mesoporous silica using the non-ionic poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) triblock copolymers (Figure 4.2) reported by Zhao *et al.* [3] Mesoporous silica with large pores and thick pore walls were obtained, with tuneable pore diameter and better hydrothermal stability than the earlier discovered MCM materials. The [PEO]<sub>x</sub> [PPO]<sub>y</sub> [PEO]<sub>x</sub> triblock copolymer consists of hydrophilic poly(ethylene oxide) tails and a hydrophobic poly(propylene oxide) core. An important characteristic of the surfactant is the fact that the solvation of the PEO chains is entropically unfavourable. Consequently, the PEO chains become more hydrophobic at higher temperatures. The aggregation of the triblock copolymer is schematically depicted in Figure 4.3. It can be seen that the core of the micelles consists of

the PPO chains, which are hydrophobic, while the PEO tails are more hydrophilic. During the synthesis of mesoporous silica using this structural directing agent, the PEO branches penetrate into the silica framework and interact with the silanol groups through hydrogen bonding. It is known that by increasing the temperature above approximately 80 °C, the interactions between the PEO chains and the silica framework become unfavourable. In order to reduce these polar interactions, the PEO chains tend to bundle together with PEO chains of adjacent micelles as shown in Figure 4.3. As the number of chains in the bundles increases with temperature, it was shown by Galarneau *et al.* that this caused an enlargement of the micropores during the synthesis of SBA-15 mesoporous silica. [10] Simultaneously, the unfavourable interactions of PEO and the polar silica framework at increasing temperatures are reduced by the interaction of the PEO chains with the PPO chains, causing the core of the micelles to swell. [10]



Figure 4.2. Structure of the triblock copolymer [PEO]<sub>x</sub> [PPO]<sub>y</sub> [PEO]<sub>x</sub>.



Figure 4.3. Schematic representation of the micelle formation and temperature dependence of PEO-PPO-PEO triblock copolymers. Image reproduced from [10].



Figure 4.4. Phase diagram of P123,  $[EO]_{20}[PO]_{70}[EO]_{20}$  (left). Phase diagram of mesophase structures obtained based on XRD measurements. The mesoporous silica was synthesized with a molar ratio of 0.017 P123/x TEOS/y BuOH/1.83 HCl/195 H<sub>2</sub>O (right). Image reproduced from [4, 11].

The pore structure, on the other hand, is affected by the nature of the triblock copolymer, temperature, additives such as salts, co-solvents, reaction temperature, surfactant to silica precursor ratio and pH. [3, 12, 13] It can be seen in Figure 4.4 that the surfactant concentration of P123 ([EO]<sub>20</sub>[PO]<sub>70</sub>[EO]<sub>20</sub>) and temperature determines the pore structure of the synthesized

silica materials. Between a surfactant concentration of 20 and 40 w% and between 10 and 45°C, P123 forms a cubic micelle structure, while a hexagonal lattice structure is obtained at higher surfactant concentrations. [4] The addition of butanol as cosolvent can also change the micelle structure as is shown in the right graph of Figure 4.4. Namely, depending on the TEOS to butanol ratio, disordered, hexagonal, mixed hexagonal-cubic and cubic micelle structures are obtained.

The ability to synthesize highly ordered mesoporous silica materials originates from the fact that the hydrolysis and condensation reactions can be precisely controlled, while the structure remains amorphous up to high temperatures. Namely, while the structural directing agent is removed by thermal decomposition in air below 550 °C the pore structure does not collapse. On the contrary, when the material would crystallize during the thermal decomposition treatment of the template, the porous would collapse due to crystal growth. The precipitation of the silica framework around the liquid crystal lattice during its synthesis can be both occur under acid (Figure 4.5a) and basic conditions (Figure 4.5b). Generally, the precipitation of silica precursor chemistry, while the reaction speed is determined by the  $OH^-$  concentration under basic conditions. Under acid conditions, a fast equilibrium is obtained between the  $\equiv Si - OR$  precursor and its protonated form, which hydrolyses to  $\equiv Si - OH$  (silanol). The speed of the condensation step is determined by the kinetics of the substitution of  $\equiv Si - O^+RH$  with  $^-O - Si \equiv$  and the elimination of R - OH.

(a) Hydrolysis

Condensation

$$-$$
Si $-$ OH +  $-$ Si $-$ O<sup>+</sup><sub>H</sub> Slow  $-$ Si $-$ O $-$ Si $-$  + R $-$ OH

(b) Hydrolysis

$$-$$
Si OR + OH  $-$ Si OH + R-C

Condensation

$$\rightarrow$$
Si-OH  $\rightarrow$   $\rightarrow$ Si-O<sup>T</sup> + H<sub>2</sub>O  $\rightarrow$ Si-OR  $\rightarrow$ Si-O-Si/T + R-O<sup>T</sup>

Figure 4.5. Reaction mechanisms of tetraethyl orthosilicate (TEOS) under (a) acidic and (b) basic conditions. Image reproduced from [14].

Under basic conditions, on the other hand, the substitution of  $\equiv Si - OR$  with  $OH^-$  is the speed determining step. As the  $OH^-$  concentration is pH dependent, it controls the reaction speed. The condensation reaction under basic conditions occurs through the deprotonation of the silanol moiety and subsequent reaction with the silica precursor.

#### 4.2.3 Evaporation induced self-assembly

In this reaction mechanism, true liquid crystal mesophases are formed at high surfactant concentrations while the inorganic precursor forms an amorphous framework around the template's liquid-crystal scaffolds, copying the pore sizes and symmetries. The high concentration of surfactant and the formation of the liquid crystal is usually achieved by evaporating the solvent as depicted in Figure 4.6. During the evaporation of the volatile solvent, a tuneable steady state is formed, which still allows altering of the mesostructure by changing the relative humidity (RH). After condensation, the structural directing template is typically removed by calcination or extraction. The method is referred to as evaporation induced self-assembly or EISA. The method has been used for the synthesis of both mesoporous carbon frameworks [15, 16] and metal oxides [17, 18].



Figure 4.6. Schematic representation of liquid-crystal templating pathways. Image reproduced from [9].

#### 4.3 Removal of the structural organic directing agent

After the soft-templating synthesis of mesoporous silica materials, the surfactant remains in the pore. Typically, the organic structural directing agents can be removed through solvent extracting, calcination or microwave digestion. An overview of the different methods is given here.

#### 4.3.1 Solvent extraction

The removal of [PEO]<sub>x</sub> [PPO]<sub>y</sub> [PEO]<sub>x</sub> structural directing agents through solvent extraction is based on the high solubility of the organic liquid crystal template in for example acetone. The process to extract the surfactant from the silica material can be compared with the washing of the silica material on a filter with boiling acetone. Since not all the surfactant is removed at once, the process is repeated multiple times. In general, a soxhlet extractor is used to automate the extraction of the surfactant. An image of this glassware is shown in Figure 4.7. In a typical extraction procedure, approximately 150 mL acetone is refluxed at a bath temperature of 110 °C for 5 h. The mesoporous silica powder is placed in a filter tube and positioned in such way that the condensed acetone drops into the filter tube. [19]



Figure 4.7. Schematic of soxhlet extractor.

#### 4.3.2 Microwave digestion

In the microwave digestion treatment, the structural directing agent is chemically removed in a solution of nitric acid and hydrogen peroxide. It is generally used for the removal of PEO-PPO-PEO type triblock copolymers. A typical characteristic of mesoporous silica treated via the microwave digestion technique is the hydrophilic nature of the surface, because all silanol moieties on the surface remain. Typically, the mesoporous silica is dispersed in 12 mL concentrated HNO<sub>3</sub> and 8 mL H<sub>2</sub>O<sub>2</sub> (30%) in a Teflon vessel and treated in a microwave oven at approximately 200 °C under a pressure of 1.3 MPa for 2 min. [20]

#### 4.3.3 Calcination

The most used method to remove the organic surfactant from the mesoporous silica is through a thermal treatment in air. Herefore, the powder is heated at a rate of 2 °C/min to 550 °C, with a dwell time of 6 h.

#### 4.4 Characterization of mesoporous materials by N<sub>2</sub> physisorption

Sorption measurements are an important characterization technique for mesoporous materials, since they provide insight into the pore structure, pore volume, pore diameter and surface area of mesoporous materials. Various gasses, such as nitrogen, argon, carbon dioxide, etc. can be used as probe gas. Typically, nitrogen adsorption at 77 K is used as it is recommended by the IUPAC for the determination of the surface area and mesopore size distribution. Adsorption in micropores (< 2 nm) is dominated by strong interactions between the probe molecules and the pore walls, which occurs at a relatively low pressure. Adsorption in mesopores (between 2 nm and 50 nm), on the other hand, is dominated by capillary condensation, which results in a quick increase of the volume of adsorbed gasses for a small increase in relative pressure. A N<sub>2</sub> sorption measurement is conducted by exposing the sample to a controlled gas environment at a constant temperature while the volume of adsorbed or desorbed gas is measured as a function of the relative pressure. [1]



Figure 4.8. IUPAC classifications of isotherms. Image reproduced from [1].

The shape of the sorption isotherms reflects the characteristics of the pore structure and can be divided into six classes as depicted in Figure 4.8. In all cases, a low surface coverage results in a linear sorption isotherm. Type I is concave in respect to the P/P<sub>0</sub> axis and reaches a saturation value as P/P<sub>0</sub> reaches 1. This reversible type of isotherm is typically observed on microporous solids with a small external surface compared to its total surface (e.g. activated carbon, microporous molecular sieves, zeolites and alumina). The steep increase of adsorbed gas at a low relative pressure is typical for microporous materials. Type I(a) isotherms are obtained from microporous materials with narrow micropores, whereas Type I(b) isotherms are observed with materials having wider micropores and possibly narrow mesopores. The reversible Type II curve is a typical isotherm for macroporous and non-porous materials, representing an unlimited monolayer-multilayer adsorption on their surfaces. Point B indicates the relative pressure at which the monolayer coverage is considered completed and multilayer coverage begins. Type III isotherms exhibit a convex curve with respect to the P/P<sub>0</sub> axis of the entire range and are not often encountered and result from a weak adsorbate-solid and strong adsorbate-adsorbate interactions, typically observed in the adsorption of water vapour on nonporous carbon. Characteristic for the Type IV(a) isotherm is the occurrence of an adsorption/desorption hysteresis which starts to occur for pore sizes larger than approximately 4 nm. The hysteresis loops originate from the difference in pressure at which the capillary condensation and capillary vaporization of the adsorbate within the mesopores occurs. A steep curve in the capillary condensation regime indicates a narrow pore-size distribution. Type IV isotherms are particularly observed in ordered mesoporous materials. **Type IV(b)** is observed for mesoporous materials with pores sizes smaller than approximately 4 nm. The initial part of the Type V isotherms follows the same trend as the Type II isotherm, namely, the monolayer-multilayer adsorption. **Type V** isotherms are uncommon and are related with the Type III isotherm. The **Type VI** isotherm represents stepwise multilayer adsorption on a uniform non-porous surface.



Figure 4.9. IUPAC classification of hysteresis loop types. Image reproduced from [1].

According to IUPAC terminology, isotherm hysteresis loops are classified into four types as shown in Figure 4.9. The shapes of hysteresis loops are often characteristic for specific pore structures. Type H1 and H4 are the most extreme cases, while the other two are more intermediate cases. The Type H1 hysteresis loop exhibits parallel and almost vertical branches, which are characteristic for mesoporous materials with a cylindrical mesopore geometry and a high uniformity in pore-sizes. **Type H2** loops are especially difficult to interpret. The steep desorption branch, as observed in the H2(a) loops, can be attributed either to poreblocking in a narrow range of pore necks or to cavitation-induced evaporation. This type of isotherms are observed for instance in SBA-16. The **Type H2(b)** loop is also associated with pore blocking, but the size distribution of neck widths is much larger, which does no longer gives the sharp desorption isotherm. Type H2(b) isotherms are observed in mesocellular silica foams. The **Type H3** loop, which does not form any limiting adsorption at high P/P<sub>0</sub>, is observed with aggregates of plate-like particles giving rise to split-shaped pores. Type H4 loop is believed to be associated with narrow split-like pores, while the Type I isotherm behaviour indicates the presence of microporosity. The **Type H5** hysteresis loop has a distinctive from associated with certain pore structures containing open and partially blocked mesopores. Typically, they are observed in plugged hexagonal templated silica materials.

The BET method of Brunauer, Emmett, and Teller is employed to determine surface area on a model of adsorption which incorporates multilayer coverage, while the BJH method of Barrett, Joyner, and Halenda is a procedure for calculating pore size distributions from experimental

isotherms using the Kelvin model of pore filling, which applies to the mesopore and small macropore size range.

An error analysis on  $N_2$  sorption measurements reported by De Lange *et al.* [21] showed that the BET surface area was determined with a confidence level of 95 % with an error of typically  $\pm 5$  % and a maximum error of  $\pm 20$  %. Further, it was reported that the pore volume at a relative pressure P/P<sub>0</sub> = 0.9 was determined with a 95 % confidence level of  $\pm$ 5 %, provided that less than 0.1 g sample is used for strongly adsorbing materials, 0.2 to 0.3 g for moderately adsorbing materials and more than 0.5 g for poorly adsorbing materials. If those guidelines are not followed, the error can be as large as  $\pm 10$  %. When determining the BJH pore size distribution, the desorption isotherm below a relative pressure  $P/P_0 = 0.42$  should not be used. This limits the minimum relevant pore diameter calculated from the desorption branch to 3.4 nm. However, lower pore diameter can still be measured when derived from the adsorption isotherm. It was further reported that the uncertainty on the pore size distribution was negligible below a pore diameter of 50 nm. However, the confidence level for the increment of the pore volume per diameter increases as the pore diameter decreases. In other words, the error on volume contribution of pores with a certain pore diameter is the largest for small pore diameters. Moreover, the magnitude of the 95 % confidence level prevented drawing quantitative conclusions for pore diameters below 10 nm.



Figure 4.10. Typical N<sub>2</sub> physisorption isotherms of SBA-15.

Nitrogen sorption experiments were performed at 77 K with a Micromeritics TriStar 3000 device. Samples were vacuum dried at 120 °C for 12 h prior to analysis. The surface area was calculated using the BET method while the pore size distribution was determined by analysis of the adsorption branch of the isotherms using the BJH method. [22, 23]

A typical N<sub>2</sub> sorption isotherm of SBA-15 is shown in Figure 4.10. At low relative pressures  $(0.01 < P/P_0 < 0.15)$ , the volume of adsorbed gas is determined by the micropores, while the adsorption in mesopores occurs at intermediate pressures and close to  $P/P_0 \approx 1$  in macropores. The intersect of the isotherm with the vertical axis at very low pressures is a measure for the micropore volume, whereas the height of the isotherm on the right-hand side (close to  $P/P_0 = 1$ ) is a measure for the total pore volume. Information about the pore size can be deduced from



the relative pressure at which the capillary condensation starts. Namely, the smaller the pores, the lower the relative pressures required for the capillary condensation to occur.

Figure 4.11.  $N_2$  sorption isotherms for (a) pore system with open mesopores and micropores inside the walls, (b) pore system with plugs at the pore orifices of the mesopores and micropores inside the walls, and (c) pore system with plugs inside the mesopores, consisting of open and blocked pores. Images modified from [24, 25].

The shape of the capillary condensation also gives information about the pore structure. Van Der Voort *et al.* reported the synthesis of plugged hexagonal templates, shown in Figure 4.11. [24, 25] In the case of cylindrical pores, the capillary condensation and evaporation are parallel (Figure 4.11a), whereas the capillary evaporation is delayed when the pore orifice are blocked (Figure 4.11b). In the case plugs were formed inside the pores rather than at the pore openings, the isotherm showed a contribution of normal capillary evaporation for cylindrical pores and a delayed evaporation due to plugs inside the pores.

#### 4.5 Overview of mesoporous silica templates used for nanocasting

#### 4.5.1 MCM-41 materials

MCM materials are typically synthesized using the ionic surfactant cetyltrimethylammonium bromide (CTAB). [2] Cylindrical pores with a diameter from 1 - 3 nm and thin pore walls of 1 - 2 nm are typically obtained. The pore structure of MCM-41 consist of a hexagonal symmetry with the *P6mm* space group symmetry. Due to the small pores and relatively low hydrothermal stability, it is challenging to use MCM materials as template for the synthesis of replica structures in its pores. Nevertheless, MCM-41 is of interest as template for nanocasting, since the isolated linear pores could be used for the synthesis of single nanowires. The material has very similar structural properties that of SBA-15, but it does not have micropores in the pore walls.

#### 4.5.2 SBA-15

#### 4.5.2.1 Structural properties

SBA-15 is a 2D ordered mesoporous silica material consisting of cylindrical pores with a hexagonal symmetry, belonging to the P6mm space group. Although SBA-15 is structurally very similar with MCM-41 [2], SBA-15 has larger pores, the pore walls are thicker and the mesopores are interconnected through micropores as depicted in Figure 4.12.



Figure 4.12. Schematic representation of SBA-15, consisting of hexagonally ordered mesopores interconnected through micropores in the pore walls and the structure's replica.



Figure 4.13. Low angle X-ray diffractogram of SBA-15 mesoporous silica (stirring for 5 h at 45 °C, ageing at 90 °C for 18 h and calcined at 550 °C for 6 h and 2 °C/min heating rate) and its carbon replicated structure named CMK-3 (impregnation of carbon precursor through refluxing in 25 v% furfuryl alcohol and 0.5 v% 0.1 mol/L  $H_2SO_4$  in toluene at 100 °C for 36 h, polymerization at 150 °C for 5 h and carbonization at 1100 °C for 1 h in  $Ar - 5 v\% H_2$ ) after chemical etching of the silica template.

Although the pore walls of mesoporous silica materials are amorphous, the ordered pore channels give rise to a long-range ordering which could be measured by low angle X-ray diffraction measurements (Figure 4.13). The larger pores of SBA-15 facilitate diffusion and the impregnation of larger molecules in the template, while the thicker pore walls provide better hydrothermal stability of the framework than its small pore counterpart MCM-41. The micropores present in the walls originate from the Pluronic surfactant that forms bridges between the mesoporous crystal lattice as shown in Figure 4.3. The presence of the micropores could not be identified via TEM imaging (Figure 4.14), however, their presence could be indirectly revealed when the silica template was used as template for the synthesis of e.g. a mesoporous carbon replicate structure via a nanocasting procedure. In summary, when a soluble carbon precursor, such as furfuryl alcohol, is impregnated in the pores of SBA-15 and subsequently carbonized, a replica of the pore structure is obtained. In case no micropores would be present, nanowires would be obtained. However, in reality, carbon

replicated structures from SBA-15 lead to rods which are interconnected with thin bridges, what confirms the presence of the micropores in the pore walls of SBA-15. Using Bragg's law,  $n\lambda = 2d \sin \theta$ , the d-spacings for the (100), (110) and (200) reflections of the pattern for SBA-15 in Figure 4.13 could be derived, giving us the values 9.00 nm, 5.41 nm and 4.72 nm, respectively. The replicated carbon structure (CMK-3) of SBA-15 resulted in the retention of the structural ordering. However, the shift of the diffraction peaks of the carbon replica compared to the parent SBA-15 structure indicate that 6-7% shrinkage occurred (calculated based on the d-spacing of the (110) reflections, which were approximately 8.4 nm and 9 nm for, respectively, CMK-3 and SBA-15). The lattice parameter for a hexagonal lattice could be calculated using Eq. 4.1:

$$\frac{1}{d^2} = \frac{4}{3} \cdot \left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$
 Eq. 4.1

The unit cell constant *a* was derived based on all reflections, with an average value of 10.7 nm. An estimation of the pore wall thickness, *t*, for a hexagonal system could be made by subtracting the pore diameter, *D*, from the cell constant, *a* as: t = a - D. [26] The pore diameter was determined using the BJH model on the adsorption branch of the N<sub>2</sub> sorption isotherm, which is given in Figure 4.17. According to the BJH pore size distribution plot, an average pore diameter of 6 nm was measured for SBA-15 calcined at 550 °C. Consequently, the thickness of the pore walls was estimated to be 4.7 nm.



Figure 4.14. Typical TEM images of SBA-15 mesoporous silica (stirring for 5 h at 45 °C, ageing at 90 °C for 18 h and calcined at 550 °C for 6 h and 2 °C/min heating rate).

As shown in §4.5.2.2, the synthesis of SBA-15 type mesoporous silica consists of three steps: the stirring step, ageing step and a thermal treatment. The same steps will return for the synthesis of SBA-16, KIT-6 and FDU-12, as it is the typical procedure for the synthesis of mesoporous silica under acid conditions, using Pluronics as structural directing agents. Galarneau *et al.* reported that the pore diameter of SBA-15 increased when the ageing temperature during the synthesis was enhanced from 60 °C to 130 °C [10]. In addition, it was shown that no micropores between the mesopores were present when the template was aged at 60 °C, while micropores of approximately 1.5 - 4 nm were formed at an ageing temperature of 100 °C. At an ageing temperature of 130 °C the micropores grew in diameter and formed mesopores with a diameter of approximately 1.5 - 5 nm as depicted in Figure 4.15.



Figure 4.15. Schematic representation of the pore diameter and micropore-mesopore interconnections during the synthesis of SBA-15 as a function of the ageing temperature. No mesopores were observed when aged around 60  $^{\circ}$ C (A), while micropore connections were formed between the mesopores when aged at 100  $^{\circ}$ C (B) and mesopore connections were present when aged at 130  $^{\circ}$ C. Figure adapted from [10].



Figure 4.16. Theoretical pore volume (a) and surface area (b) of SBA-15 as a function of the wall thickness, *t*, and cell parameter, a. The dashed line indicates the cell parameters for SBA-15 materials. Figure replicated from [10].

Theoretical values of the surface area and pore volume as a function of the wall thickness and cell parameters of SBA-15 type mesoporous silica reported by Galarneau *et al.* are shown in Figure 4.16, which shows that for a fixed lattice parameter a, the surface area and pore volume increases when the pore wall thickness reduces.

#### 4.5.2.2 Synthesis

SBA-15 was synthesized by dissolving 4 g P123 ([EO]<sub>20</sub>[PO]<sub>70</sub>[EO]<sub>20</sub>) in 120 mL 2M HCl and 30 mL distilled water at RT. Next the solution was heated to 45 °C and 9.1 mL TEOS was added while stirring at 700 rpm. The mixture was stirred at that temperature for 5 h and

subsequently aged at 90 °C for 18 h under static conditions. Finally, the precipitate was collected via filtration, dried overnight at RT and calcined at 550 °C for 6 h in air, using a heating rate of 2 °C/min. [3] The synthesis of SBA-15 could be easily scaled up in a 2 L round bottom flask, provided that the solution was stirred vigorously. Typically, an egg shaped stirring bar of 50 x 25 mm was used, which provided sufficient stirring power for a 2 L round bottom flask.

#### 4.5.2.3 Influence of the synthesis parameters on the material properties

Typically, the SBA-15 mesoporous silica material synthesized here was aged at 90 °C what resulted in mesopores with a diameter of approximately 7 nm, a pore volume of approximately 0.8 cm<sup>3</sup>/g and a BET surface area of 850 m<sup>2</sup>/g after calcination at 550 °C. The influence of the ageing temperature on the pore diameter was not studied on SBA-15, but the knowledge acquired by Galarneau *et al.* was tested on KIT-6 mesoporous silica.

#### 4.5.2.4 Thermal stability of SBA-15

The thermal stability of SBA-15 mesoporous silica was studied by synthesizing the material using a stirring step at 45 °C, an ageing step at 100 °C and performing the calcination at 550, 700, 800 and 850 °C for 6 h. The samples were heated in air with a rate of 2 °C/min. The N<sub>2</sub> sorption isotherms and BJH pore size distribution plots of the material calcined at different temperatures are depicted in Figure 4.17.

A summary of the mesopore properties obtained via N<sub>2</sub> sorption measurements of the samples calcined at different temperatures is shown in Table 4.1. It can be seen that particularly the micropore surface area drops between 550 and 700 °C, followed by a quick reduction of the BET surface area above 800 °C. At 850 °C, no micropore surface area remained while the pore diameter, D, dropped from 6 nm to 5 nm when calcined at 550 and 850 °C, respectively. Note that SBA-15 calcinated at 850 °C does not lead anymore to a mesoporous replica when it is used as template material in the nanocasting procedure, but to individual nanowires. Namely, as the micropores (derived via the t-plot method) completely disappeared, no structural interconnections between the mesopores remain. In this case, the template has become similar with MCM-41, which also possesses cylindrical pores without micropores in its walls.



Figure 4.17. (a) Nitrogen sorption isotherms of SBA-15 calcined at different temperatures (stirring at 45 °C for 5 h, ageing at 90°C for 18 h and at 550, 700, 800 and 850 °C for 6 h and 2 °C/min heating rate). (b) BJH pore size distribution plot calculated on the adsorption branch of the  $N_2$  sorption isotherm for SBA-15 calcined at different temperatures.

	Calcination Temp. (°C)	BET Surface Area (m²/g)	Micropore Area (m²/g)	Vp (cm³/g)	D (nm)
SBA-15	550	875	252	0.8	6.0
SBA-15	700	737	196	0.7	5.6
SBA-15	800	404	27	0.6	5.2
SBA-15	850	286	0	0.45	4.9

Table 4.1. Mesopore characteristics of SBA-15 calcined at different temperatures (stirring at 45 °C for 5 h, ageing at 90°C for 18 h and calcined at 550, 700, 800 and 850 °C for 6 h and 2 °C/min heating rate).

#### 4.5.3 SBA-16 mesoporous silica

#### 4.5.3.1 Structural properties



Figure 4.18. Cage like 3D ordered pore system of SBA-16 and its replicated structure. Images reprinted from [27, 28].

SBA-16 is a 3D ordered cubic mesoporous material with the  $Im\overline{3}m$  space group symmetry. The pore system consists of cavities connected through smaller pores, called windows. Similar to SBA-15, the pore walls possess micropores, but they are not essential to support the structure when its carbon replica for instance is made. Namely, the replicated pore cavities are interconnected through the replicated windows (Figure 4.18) and not the micropores as is the case for SBA-15.



Figure 4.19. (a) Typical TEM images of SBA-16 (stirring for 20 h at 45 °C, ageing at 80 °C for 24 h and calcined at 550 °C for 6 h and 2 °C/min heating rate) (b) TEM image of SBA-16 along (100) direction, reprinted from Ref. [27].

Figure 4.19 compares the TEM images of SBA-16 (a) synthesized in house, and (b) a HR TEM image reported by Sakamoto *et al.* [27] In the latter case, similar images were obtained along the (110) and (111) crystallographic axes, what confirms the 3D oriented cubic pore system. The TEM image of our sample shown in Figure 4.19a seems less ordered than Figure 4.19b

obtained from Ref. [27], but this may also be due to the random orientation of the particle. The pore diameter and wall thickness are of comparable dimensions.

Figure 4.20 shows a typical low angle X-ray diffraction pattern of SBA-16 synthesized via the conditions described in §4.5.3.2. The pattern reveals the long-range ordering of the pores of the material. Similarly, as before, the lattice parameter could be derived from the diffraction peaks. An average value of the lattice parameter a = 15.2 nm was derived using Bragg's law and Equation 4.2 for the calculation of the lattice parameter of a cubic unit cell:



Figure 4.20. Low angle X-ray diffraction pattern of SBA-16 mesoporous silica (stirring for 20 h at 45 °C, ageing at 80 °C for 24 h and calcined at 550 °C for 6 h and 2 °C/min heating rate).

It was calculated by Ravikovitch *et al.* that the wall thickness of a cubic  $Im\overline{3}m$  structure could be estimated as:  $t = \frac{\sqrt{3}}{2}a - D$ . [26] N<sub>2</sub> sorption measurements were performed in order to estimate the pore diameter of the SBA-16 sample. The average pore diameter based on the BJH pore size distribution plot shown in Figure 4.21b is approximately 6.8 nm. Consequently, the estimated pore wall thickness of the synthesized SBA-16 is approximately 6.4 nm.

It can be seen from the desorption isotherm in Figure 4.21a that a delayed capillary evaporation occurs, which is typical for mesoporous materials exhibiting two types of pores. Namely, the pores consist of cages, connected via smaller pores causing the capillary evaporation to occur at a lower partial pressure than the capillary condensation of  $N_2$  gas. The presence of two types of pores could also be identified from the asymmetry in the BJH pore size distribution plot shown in Figure 4.21b. Namely, the pore volume as a function of pore diameter is higher for bigger pores than for smaller ones, which shows that the cages contribute for a larger fraction to the total pore volume compared to the small ones.

The size of the pore entrances or "windows" of SBA-16 can be controlled by changing the ageing temperature. It was shown already for SBA-15 that the PEO chains aggregate at higher temperatures as the interaction with the silica framework becomes less favorable. Consequently, the aggregated bundles of PEO increase in diameter with temperature and time, which form the pore entrances after template removal. [29]



Figure 4.21. (a)  $N_2$  sorption isotherms of SBA-16 (stirring for 20 h at 45 °C, ageing at 80 °C for 24 h and calcined at 550 °C for 6 h and 2 °C/min heating rate) and (b) BJH pore size distribution plot calculated from the adsorption isotherm of SBA-16.

#### 4.5.3.2 Synthesis

SBA-16 was synthesized by dissolving 4 g F127 ( $[EO]_{106}[PO]_{70}[EO]_{106}$ ) in 129.4 mL distilled water and 20.6 mL 36% HCl at RT. Next the solution was heated to 45 °C and 12 mL TEOS was added while stirring at 700 rpm. The mixture was stirred at that temperature for 20 h and subsequently aged at 80 °C for 24 h under static conditions. Finally, the precipitate was collected via filtration, dried overnight at RT and calcined at 550 °C for 6 h in air with a heating rate of 2 °C/min. [3]

#### 4.5.3.3 Results and discussion

The asymmetry in the BJH pore size distribution plot in Figure 4.21b indicates the presence of pores with different diameters. The estimated size of the windows is approximately 2 - 5 nm, what makes the material useful as template for the nanocasting technique (see Chapter 5).

#### 4.5.4 KIT-6 mesoporous silica

#### 4.5.4.1 Structural properties

KIT-6 mesoporous silica consists of two sets of mesopores, forming a bicontinuous pore system with a cubic crystal symmetry and  $Ia\overline{3}d$  space group. In contrast to SBA-16, KIT-6 has cylindrical pores, which can also be deduced from the parallel capillary condensation and capillary evaporation in the N<sub>2</sub> sorption isotherms depicted in Figure 4.25 and Figure 4.26 or



Figure 4.22. Schematic representation of the pore structure of KIT-6 and its replica. Image modified from [30].

symmetry in the BJH pores size distribution plot.

KIT-6 has is often used as template for nanocasting, however, the bimodal pore system can lead to a partial replication of the template as shown in Figure 4.22. The latter leads to bigger pores, and a change of space group symmetry.



Figure 4.23. Low angle diffraction pattern of KIT-6 mesoporous silica aged at 100 °C (stirring for 24 h at 35 °C, ageing at 100 °C for 24 h and calcined at 550 °C for 6 h and 2 °C/min heating rate).



Figure 4.24. (a) Typical TEM image of KIT-6 mesoporous silica (stirring for 24 h at 35 °C, ageing at 100 °C for 24 h and calcined at 550 °C for 6 h and 2 °C/min heating rate). (b) TEM image of KIT-6 mesoporous silica, reprinted from Ref. [31].

A typical low angle diffraction pattern of KIT-6 is depicted in Figure 4.23. The most intense reflection used to calculate the lattice parameter were (211) and (220), with an average a = 19.8 nm (Figure 4.23). Using the pore diameter obtained from the BJH pore size distribution plot (Figure 4.25), an estimate of the wall thickness for an  $Ia\overline{3}d$  cubic structure could be can be made as:  $t = \frac{a}{2} - D$ , giving a wall thickness of approximately 2.4 nm. Typical TEM images of KIT-6 synthesized in house and reported by Xu et al. are depicted in Figure 4.24.

#### 4.5.4.2 Synthesis

KIT-6 was synthesized by dissolving 4 g P123 in 150 mL 0.5 mol/L HCl solution and 4.9 mL butanol at RT. Next the solution was heated to 35 °C and 9.2 mL TEOS was added while vigorous stirring. The mixture was stirred at that temperature for 24 h and subsequently aged at 90 °C for 24 h under static conditions. Finally, the precipitate was collected via filtration,

dried overnight at RT and calcined at 550 °C or 700 °C for 6 h in air with a heating rate of 2 °C/min. [4] Similarly, as for SBA-15, the synthesis of KIT-6 could be easily scaled up in a 2 L round bottom flask provided that the solution was stirred with an egg shaped stirring bar of  $50 \times 25$  mm.

#### 4.5.4.3 Results and discussions

Influence of ageing temperature on pore diameter of KIT-6



Figure 4.25. (a)  $N_2$  sorption isotherms and (b) BJH pore size distribution plot of KIT-6 synthesized with different ageing times (stirring for 24 h at 35 °C, ageing at 100 °C or 150 °C for 24 h and calcined at 550 °C for 6 h and 2 °C/min heating rate).

The pore diameter of the KIT-6 materials synthesized by us were typically between 5 and 7 nm. The standard synthesis conditions of KIT-6 involve a stirring step at 35 °C, ageing step at 90 °C and a thermal treatment at 550 °C. However, the pore diameter could be doubled by increasing the ageing temperature and ageing time.

The N<sub>2</sub> sorption isotherm in Figure 4.25 shows how the pore diameter and pore volume increase as the ageing temperature is increased from 100 to 150 °C. Namely, the shift of the capillary adsorption and desorption isotherms towards higher relative pressures  $P/P_0$  indicates an enlargement of the pores while the stretch along the vertical axes shows that the total pore volume increased. The effect of the ageing temperature on the creation of larger micropores of the micelles was explained in §4.5.2.1 for SBA-15 mesoporous silica.

#### **Thermal stability of KIT-6**

A summary of the BET surface area, micropore volume, total pore volume and the pore diameter of KIT-6 synthesized with different ageing times and calcination times are given in Table 4.2. It can be seen from the downwards shift of the N<sub>2</sub> sorption isotherms in Figure 4.26 and the reduction of the micropore surface area in Table 4.2 that the micropores disappear when the calcination temperature was increased from 550 °C to 700 °C. Also, the total BET surface area and the total pore volume reduced slightly. However, both the surface area and pore volume dropped completely when the sample was calcinated at 850 °C. SBA-15, on the contrary, loses all its micropores, but keeps most of its mesopores at that temperature. Consequently, the thermal stability of KIT-6 is inferior to that of SBA-15 mesoporous silica. It will be clear later that this is important in the nanocasting procedure of oxides since the silica material is what acts as rigid template for the synthesis of its replicated structure.


Figure 4.26.  $N_2$  sorption isotherms of KIT-6 mesoporous silica calcinated at different temperatures (stirring for 24 h at 35 °C, ageing at 100 °C for 24 h and calcined at 550, 700 and 850 °C for 6 h and 2 °C/min heating rate).

Table 4.2. Mesopore characteristics of KIT-6 synthesized with different ageing and calcination temperatures (stirring for 24 h at 35 °C, ageing at 90, 100 or 150 °C for 24 h and calcined at 550, 700 or 850 °C for 6 h and 2 °C/min heating rate).

	Ageing Temp. (°C)	Calcination Temp. (°C)	BET Surface Area (m²/g)	Micropore Area (m²/g)	Vp (cm³/g)	D (nm)
KIT-6	100	550	649	56	0.95	8.0
KIT-6	150	550	564	33	1.80	13.5
KIT-6	90	550	646	133	0.70	7.0
KIT-6	90	700	418	38	0.50	6.0
KIT-6	90	850	89	0	0.09	-

We see that the pore volume and surface area of KIT-6 dropped significantly when calcined at 850 °C. The isotherm does not show a hysteresis loop anymore, indicating that the mesopores collapsed during the calcination treatment. Consequently, KIT-6 is not suitable as template material when a high calcination temperature is required to convert its impregnated precursor to the desired target material. This involves that KIT-6 is more suitable as template for the replication of Bi nanostructures than SrTiO<sub>3</sub> for instance.

### 4.5.5 FDU-12 mesoporous silica

#### 4.5.5.1 Structural properties

Figure 4.27 (a) shows the TEM image of FDU-12 mesoporous silica made in house, while (b) was reported by Huang *et al.* [32] Compared to the right image, which shows highly ordered cages, only poorly ordered structures were obtained in this work. The material possesses a face-centered cubic symmetry with  $Fm\overline{3}m$  space group. The cell parameter of the cubic unit cell can be calculated as shown by Equation 4.2. An estimate of the wall thickness for a fcc structure can be made as:  $t = \frac{\sqrt{2}}{2}a - D$ . [26]

Zhao *et al.* reported the synthesis of FDU-12 with large pores using TMB as swelling agent and KCl as additive. [33] Pore sizes up to 10 - 12.5 nm could be obtained when the synthesis consisted of a stirring step at 40 °C and ageing step between 100 and 140 °C. [6] However, larger pores could not be obtained when more TMB was added. The same was observed for SBA-15 type silica, which formed mesostructured cellular foam upon the addition of extra TMB. [34] Nevertheless, it was discovered that the synthesis of large cages was favored when the stirring step was performed between 15 and 20 °C instead of 35 - 40 °C. Fan *et al.* postulated that the hydrophobic TMB molecules only penetrates the PEO "shell" of the micelles when it is loosely packed and not when a densely PEO "shell" is formed. It was observed that below 10 °C no precipitation occurred, while the critical micelle temperature (CMT) was reached between 10 and 20 °C. In the temperature range of 15 - 23 °C, TMB penetrated the PEO "shell" easily, whereas diffusion became limited above approximately 23 °C. It is believed that an equilibrium between free block copolymers and loosely packed micelles are present when the stirring step is performed at 15 °C, what enables easy diffusion through the PEO layer. The micelles under those synthesis conditions exhibit the ability to absorb large amounts of TMB, leading to ultra large pore FDU-12. [33, 35]



Figure 4.27. (a) TEM image of FDU-12 mesoporous silica (stirring for 24 h at 30 °C, ageing at 100 °C for 24 h, treated for 48 h in an autoclave at 150 °C and calcined at 550 °C for 6 h and 2 °C/min heating rate). (b) TEM image of large pore FDU-12 along (110) direction, with a pore diameter of 23 nm and pore entrances smaller than 5 nm, reprinted from Ref. [32, 33].



Figure 4.28. Schematic representation of the micelle swelling ability at different temperatures. Green part represents poly(ethylene oxide) (PPO), dark blue represents poly(propylene oxide) (PPO) and red stands for 1,3,5-trimethylbenzene (TMB). It is shown that no micelles are formed below 10 °C, while an easily impermeable soft PEO shell surrounds the PPO core between 15 and approximately 23 °C. A badly permeable PEO shell is believed to form above 23 °C, which is much higher than the critical micelle temperature (CMT). Image reproduced from [35].

Although the swelling agents increase the pore diameters of the silica material, it also causes more structural shrinkage when the samples are calcined. Huang *et al.* reported that the shrinkage could be limited by performing an acid treatment. Typically, a hydrothermal treatment is performed in a 2 mol/L HCl solution between 100 and 140 °C for several days. As a result, highly ordered ultra large pores could be synthesized without structural collapse during the calcination procedure. [32]

Control of the pore entrances could be obtained by performing the hydrothermal ageing step at different temperatures. The mechanism of the pore enlargement is similar as for SBA-15 and KIT-6 mesoporous silica as described earlier in §4.5.2.1. [6] Note that it is important to use a sufficiently high ageing temperature to prevent the formation of closed pores. It is generally preferable to have relatively large pore entrances as it improves diffusion of larger molecules in the material. The electrostatic potential maps of FDU-12 synthesized under different conditions are depicted in Figure 4.29.



Figure 4.29. 3D electrostatic potential maps of FDU-12 mesoporous silica stirred at 15 °C, aged at 100 °C for 3 days (left), stirred at 35 °C, aged at 100 °C for 1 day (middle) and stirred at 35 °C and aged at 120 °C for 2 days (right). Images reprinted from [33].

# 4.5.5.2 Synthesis

Typically, pore expanded FDU-12 was synthesized by dissolving 10 g F127 Pluronic and 25 g KCl in 600 mL of 2 M HCl together with 22 g trimethylbenzene (TMB). The solution was stirred vigorously at 35 °C for 24 h in a closed round bottom flask. Next, 41 g of TEOS was added to the solution and stirred for another 24 h at 35 °C. Subsequently, the solution was aged under static conditions at 100 °C for 24 h. The solid was collected through filtration and dried at room temperature. 0.2 g of the dried powder was mixed with 20 mL of 2 M HCl and stirred for 30 min. The obtained slurry was transferred to an autoclave and kept between 100 and 150 °C for 24 to 72 h. Finally, the surfactant was removed by heating the sample in air at 2 °C/min to 550 °C and holding for 6 h. [2] Note that we were unable to control the stirring temperature at 15 °C, therefore the standard stirring temperature for the synthesis of mesoporous silica was used instead.

### 4.5.5.3 Results and discussion

### Influence of ageing temperature on pore diameter of FDU-12 mesoporous

The N<sub>2</sub> sorption isotherms and the pore size distribution plot of FDU-12 are depicted in Figure 4.30. The red curve depicts the isotherms of the sample aged at 100 °C. It can be seen that desorption branch exhibits a delayed capillary evaporation at a much lower pressure than the capillary condensation. This is caused by the small pore entrances. When the ageing temperature and time were increased to 120 °C and 2 days respectively, the capillary desorption shifted to higher pressures, following a H2(b) type hysteresis loop, typical for bottle neck pores with a large range of diameters. Consequently, this can be interpreted as an increase of the pore entrance diameter. Further enhancement of the pore diameter occurred when the samples were aged at 150 °C for 2 days.



Figure 4.30.  $N_2$  sorption isotherms of FDU-12 mesoporous silica aged at 100, 120 and 150 °C. Inset: pore size distribution plots calculated on the adsorption branch of the isotherms.

Table 4.3 gives a summary of the properties of FDU-12. It can be seen that the pore volume increases significantly after performing a hydrothermal treatment at 120 °C. However, no further increase in pore volume was observed when annealed at 150 °C. Another strategy to enlarge the pore diameter of FDU-12 is based by performing the stirring step at 14 - 15 °C instead of 35 °C. Huan *et al.* reported the synthesis of ultra large pore FDU-12 with pore diameters up to 32 nm when the synthesis was performed at 14 °C and xylene used as pore expander with a mass ratio of 4.5 g xylene/g P127 and an acid treatment of 4 days at 130 °C. [32]

	Ageing Temp. (°C)	Ageing time (days)	Calcination Temp. (°C)	BET Surface Area (m²/g)	Micropore Area (m²/g)	Vp (cm³/g)	D (nm)
FDU-12	100	1	550	482	78	0.47	9.0
FDU-12	120	2	550	676	144	0.93	12.0
FDU-12	150	2	550	240	17	0.9	15.0- 40.0

Table 4.3. Summary of pore properties of FDU-12 mesoporous silica.

# 4.6 Conclusions

Analysing the aforementioned types of mesoporous silica materials, based on their high pore volume, 3D interconnected pore structure and large pore sizes, we can conclude that KIT-6 and FDU-12 mesoporous silica come up as the best candidates for their use as template material in the nanocasting process. Namely, KIT-6 could be synthesized with a relatively large uniform pore diameter up to 13 nm and a pore volume up to 1.8 cm<sup>3</sup>/g. The latter corresponds with a porosity of 82.5 v%. However, the thermal stability of the material is rather low compared to SBA-15 for instance.

FDU-12, on the other hand, had a lower pore volume than KIT-6, but larger pore diameters when the ageing temperature during the synthesis was performed at 150 °C. It has been reported that ultra large pore FDU-12 with diameters up to roughly 32 nm could be synthesized when performing the stirring step at 14 °C and ageing at 140 °C, however, we have not been able to reproduce such large pore diameters. The low temperature stirring step was not used

here because we were not equipped to do so. Note that it is important to perform an acid treatment at 130 - 140 °C to limit structural shrinkage of the silica framework upon calcination. Also, it enlarged to pore entrances, facilitating diffusion through the template.

Although the 2D pore structure of SBA-15 is undesirable in order to form percolation paths, the material was used to study and optimize the impregnation procedure, since the filling of 2D cylindrical pores are easier to study via  $N_2$  sorption experiments than a 3D interconnected pore system.

Some aspects which were not studied here but should be considered is the mechanical stability of the templates at the temperatures used during sintering of the nanocomposites. Namely, the materials were typically sintered between 180 and 260 °C at a pressure of 50 MPa for up to 90 min. Also, the morphology of the mesoporous particles may influence their packing and consequently the density of the sintered composite and affect the formation of percolation paths. For that reason, we believe spherical particles would be the best morphology.

# 4.7 References

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# 5

# Nanocasting

Nanocasting is a versatile technique for the synthesis of nanostructured and mesoporous materials, typically using the pores of mesoporous silica as nano-reactor. The silica materials discussed in previous chapter were used as hard template. The principles, advantages, limitations and the comparison of state of the art nanocasting techniques with the impregnation method developed throughout this research are discussed. It is shown how the impregnation of the template is affected by its surface chemistry and precursor composition and how these parameters could be optimized to improve the nanocasting process.

# 5.1 Introduction

Casting is a manufacturing process in which a mould, consisting of cavities in the shape of the desired structure, are filled with a melt or fluid which is allowed to solidify. Subsequently, the structure within the mould is removed through chemical etching and a perfect negative or replica is obtained.

In the case of nanocasting, the template consists of nanometre sized thin channels, typically the pores of microporous zeolites or mesoporous silica templates. In contrast to industrial moulds, microporous/mesoporous materials cannot be infiltrated with a melt under high pressure due to diffusion limitations. Several methods are available to infiltrate a metal/metal oxide precursor into a porous template. They can be classified in three general routes: wet chemistry impregnation, chemical/physical vapour impregnation and electrochemical impregnation. The method we will discuss here is the wet chemistry impregnation method, since it has the advantage over the other methods that porous powderous materials can be impregnated with the precursor solution. Mesoporous silica materials are used here as template material for the synthesis of replica structures in their pores. Typically, the precursor solutions are prepared by dissolving a metal salt or a mixture of metal salts in water or ethanol. Subsequently, the pores are impregnated with a diluted precursor solution and the solvent is evaporated. A thermal treatment converts the impregnated metal precursor to the desired material. Finally, the mesoporous replica structure is obtained when the template is chemically etched. For the removal of a silica template, a sodium hydroxide or hydrofluoric acid solution can be used.

In order to form a continuous self-supporting network of nanowires or a mesoporous material within the template, it is beneficial that the pore structure consists of interconnected pores. Therefore, the influence of the template's structural properties on the replicated structures and strategies to enhance the pore filling degree are discussed. Secondly, the surface chemistry of the mesoporous silica template is discussed, since that affects the interaction with the polar precursor solution which infiltrates the pores. The calculation of the pore loading is shown as it is used to assess how much material is deposited inside the pores and how much is deposited on the external surface of the template, as well as the pore filling efficiency. An overview of state-of-the-art nanocasting techniques is discussed and compared to the continuous flow nanocasting method developed in this work. The different filling mechanisms of mesoporous silica materials proposed by Lu et al. are compared with the materials synthesized here.[1] It is shown that both surface modification of the silica template as the modification of the polar precursor solution can be performed to improve the affinity of the precursor and the template. The latter affects the impregnation kinetics, while the pore loading influences the quality of the obtained nanowires or mesoporous replicated structures. Mechanism to enhance the pore loading are based on the decomposition of the precursor salt.

# 5.2 The influence of the template material on nanocasting

The type of mesoporous template employed for the nanocasting procedure determines the structural properties of the replicated material. This involves the symmetry of the pore structure, pore diameter, pore wall thickness and the size of the mesoporous grains. In addition, also the surface chemistry of the template material plays a crucial role in the impregnation process, more specifically, the wetting behaviour of the precursor solution on the surface of the template. The interactions between the precursor and a silica template, for instance, can also be altered through surface modification in order to improve the wettability and the impregnation kinetics. Examples of template materials are mesoporous carbon and mesoporous silica and are described in detail in the previous chapter [2, 3]. Due to the simplicity of the synthesis of mesoporous silica and the ability to tune the pore structure and pore diameter, silica is most commonly used for the nanocasting technique and is also used here.

# 5.2.1 Structural influence of the template on the nanocasted replica

Commonly used silica templates with a 2D pore structure are MCM-41 and SBA-15. Replication of these templates results in nanowires. As already mentioned in Chapter 4, the main difference between MCM-41 and SBA-15 is the fact that the former has a smaller pore diameter and does not possess micropores within the walls. Single nanorods with a diameter of approximately 2 to 4 nm are obtained from MCM-41. SBA-15 derived nanowires are typically connected with each other by thin rods which originate from the template's micropores within the pore walls connecting the meso channels. To increase the number and strength of the interconnections it is recommended to hydrothermally treat the SBA-15 template at 130 °C instead of 100 °C. [4] Consequently, bundles of nanowires are obtained in the latter case.

KIT-6 is a silica template with 3D helix channels with a cubic symmetry  $(Ia\overline{3}d)$  and contains 3D bicontinuous mesochannels. Consequently, replicating KIT-6 leads often to dislocations or only one set of the channels is filled. [5]

SBA-16 and FDU-12 are frequently used hard templates with cage-like pores. The interconnections between the cages are often called "windows" or entrances of the meso-structures and their size depends on the overlaps of the spherical pores. Sufficiently large entrances are required to fill the caged pores easily and it also improves the robustness of the obtained replica structures. The window size is rather small when a conventional hydrothermal treatment at 100 °C is performed. Therefore a higher ageing temperature, such as 130 °C is recommended. [6]

Since nanocasting is a faithful replication of the pore structure of the template material, the structure of the desired material could be altered by using silica templates with different pore structures as depicted in Figure 5.1.



Figure 5.1. Schematic representation of nanocasting principle with SBA-15 (top) and KIT-6 (bottom) mesoporous silica as template, yielding bundles of linear nanowires and 3D interconnected nanowires, respectively. In practice, the impregnated material shrinks significantly during the nanocasting process, which is not shown here.

### 5.2.2 Surface properties of the mesoporous silica template

In order to successfully cast the mesoporous channels of a silica template, it is required to achieve a high pore loading and no material should be deposited on the material's external surface. When a metal salt solution is added to a mesoporous silica template, it is reported that the pores are filled through capillary force [7]. Nevertheless, also the interaction between the precursor and the pore surface and the tendency of the precursor ions to migrate or aggregate within the pores affects the impregnation significantly. Namely, if the precursor aggregates randomly within the pores blockage could occur which would prevent further impregnation. [8] On the other hand, if the interactions are too strong the precursor may block the pore openings and prevent further impregnation. [1]

Since the precursor solution is generally water based, it is desirable to use a hydrophilic template to improve interactions with the precursor. The hydrophilicity of a mesoporous silica template is greatly affected by the concentration of silanol ( $\equiv$ Si-OH) moieties on its surface. Therefore, we must look how the number of silanol functional groups on the silica surface can be altered. Mesoporous silica is synthesized through a condensation driven polymerization of a silica precursor around a structural directing agent (Figure 5.2). After the ageing step (see Chapter 4), the as synthesized silica possesses the maximum concentration of silanol groups. Since the condensation of two  $\equiv$ Si-OH moieties results in the formation of a  $\equiv$ Si-O-Si $\equiv$  chain and the release of water, the crosslinking proceeds faster at elevated temperatures. Depending on the method used for the removal of the structural directing agent, the surface silanol groups may either crosslink to  $\equiv$ Si-O-Si $\equiv$  or be preserved. In the case of solvent extraction, almost all silanol moieties remain due to the low temperature of the treatment (< 100 °C).



Figure 5.2. General synthesis route of amorphous silica and the origin of silanol moieties on the surface. (Modified from [9])

Although the silanols are retained when the organic structural directing agent is removed via solvent extraction, there are always some surfactant molecules remaining which could cover the pore surface and prevent the silanol moieties to be exposed. Consequently, another technique called microwave digestion was developed to remove all surfactant molecules while maintaining the surface hydroxyl groups [9]. The microwave digestion is performed at approximately 200 °C. Due to the relatively low temperatures used during the solvent extraction and microwave digestion treatment, limited structural shrinkage of the mesoporous silica occurs. When the structural directing agent is removed by a calcination treatment at 550 °C, then the silanol groups tend to crosslink and release water, what also causes shrinkage of silica template. As the number of silanols reduce at elevated temperatures (Table 5.1), the template becomes more hydrophobic.

Calcination temperature (°C)	Conc. of silanol groups (OH/nm <sup>2</sup> )
200	4.6
300	3.55
400	2.35
500	1.8
600	1.5
700	1.15
800	0.7
900	0.4
1000	0.25
1100	0.15
1200	0

*Table 5.1.* Surface concentration of different types of OH groups as a function of the calcination temperature in vacuum. Data reproduced from [9, 10].

We can conclude that microwave digested silicates with large pore volumes and a high concentration of silanols would be the ideal hard templates for nanocasting replicas. Nevertheless, only the calcination treatment was used here due to the ability to process several tens of grams of silica template at a time and the simplicity of the method.

#### 5.2.3 Pore filling mechanisms of mesoporous templates

Due to the small pore size of mesoporous templates (2 - 50 nm), the precursor cannot be mechanically pressed into the pores. Instead, it must migrate within the pores through capillary force and/or hydrophilic affinity. In order to obtain a successful replication of the

template, the precursor also has to be converted within the pores to the desired material without leaching out of the channels. Namely, either the metal salt or the desired product could melt during the thermal treatment and escape the pores. Taking Bi as an example, temperature is particularly critical for  $BiCl_3$  salts and metallic Bi, which have a melting temperature of respectively 227 and 271.5 °C. In addition, transition metal nitrate salts could also have hydrate salts with a melting temperature below 100 °C.

To obtain an easy filling of the template's pore channels, the precursor should be soluble in a solvent that possesses a good affinity with the template or the precursor should be in the liquid or gaseous state/phase. Mostly, the precursor salt is dissolved in water or ethanol before infiltration. However, some transition metal nitrates form low melting salts, which can be directly impregnated. In the case of a precursor solution, the capillary force, wettability and mobility of the precursors are key to a successful impregnation. On the one hand, the affinity between the precursor and the template's surface should be sufficiently high to have a good wettability and subsequently capillary impregnation, but on the other hand too strong interactions between the precursor and the pore surface may impede the migration of the precursor within the channels causing pore blocking at the pore orifices. [1] Also, the impregnated precursor should aggregate together and form a continuous network when the precursor solvent is removed.



Figure 5.3. Typical distributions of target product during the thermal treatment of impregnated template in the nanocasting process: (a) the desired product enriches and/or aggregates at small domains within the mesopore channels of the template, leaving the majority of the pores empty; (b) the target material fills the entire pore channels with the formation of micropores; (c) the contracting precursor forms a homogeneous film which covers the entire pore wall of the template. Figure adapted from [1].

To obtain the desired product, the precursor must be converted in situ with as little shrinkage as possible. However, contraction of the impregnated material is inevitable as the precursor has a much lower density and a higher molecular weight than the target product. This results in a drastic loss of the occupied volume upon conversion of e.g. a metal salt to its oxide or metallic form. Nevertheless, materials which tend to migrate and aggregate within the pore channels can form completely filled domains of the target product within the template and therefore are preferred for nanocasting (Figure 5.3a). Most mesoporous metal oxide replicas are synthesized according to this pathway. [3, 4, 11, 12]

In the second case (Figure 5.3b), the product fills the entire pore channels without any significant shrinkage. Instead, homogeneously distributed micropores are formed to compensate for the constriction due to mass loss and increase in density of product compared to the precursor. Typically, nanocasting carbons follow this filling behaviour; the conversion of carbon precursors, such as sucrose, furfuryl alcohol, or low molecular weight polymers thermally polymerizes to rigid amorphous carbon occupying the entire mesochannels with micropores caused by the release of gaseous molecules. [2, 13] Mesoporous carbon replicated from SBA-15 are denoted CMK-3 and possess an excellent replica of the pore channels.

The third behaviour, shown in Figure 5.3c, is rather uncommon and is only observed in the synthesis of CMK-5 mesoporous carbon, which is the replication of an SBA-15 mesoporous silica template by a carbon replica when the pores are insufficiently filled with precursor, forming hollow rods. [14] During this synthesis, the precursor possesses a strong interaction with the template, which forms a film on the pore walls. The insufficient filling of the template's pores leads to hollow tubes after the thermal polymerization process. [15, 16]

# 5.3 Calculation of the pore filling efficiency

The calculations discussed here are applied to the impregnation of  $BiCl_3$  into a mesoporous silica template and the reduction to metallic Bi. In order to synthesize conducting Bi nanowire composite material, it is crucial to obtain a sufficiently high loading of  $BiCl_3$  within the template's pores. Namely, if the loading is too low, fragmented nanowires within the pores would be obtained which do not form any electrical percolation path within the silica grains.

When the pore channels are completely filled with  $BiCl_3$ , only 32 v% is occupied by metallic Bi after reducing the precursor. This is considered the theoretical maximum loading efficiency of bismuth with  $BiCl_3$  as precursor salt. In reality, if the impregnation is not performed properly, some material might be deposited on the external surface of the template, what could reduce the actual loading efficiency. The two extreme scenarios which can occur during the impregnation of a mesoporous silica template are schematically depicted in Figure 5.4. In the first case, all material is present inside the pore, whereas the same amount of material is completely deposited on the external surface of the template.



Figure 5.4. Determination of internal and external deposited material.

The filling degree of any impregnated salt was calculated from data obtained from  $N_2$  sorption measurements as follows(BiCl<sub>3</sub> as example):

- Properties of the metal salt:
  - Mwt (BiCl<sub>3</sub>) = 315.34 g/mol
  - Density (BiCl<sub>3</sub>) =  $4.75 \text{ g/cm}^3$
- Properties of the template material (SBA-15 silica) measured by N<sub>2</sub> sorption:
  - Pore volume:  $Vp = 0.8 \text{ cm}^3/g$

- Mwt (SiO<sub>2</sub>) =  $60.08 \text{ g/cm}^3$
- Density  $(SiO_2) = 2.648 \text{ g/cm}^3$  (overestimation)
- Properties of the desired product (metallic bismuth):
  - Mwt(Bi) = 208.9804 g/mol
  - Density (Bi) =  $9.78 \text{ g/cm}^3$
- Maximum pore loading of metallic bismuth when the pores were completely filled with BiCl<sub>3</sub>:
  - Mass impregnated salt = mass template  $\times Vp \times density$  (BiCl<sub>3</sub>)
  - Mass impregnated salt =  $1g \times 0.8 \frac{cm^3}{a} \times 4.75 \frac{g}{cm^3} = 3.8 g BiCl_3$
  - Inital pore volume of the template:  $Vp = 0.8 \ cm^3/g$
  - $Volume \ occupied \ by \ metallic \ bismuth: V_{Bi} = \frac{mass \ (BiCl_3)}{Mwt \ (BiCl_3)} \times \frac{Mwt(Bi)}{density \ (Bi)}$
  - Volume occupied by metallic bismuth:  $V_{Bi} = \frac{3.8 g}{315.14 g/mol} \times \frac{208.98 g/mol}{9.78 g/cm^3} = 0.2577 cm^3$
  - Maximum fraction of the pores filled with  $Bi = \frac{V_{Bi}}{Vp}$
  - Maximum fraction of the pores filled with  $Bi = \frac{0.2577 \text{ cm}^3}{0.8 \text{ cm}^3} = 32.2\%$

#### Maximum pore volume of silica-Bi composite measured by N<sub>2</sub> sorption:

- $mol(Bi) = mol impregnated salt = \frac{mass(BiCl_3)}{Mwt(BiCl_3)} = \frac{3.8 g}{315.34 g/mol} = 0.012 mol(BiCl_3)$
- mass  $Bi = mol(Bi) \times Mwt(Bi) = 0.012 mol \times 208.98 g/mol = 2.5 g$
- V<sub>p</sub> when material is 100% inside the pores:
- Vp, max internal =  $\frac{initial \text{ pore volume:} Vp-volume \text{ occupied by } Bi: V_{Bi}}{V_{Bi}}$
- Vp, max internal =  $\frac{0.8 \ cm^3 0.2577 \ cm^3}{1 \ g + 2.5 \ g} = 0.155 \ cm^3/g$  V<sub>n</sub> when motorial
- V<sub>p</sub> when material is 100% outside the pores:

**Bismuth nanowires** confined within the template's channels

- $Vp, max \ external = \frac{initial \ pore \ volume: Vp}{mass(SiO_2) + mass(Bi)} = \frac{0.8 \ cm^3}{1 \ g + 2.5 \ g} = 0.229 \ cm^3/g$
- Fraction of material inside and outside the template:
- fraction inside + fraction outside template = x + y = 1
- Vp, max internal  $\cdot x + Vp$ , max external  $\cdot y = Vp$ ,  $N_2$  sorption



**Bismuth spheres** outside the template

Figure 5.5. Indication of bismuth nanowires within the template and external spheres.

It can be understood from the calculations above that the amount of material within and outside the pores can be calculated when the density and molecular weight of the precursor and desired material and the pore volume of the composite are known. The SBA-15 silica template depicted in Figure 5.5 was filled completely with BiCl<sub>3</sub> and subsequently reduced at 220 °C for 10 h in an atmosphere of N<sub>2</sub>H<sub>4</sub> vapour in a flow of Ar – 5 % H<sub>2</sub> gas. More details about the synthesis are shown in §5.5.2.3. Although the theoretically maximum filling degree is 32 v% Bi, it could be calculated as shown above that only 27 v% of the pores was filled with bismuth. It was determined that 86 v% of the impregnated material was inside the template while 14 v% was leached out.

# 5.4 State of the art wet chemistry nanocasting techniques

Various wet chemistry nanocasting methods have been developed each to address one of the issues involved with nanocasting, such as improving the pore loading efficiency, or reducing the amount of external deposited material. The simplest wet chemistry impregnation is the conventional solvent impregnation method, in which a large amount of precursor solution is added to a template material. [17] Only a small fraction of the metal precursor infiltrates into the pores through diffusion, while some will deposit on the outer surface of the template, generating large aggregates after drying and/or thermal treatment. The major part of the precursor solution is filtered off. This method typically leads to a low loading, but is useful for the synthesis of nanoparticles within the pore channels of the template. It was reported that the impregnation of a precursor solution in the template's pores could be facilitated under reduced pressure. [11] TEM images of ordered mesoporous Co<sub>3</sub>O<sub>4</sub> and NiO synthesized via this method are shown in Figure 5.6. The ordered structure of the replicas can be noticed from the figures, indicating a successful replication of the KIT-6 template. However, the size of the mesoporous metal oxide particles are significantly smaller than the size of their parent template, which is typically several µm. [18] This suggests that the metal precursor aggregated into dense domains as shown in Figure 5.3a. In contrast to Co<sup>3+</sup> ions, it was reported that Ni-ions do not aggregate easily due to their poor mobility on the silica surface, which explaining the smaller size of the replicated NiO grains than Co<sub>2</sub>O<sub>3</sub> grains in Figure 5.6. [11]



Figure 5.6. TEM images of ordered mesoporous (a)  $Co_2O_3$  and (b) NiO replicated from KIT-6 mesoporous silica. Images reprinted from [11].

A variation on the conventional impregnation is evaporation induced impregnation. In this technique, the metal salt is dissolved in a low boiling solvent such as ethanol and stirred until the solvent is completely evaporated while the metal salt crystallizes inside the pores. Typically, it is applied for the impregnation of transition metal nitrates since they have a high solubility in ethanol. However, when the metal salts do not possess a sufficiently high solubility in ethanol or the salt is sensitive towards hydrolysis this method cannot be used.

The evaporation induced impregnation usually leads to a higher loading than the aforementioned conventional impregnation methods, but it does not prevent the deposition of material on the external surface of the template and it requires large amounts of solvent. [1, 19] The technique was successfully used for the synthesis of mesoporous NiCo<sub>2</sub>O<sub>4</sub>, shown in Figure 5.7. Large mesoporous particles were obtained using a nitrate salts dissolved in ethanol as precursor. [20]



Figure 5.7. TEM image of NiCo<sub>2</sub>O<sub>4</sub> obtained via the evaporation induced impregnating method. 0.15 g SBA-15 was impregnated with 0.29 g nitrate salts in 5 g ethanol, stirred for 30 min and left for ethanol evaporation overnight. Image reprinted from [20].

A method used to limit the amount of material deposited on the surface of the template is the incipient wetness technique, also called dry impregnation, as an amount of precursor solution less or equal to the pore volume of the template material is added to the template so that no material is deposited on the external surface of the template [21]. Typically, a metal salt is dissolved in water or ethanol as precursor. The dry powder is stirred to enable all of the precursor solution to draw into the template's pores. The precursor is believed to infiltrate into the pores through capillary action rather than through diffusion. After impregnation, the material is dried and subjected to a thermal treatment. A disadvantage of this method is that the maximum loading is limited by the solubility of the precursor in the solvent. Furthermore, this methodology leads to inhomogeneous impregnation due to the difficulty to homogenize the precursor solution and the dry mesoporous silica powder. When repeated dry impregnations are performed, the pores tend to block, what makes it difficult to enhance the loading of material in the pores.

A more advanced version of the incipient wetness technique, referred to as the "double solvents" method [22, 23], was initially used to impregnate a water-based precursor solution into mesoporous silica and recently for the impregnation of nanoparticles inside metal-organic frameworks ("MOFs") [24]. A non-polar solvent, such as hexane, is added in a large quantity to the template material followed by the addition of a volume of water-based precursor solution less or equal to the total pore volume of the template. In this way, no external material is deposited and homogeneous filling of the template is obtained, but this methodology still faces the problem that many steps are required to obtain a high loading. An example of this method used for the synthesis of mesoporous MnO<sub>2</sub> is shown in Figure 5.8. The low loading can be observed from the TEM image, in which the dark areas are MnO<sub>2</sub> aggregates and the light area is the silica template. Specifically, it can be calculated from the pore volume (1 cm<sup>3</sup>/g), the mass of the added template (1 g), the volume and concentration of the precursor added (1 cm<sup>3</sup> and 2.34 mmol/cm<sup>3</sup>, respectively), the molecular weight of the target material (Mwt MnO<sub>2</sub> = 86.94 g/mol) and its density ( $\rho$  MnO<sub>2</sub> = 5.026 g/cm<sup>3</sup>) that the

loading of the template was only 4.1 v%. [25] The low loading in this example is due to the low metal salt concentration of the impregnated precursor solution. Subsequent impregnations and drying steps could enhance the loading.



Figure 5.8. TEM images of  $MnO_2$  structures synthesized within the pores of SBA-15. The template was impregnated with a 2.34 mol/L aqueous solution of  $Mn(NO_3)_2.4H_2O$  using the "double solvent" method with dry hexane as nonpolar solvent and subsequently calcined for 3 h at 400 °C. Image reprinted from [25].

# 5.4.1 Limitations of available techniques

Problems associated with the current impregnation methods of porous templates include incomplete and inhomogeneous filling of the pores, as well as deposition of material on the external surface of the template. In many cases, multiple loading steps are required to obtain an acceptable degree of loading. The evaporation induced impregnation of an ethanol based precursor and the double solvent has been very successful for the synthesis of various transition metal oxides, but the technique is limited to nitrate salts which do not hydrolyse and possess a high solubility in ethanol. The double solvent impregnation method enables a faithful replication of the silica template and prevents deposition of precursor on the exterior surface of the template. However, the pore loading for each impregnation step remains low.

Since we are interested in electrically conducting nanowire networks, a high filling degree of precursor material in the pore channels is required to obtain an electrical percolation path through the nanowires when, for example, the mesoporous silica – bismuth nanocomposite powder is pressed into pellets. Therefore, we developed an impregnation process consisting of the continuous infiltration of a diluted polar precursor solution, the simultaneous evaporation of the polar precursor solvent and continuous deposition of solid precursor salt in the template's pore channels. The method is related with the double solvent impregnation, but differs in the way the aqueous precursor is added. As will be shown more detailed later on, the method developed here adds a continuous flow of precursor solution while the "double solvent" is refluxed.

# 5.5 Experimental section

### 5.5.1 Materials

### 5.5.1.1 Mesoporous silica synthesis

98 % reagent grade tetraethylorthosilicate (TEOS), Pluronics P123 ( $EO_{20}PO_{70}EO_{20}$ , Mw = 5800 g/mol) and 36 % hydrochloric acid were purchased from Sigma Aldrich. All reagents were used as received.

# 5.5.1.2 Nanocasting of C, Bi, Ni and TiO<sub>2</sub>

furfuryl R/S)+alcohol and 36 % hydrochloric acid were purchased from Sigma Aldrich. 98 % bismuth(III) chloride, 30 % hydrogen peroxide, 97 % titanium(IV) isopropoxide and 99 % bismuth(III) oxide were supplied by Alfa Aesar. 98.5 % xylenes, 99% toluene and 98 % methanol were supplied by Fiers. 98.5% bismuth(III) nitrate was purchased from Chem-Lab NV and 97% n-octane was supplied by TCI Europe N.V. All reagents were used as received.

# 5.5.1.3 Reduction treatment of Bi salts and reactive vapor treatments with $H_2$ Se and $Me_3$ Sb

Sulfuric acid (> 95 %), 30 % hydrogen peroxide, 98 % sodiumborohydride and methylmagnesium bromide 3 M solution in diethylether were purchased from Sigma Aldrich. 99% antimony(III) chloride, 99.5 % selenium powder, 98% hydrazine monohydrate and 99% tetrahydrofuran stabilized with 250-350 ppm BHT were supplied by Alfa Aesar. All reagents were used as received.

# 5.5.2 Synthesis

# 5.5.2.1 SBA-15 and KIT-6 mesoporous silica template

The synthesis of SBA-15 and KIT-6 is extensively described in Chapter 4.

# 5.5.2.2 CMK-3 and CMK-5 mesoporous carbon

Prior to the synthesis of CMK-3 the pore volume of the SBA-15 mesoporous silica template is determined by  $N_2$  adsorption measurements. CMK-3 is synthesized by impregnating a diluted solution of 25 v% furfuryl alcohol in toluene. The amount of furfuryl alcohol is a 5-fold of the total pore volume of the silica template impregnated. To catalyse the polymerization of furfuryl alcohol, 2 v% 0.1 M  $H_2SO_4$  of the volume of furfuryl alcohol is added. Typically, the synthesis is performed in a 250 mL round bottom flask equipped with a reflux cooler.

For 2.5 g SBA-15 with a pore volume of 0.8 mL/g, the total pore volume equals 2 mL. 10 ml furfuryl alcohol is added and diluted with 30 ml toluene. Next 200  $\mu$ l 0.1 M H<sub>2</sub>SO<sub>4</sub> is added while stirring at 700 rpm for 36 h at 100 °C. The impregnated silica powder is filtered off with a glass filter and washed 3 times with toluene. The powder is dried at 150 °C for 5 h in a muffle furnace with a heating rate of 2 °C/min. the composite material is carbonization at 1100 °C for 1 h in a tube furnace under Ar - 5 % H<sub>2</sub> atmosphere with a heating rate of 2 °C/min and a gas flow rate of 0.25 L/min. The silica is chemically etched with a 10 % HF solution for minimum 6 h whilst stirring. [26]

CMK-5 mesoporous silica is synthesized in the same manner, except that the amount of furfuryl alcohol is only a 2 fold of the total pore volume of the silica template impregnated. [14]

# 5.5.2.3 Continuous flow nanocasting procedure for the synthesis of mesoporous Bi

The impregnations were performed by the same procedure for both SBA-15 and KIT-6 mesoporous silica templates. Prior to the impregnation, the pore volume of the template was measured by means of N<sub>2</sub> sorption analysis in order to calculate the amount of precursor salt that the pores could contain based on its density. The templates were loaded with bismuth salt by impregnating with a solution of Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O dissolved in diluted nitric acid or BiCl<sub>3</sub>



dissolved in diluted hydrochloric acid. The polar precursor solution is defined as an aqueous solution of a metal salt dissolved in water or a diluted acid.

Figure 5.9. Schematic representation of the impregnation setup. Patent pending.

Typically, BiCl<sub>3</sub> was used as bismuth precursor for the synthesis of Bi nanowire structures. The salt was dissolved in a mixture of HCI and H<sub>2</sub>O, with methanol and formic acid as cosolvents to improve the impregnation kinetics. All the aforementioned solvents are referred to as the precursor solvents. On the other hand, the non-polar solvents were typically toluene, xylene or n-octane and were used in such combination that they would be immiscible with the polar precursor solution. Taking BiCl<sub>3</sub> as example, 1 g KIT-6 mesoporous silica template material with a pore volume of 1 cm<sup>3</sup>/g was dispersed in 100 mL n-octane, while stirring at 700 rpm, in a 250 mL perfluoroalkoxy alkane (PFA) round bottom flask equipped with a dean stark separator (Figure 5.10). The recipient was heated to 160°C to enable gentle refluxing of the solvent. Subsequently, 4.78 g BiCl<sub>3</sub> was dissolved in 15 mL 30 w% HCl and 60 mL MeOH and added to the reaction vessel using a syringe pump. The precursor was added in a continuous manner to the PFA flask at a rate of 4 mL/h until all bismuth precursor solution was added to the suspended template solution. Meanwhile, the diluted acid mixture was continuously eliminated from the system with the dean stark separator. After impregnating the silica template, the yellowish powder was collected through filtration, washed with hexane and dried overnight at 60 °C.

An image of the impregnation setup is shown in Figure 5.10. The heating plate was equipped with an aluminum block as heat exchanger, which fitted the PFA round bottom flask. The impregnation was performed under refluxing conditions, while the evaporation speed could be adjusted by changing the temperature of the heating plate. A modified Dean Stark separator was attached to the flask. The precursor was injected in the round bottom flask using a syringe pump. Herefore, a PTFE tube was inserted in the flask through a septum, whereas the addition speed could be controlled with the syringe pump. A volume up to 45 mL could be added to the reaction vessel, which was also the volume of the collection reservoir.

In operation, the flask was insulated to enable efficient removal of water during the impregnation. The pressure during the impregnation could be adjusted by means of a pressure controllor that could be attached to the system.



Figure 5.10. Impregnation setup: heating plate, PFA round bottom flask, dean stark separator, condenser and syringe pump.

#### 5.5.2.4 Reduction of BiCl<sub>3</sub> – silica composite powder

Approximately 0.5 g of the material was placed in a ceramic crucible and placed in a horizontal flow furnace to perform the reduction of the salt. Herefore, a gas flow of Ar – 5 % H<sub>2</sub> bubbled through a solution of 98 % hydrazine monohydrate was used as reducing atmosphere. The reduction was performed between 220 and 265 °C for 12 h.

#### 5.5.2.5 Gas phase doping and alloying of BiCl<sub>3</sub> – silica composite powder

It was demonstrated that the impregnated material could also be chemically converted through the reaction with a reactive chemical vapour deposition (CVD) precursor such as Me<sub>3</sub>Sb. The volatile CVD precursor was generated in situ prior to entering the furnace (Appendix B Figure 2) by adding SbCl<sub>3</sub> dissolved in tetrahydrofuran (THF) to a solution of Grignard reagent MeMgBr, following the reaction mechanism shown in Eq. 5.1 [27].

$$SbCl_{3(THF)} + 3MeMgBr_{(THF)} \xrightarrow{THF} SbMe_{3(l)} + 3MgBrCl_{(THF)}$$
 Eq. 5.1

Herefore, a syringe pump was used to control the addition of SbCl<sub>3</sub> to MeMgBr and consequently the rate at which Me<sub>3</sub>Sb was generated. The BiCl<sub>3</sub> – silica composite powder was placed in a horizontal flow furnace heated to 120 °C, while the Me<sub>3</sub>Sb vapours were carried through the furnace in a flow of Ar gas. The amount of antimony that reacted with the impregnated BiCl<sub>3</sub> could be controlled by varying the duration of the exposure time. Note that

the latter is a pyrophoric and toxic liquid. Therefore, it was prepared in situ, carried by argon gas into the tube furnace, while the outlet was chemically oxidized.

#### 5.5.2.6 Template removal of metal – silica composite powder

After completing the nanocasting process, the replica was separated from the silica template by etching the latter with a 1 mol/L sodium hydroxide solution or 10 % hydrofluoric acid solution for 3 h. Typically, NaOH was preferred over HF as it is safer to handle and it usually does not react with the replicated material. The nanostructures were recovered through centrifugal separation and washed twice with water and ethanol.

#### 5.5.2.7 Synthesis of mesoporous TiO<sub>2</sub>

Typically, 1 g KIT-6 template material was used, which has a pore volume of approximately 1 mL/g as determined by N<sub>2</sub> physisorption measurements. The mesoporous silica template was dispersed in 100 mL toluene or xylene and brought into a 250 mL PFA round bottom flask equipped with a Dean Stark separator and reflux cooler. The entire system was connected to a vacuum pump with pressure controller to adjust the boiling temperature of the non-polar solvent. Prior to the addition of the precursor solution, the recipient was heated to 120 °C while the pressure was reduced to 50 mbar. This process was used to remove all water within the template's pores and was conducted for 2 h. The titania precursor solution was prepared by hydrolysis of 6.3 mL titanium tetraisopropoxide (TTIP) in distilled water, washing the Ti(OH)<sub>4</sub> precipitate with excess water on a glass filter and dissolving the white powder in 36 % hydrochloric acid or 68 % nitric acid until a metal concentration of 1 mol/L was obtained. The polar precursor solution was added to the reaction flask at a rate of 4 mL/min using a syringe pump using the impregnation method described in §5.5.2.3.

The temperature of the reaction mixture was set 40 °C above the boiling point of the nonpolar solvent at the applied pressure. The impregnation was continued until all precursor solvent was removed from the reaction mixture by means of the Dean Stark separator. The composite powder (silica + titania) was filtered off, heated at a rate of 2 °C/min, calcined at 450 °C for 4 h in air and chemically etched with 0.5 mol/L NaOH solution for 4 h to yield mesoporous titania. The obtained powder was washed 3 times with water and collected via centrifugation.

#### 5.5.2.8 Synthesis of mesoporous Ni

Typically, KIT-6 mesoporous silica template material was loaded with nickel nitrate salt by impregnating a solution of Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O dissolved in a mixture of H<sub>2</sub>O, formic acid (FA) and methanol (MeOH) by the continuous flow impregnation method described in §5.5.2.3 for Bi. 2.5 g KIT-6 mesoporous silica template material with a pore volume of 0.92 cm<sup>3</sup>/g was dispersed in 100 mL n-octane in a 250 mL perfluoroalkoxy alkane (PFA) round bottom flask while stirring at 700 rpm. The recipient was equipped with a dean stark separator and heated to 165 °C to enable gentle refluxing of n-octane. Subsequently, 7.73 g Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O was dissolved in 10 mL H<sub>2</sub>O, 10 mL FA and 70 mL MeOH and added to the reaction vessel using a syringe pump. The precursor solution was added in a continuous manner to the PFA flask at a rate of 4 mL/h until all Ni precursor solution was added to the suspended template solution. Meanwhile, the aqueous mixture was continuously eliminated from the system with the Dean Stark separator. After impregnating the silica template, the powder was collected by filtration, washed with n-hexane and dried overnight at 60 °C.

The silica template was removed in a 1 mol/L NaOH solution for 3 h and washed twice with water and twice with ethanol. The powder was collected by centrifugal separation.

# 5.5.3 Characterization

using a flow rate of 10 mL/min.

X-Ray powder Diffraction (XRD) patterns were recorded on a Thermo Scientific ARL X'TRA X-Ray Diffractometer with the Bragg–Brentano theta-2 theta configuration and using Cu K  $\alpha$  radiation. Nitrogen sorption experiments were performed at 77 K with a Micromeritics TriStar 3000 device. Samples were vacuum dried at 120 °C for 12 h prior to analysis. The surface area was calculated using the BET method while the pore size distribution was determined by analysis of the adsorption branch of the isotherms using the BJH method. Thermogravimetric analysis (TGA) were performed on a NETZSCH STA 449-F3 Jupiter device and TEM images were taken with a JEOL JSM-207 7600F device. The contact angles were determined using an optical tensiometer (Kruss DSA30). Droplets with a volume of 5  $\mu$ I were deposited on the surface using a syringe with a needle with a diameter of 0.506 mm. The contact angle was determined using a drop shape analysis software, using the Laplace-Young fitting method. Measurements were repeated three times and the average value was reported.

# 5.5.4 Results and discussions

#### 5.5.4.1 KIT-6 and SBA-15 mesoporous silica



Figure 5.11. (a) Low angle XRD diffractogram, (b)  $N_2$  sorption isotherms and (c) BJH pore size distribution plot of SBA-15 and KIT-6 mesoporous silica.

Based on the diffraction patterns shown in Figure 5.11a, it could be calculated that the synthesized KIT-6 mesoporous silica possesses a cubic interconnected pore system with the *Ia3d* space group symmetry, whereas SBA-15 possesses a *P6mm* hexagonally ordered pore system. The pore diameter of KIT-6 according to the BJH model calculated on the desorption branch of the isotherm shown Figure 5.11b,c are approximately 7.0 nm, while the BET surface area ranges from 700 to 900 m<sup>2</sup>/g and the pore volume is 0.8 to 1.2 mL/g. SBA-15, on the other hand has pores with a diameter of approximately 7.5 nm. The BET surface area and pore volume were typically between 600 and 1000 m<sup>2</sup>/g and 0.7 to 1 mL/g, respectively

[28]. Generally, SBA-15 was used as template material since its linear pores and the impregnation of it was easier to study with TEM than KIT-6.

#### 5.5.4.2 Evaluation of different impregnation mechanisms

Here we compare the volume contraction mechanism of the impregnated precursor solution during nanocasting discussed in Figure 5.3 with the materials synthesized in this work. We define the different mechanisms as:

- a) the desired product enriches and/or aggregates in small domains within the mesopore channels of the template, leaving the majority of the pores empty;
- b) the target material fills the entire pore channels with the formation of micropores;
- c) the contracting precursor forms a homogeneous film which covers the entire pore wall of the template.

The most suitable way to distinguish filling mechanism (a) and (c) is by means of  $N_2$  sorption measurements. Namely, in scenario (a) there is no reduction of the average mesopore diameter according to the BJH model, while the diameter does reduce in scenario (c). The total pore volume reduces in both cases. It can be seen from the example in Figure 5.12 that both the pore diameter and the total pore volume reduce. The reduction in pore diameter indicates that the material "coats" the surface of the pores during impregnation. On the other hand, the total pore volume drops regardless whether material is deposited inside or outside the pores since the density of the sample usually increases during the impregnation.



Figure 5.12.  $N_2$  sorption isotherms of SBA-15 mesoporous silica template, partially loaded SBA-15 with furfuryl alcohol (FA) carbon precursor and fully loaded SBA-15 with furfuryl alcohol.

Examples of materials which can easily be replicated are  $Co_3O_4$  and  $In_2O_3$ . [5, 12, 29] On the other hand, mesoporous  $Fe_3O_4$  and NiO are more difficult to synthesize as the precursor tends to form nanoparticles rather than a continuous network, which is due to the lower migration rate of Fe and Ni ions on the silica surface compared the Co and In ions.

In the case gaseous precursors are used to load the pores, a chemical vapour deposition (CVD) process is the most suitable way. The impregnation of a CVD precursor is mainly affected by the diffusion, capillary forces and deposition rate of the precursor. Often, the precursor deposits or decomposes at the pore orifice and causes pore blocking preventing any further impregnation. However, when the deposition rate is slow, a low loading of the precursor or its decomposition product is obtained within the channels and a poor replication is obtained. Alternatively, a CVD precursor could be used to dope an impregnated sample.

For example, a template loaded with  $BiCl_3$  can be doped with antimony by letting the former react with the CVD precursor Me<sub>3</sub>Sb.

An example of pore blockage occurred during the impregnation of a diluted hydrochloric acid based  $TiO_2$  precursor solution in KIT-6 mesoporous silica. It can be seen from the BJH pore size distribution plot on the desorption isotherm of the  $TiO_2$  loaded KIT-6 template in Figure 5.13 that two apparent pore diameters are present. Firstly, the main pore diameter is slightly smaller than the original diameter of the template due to filling of the pores. Nevertheless, it is doubtful to say that there is an actual difference in pore diameter if we consider that some parts of the pores might be completely filled, while other regions are clear. Secondly, an artificial pore size distribution occurs due to spontaneous capillary desorption at a relative pressure of approximately 0.42. It indicates the occurrence of partially blocked pores, which is in resemblance with the H5 type hysteresis loop shown in Figure 4.9 for plugged pore systems.



Figure 5.13. (a)  $N_2$  sorption isotherm and (b) BJH pore size distribution plot on the desorption branch of KIT-6 mesoporous silica and TiO<sub>2</sub> loaded KIT-6 template. Note the two steps capillary desorption, which is typical for plugged pores. The presence of two pore diameters can also be seen in the BJH pore size distribution plot calculated on the desorption branch of the isotherms.



Figure 5.14. (a)  $N_2$  sorption isotherms and (b) BJH pore size distribution plots on the desorption branches of SBA-15 mesoporous silica template (red) and the nickel formate loaded SBA-15 template (blue).

Figure 5.14. shows a typical isotherm and pore size distribution plot of SBA-15 template impregnated with a metal (Ni) salt which agglomerates. This involves that some pores are completely filled while others remain empty. The drop of the isotherms in Figure 5.14b for the filled template indicates that the pore volume of the sample reduces, which is due to the occupied pores and an increase of the sample's mass. The parallel adsorption and desorption isotherms indicate that no pore blockage occurs, which is preferred during

nanocasting. The pore size distribution plot in Figure 5.14b shows that the pore diameter hardly changes, which can be attributed to the pores which are mainly empty.

# 5.5.4.3 Influence of the polar precursor solution chemistry on the impregnation procedure

We discovered that the following process parameters affected the impregnation procedure:

- the polar precursor solvent and the template interaction;
- the non-polar solvent and the template interaction;
- the polar precursor solvent and non-polar solvent combination;
- the precursor salt.

Each parameter will be discussed in the following paragraphs.

#### 5.5.4.4 Influence of the polar precursor solvent on the impregnation procedure

The impregnation of a mesoporous silica template with an aqueous precursor solution is based on capillary impregnation. However, during the "double solvent" impregnation method, the silica's pores are filled with the non-polar solvent in which it is dispersed. When the aqueous precursor is added, it preferentially impregnates the pores. This means that there is a competitive wetting of the silica template with either the non-polar solvent and the aqueous precursor solution. We can say from the visual representation of the double solvent impregination in Figure 5.15 that Presoporous silica possessed a better wettability by the polar precursor solution than the non-polar solvent. The dark orange coloured peroxo titania precursor solution was obtained by hydrolysis of titanium (IV) isopropoxide in water and dissolving the obtained precipitate in diluted hydrochloric acid and hydrogen peroxide. This aqueous precursor solution was added to a beaker of toluene while vigorous stirring. Note that any non-polar solvent which is immiscible with the precursor solution could be used. In images (a-c) small spheres of the aqueous phase appear in the nonpolar solvent. At the moment mesoporous silica is added to the mixture, it can be observed from images (d-g) that the precursor infiltrates its pores until the mesoporous silica particles are finely dispersed. Importantly, the volume of the aqueous precursor solution must be equal or less than the total pore volume of the silica template. Only in that case, the majority of the precursor



Figure 5.15. Visual representation of "double solvents" impregnation method: a titanium peroxo complex in diluted hydrochloric acid (dark orange aqueous precursor solution) in toluene while vigorous stirring (a-c). Titania precursor solution in toluene and mesoporous silica template after 0,2,5 and 10 min stirring, respectively (d-g).

infiltrates the pores due to the capillary impregnation. The kinetics of this impregnation affect the amount of material which infiltrates the pores or deposits on the template's exterior.

In a similar manner as the example given in Figure 5.15, the kinetics of the impregnation of a methanol, aqueous and acidic based precursor solution were studied. It was observed that a methanol based precursor infiltrates the pores within seconds, while it took about 30 seconds for an aqueous precursor and several minutes before a 36 w% hydrochloric acid precursor infiltrated the pores completely. The speed of infiltration in a mesoporous silica template may also be affected by the pore diameter, pore structure, viscosity of the precursor solution and the surface chemistry of the pore walls. However, further research is required to investigate these process parameters.

Table 5.2. Contact angles of various precursor solvents and non-polar solvents on glass substrates. Note that water-methanol mixtures with a composition beyond 20:80 showed better wettability of the glass substrates than 92 v% n-octane + 8 v% toluene. Consequently, a polar precursor and non-polar solvent combination with these compositions are expected to give the best impregnation kinetics. Average contact angle of 4 measurements is given.

Solvent mixture	Contact angle on glass (°)
H <sub>2</sub> O	28.5 ± 3.7
90 v% H₂O + 10 v% FA	27.7 ± 1.4
80 v% H <sub>2</sub> O + 20 v% FA	22.3 ± 2.5
50 v% H₂O + 50 v% FA	14.3 ± 0.9
20 v% H₂O + 80 v% FA	16.5 ± 1.7
10 v% H₂O + 90 v% FA	18.3 ± 1.3
FA	14 ± 2.3
90 v% H₂O + 10 v% MeOH	31.7 ± 2.6
80 v% H <sub>2</sub> O + 20 v% MeOH	34.5 ± 2.8
50 v% H <sub>2</sub> O + 50 v% MeOH	27.1 ± 1.8
20 v% H <sub>2</sub> O + 80 v% MeOH	10.5 ± 3.3
10 v% H <sub>2</sub> O + 90 v% MeOH	0
MeOH	0
90 v% H <sub>2</sub> O + 10 v%, 36 w% HCl	35.4 ± 1.3
80 v% H₂O + 20 v%, 36 w% HCI	29.2 ± 3.5
50 v% H <sub>2</sub> O + 50 v%, 36 w% HCl	33 ± 1.1
20 v% H <sub>2</sub> O + 80 v%, 36 w% HCl	32.7 ± 1.1
10 v% H₂O + 90 v%, 36 w% HCI	35.7 ± 1.1
36 w% HCI	33.9 ± 3
toluene	8.1 ± 0.6
xylene	$6.8 \pm 0.8$
n-octane	0
92 v% n-octane + 8 v% toluene	6.2 1.4

The first step of the continuous flow nanocasting process is the infiltration of the polar precursor into the template's pore, which is influenced by the difference in wettability of the silica template by the polar precursor solvent and the non-polar solvent. The interaction of both solvents with the silica template was assessed by contact angle measurements of the polar precursor solution and the non-polar solvent onto a glass (SiO<sub>2</sub>) substrate, reported in Table 5.2. Although the surface properties of glass are very different from those of mesoporous silica, it was used to give us a trend in the wetting behaviour with different solvents. In addition, the influence of the surface roughness was ignored during our experiments. The choice of the co-solvents was limited to solvents which are immiscible with the non-polar solvent, typically toluene, xylene, n-octane or mixtures of these. The glass plates were cleaned in the ultrasonic bath in isopropanol (IPA) and rinsed with water and acetone and were dried before use. The data shows that formic acid (FA) has only a weak effect on the contact angle of water on the glass substrate. On the contrary, the contact

angle of water – methanol mixtures on glass increases when 10 and 20 v% MeOH is added, while it only drops significantly when the mixture consists over 80 v% of MeOH. The contact angles of water – HCl mixtures show that the acidity of the precursor solution does not strongly influence the contact angle. On the other hand, the contact angles of the non-polar solvents show that the wettability increases in the order: toluene > xylene > n-octane. From this data, we can say that the wettability of a polar precursor solution with a composition of 90 v% MeOH possesses a better wetting behaviour of the substrate than toluene, xylene or 92 v% n-octane with 8 v% toluene as non-polar solvent. Based on this principle, the impregnation of the polar precursor solvent into the template can be facilitated. Alternative methods to improve the impregnation kinetics of the polar precursor solution involve surface modification of the template.

#### 5.5.4.5 Influence of the metal salt and non-polar solvent on the impregnation process

Since the molecular weight of the precursor salt is usually higher and the density lower than the desired product, volume constriction of the impregnated precursor during the conversion of a metal salt to its oxide or metallic form is inevitable. However, the loading efficiency of a certain material can be enhanced if the molecular weight difference between the decomposed precursor and the target product is reduced. Firstly, one could simply choose another precursor or the precursor could be thermally decomposed to a denser intermediate during the impregnation. Alternatively, oxidizing or reducing agents could be added to the precursor solvent to chemically and/or thermally decompose the precursor to a denser intermediate during the impregnation.

The decomposition of BiCl<sub>3</sub> to BiOCI during the impregnation is an example how the pore loading can be enhanced. Table 5.3 shows the theoretical maximum pore loading efficiencies of Bi for the impregnation of Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O and BiCl<sub>3</sub> salt and depending on their decomposed intermediate during the impregnation. In the first example, the amount of Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O necessary to fill the template's pores completely with the salt is impregnated. Once the Bi salt is reduced, the pore loading efficiency of metallic Bi is 12 v%. In the second case, the amount of Bi salt impregnated is larger than before, because we consider the decomposition of the precursor during the impregnation to the denser intermediate BiONO<sub>3</sub>. In other words, we assume complete pore filling with BiONO<sub>3</sub>. Upon reduction of BiCl<sub>3</sub> salt is considered, which can lead to a maximum pore filling degree of 32.2 v% metallic Bi when no decomposition occurs and to 60.5 v% when the pores are completely filled with BiOCI.

The higher density and the lower molecular weight of BiCl<sub>3</sub> compared to Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O enables a 2.5 times higher loading of metallic bismuth after the reduction when BiCl<sub>3</sub> is impregnated. The impregnated BiCl<sub>3</sub> salt could decompose inside the pores, leading to a reduction of the occupied pore volume. As a result, more precursor could be added, what enables a further enhancement of the pore loading. The expected mass loading for Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O and BiCl<sub>3</sub> were confirmed by means of XRF analysis.

Table 5.3. Theoretical maximum pore loading efficiencies depending on the decomposed precursor formed during the impregnation of  $Bi(NO_3)_3 \cdot 5H_2O$ ,  $BiCl_3$ . The date shows that a higher pore loading can be achieved when the precursor salt decomposes during the impregnation compared to the case when this does not occur.

Precursor salt	Decomposed intermediate	Target product	Pore loading efficiency (%)
Bi(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	Bi(NO <sub>3</sub> ) <sub>3</sub> .5H <sub>2</sub> O	Bi	12.5
Bi(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	BiONO₃	Bi	36.7
BiCl₃	BiCl₃	Bi	32.2
BiCl <sub>3</sub>	BiOCI	Bi	60.5

The decomposition of the precursor salt is possible due to the high temperature used during the impregnation. Namely, the impregnation was performed in refluxing n-octane, which has a boiling temperature of approximately 127 °C. Due to the removal of the acidic precursor solvent (diluted HCI), the metal salts hydrolysed.

To acquire a better understanding of the decomposition process of the precursor salt during the impregnation, TGA measurements were performed. Note that this gives us only information about the thermal decomposition and not about the influence of the polar solvent or pH of the solution. The decomposition of Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O and BiCl<sub>3</sub> in air are given here as example (Figure 5.16). It can be calculated from the analysed mass loss that the nitrate salt lost 4.4 hydrate water molecules when heated to 108 °C, which is the boiling temperature of toluene, while a mass loss equivalent to 6 water molecules was obtained at 127 °C, the boiling temperature of n-octane. The latter suggest that on top of the removal of all water molecules of  $Bi(NO_3)_3.5H_2O$ , the nitrates started to decompose too. Dry  $BiCl_3$ , on the other hand, starts to decompose only above 250 °C. The DTA signal, indicates the melting of the salt between 220 and 230 °C. Tthe drastic weight loss of BiCl<sub>3</sub> between approximately 200 and 330 °C was due to evaporation of the precursor. The evaporation of BiCl<sub>3</sub> could be suppressed by using humidified air, which hydrolyses the salt to BiOCI with the release of HCl. 17.5 m% of the weight loss of the BiCl<sub>3</sub> precursor could be attributed to the conversion to BiOCI when the TGA data of BiCl<sub>3</sub> was recorded in humidified air, while the remaining 12 m% weight loss was presumably due to evaporation.



Figure 5.16. Thermogravimetric analysis of Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O and BiCl<sub>3</sub> in air at 2 °C/min heating rate.

When the BiCl<sub>3</sub> was dissolved in diluted hydrochloric acid with n-octane as non-polar solvent, the precursor salt hydrolyses due to removal of the acidic precursor solvent. For example, BiCl<sub>3</sub> remains soluble in a 4 mol/L HCl solution, but BiOCl precipitate forms when the solution is diluted to a 1 mol/L HCl solution. As the HCl-water mixture boils off during the impregnation (due to the refluxing conditions), this hydrolysis takes place. Consequently, the hydrolysis of BiCl<sub>3</sub> to BiOCl during the impregnation enables a drastic enhancement of the loading efficiency. Figure 5.17 shows that BiOCl was formed when a polar precursor solution composed of 15 mL 30 w% HCl and 60 mL methanol, both with and without the addition of 15 mL formic acid, was impregnated in a mesoporous silica template dispersed in n-octane. The decomposition products of Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O could not be identified.



Figure 5.17. XRD diffractogram of SBA-15 mesoporous silica sample impregnated with BiCl<sub>3</sub> dissolved in HCl, H<sub>2</sub>O and MeOH or HCl, H<sub>2</sub>O, MeOH and formic acid (FA), while octane was used as nonpolar solvent.





Figure 5.18. (a) TEM image of 12 v% Bi loaded in SBA-15.  $Bi(NO_3)_3$  was dissolved in 20 w% HNO\_3, impregnated and subsequently reduced at 220 °C in a hydrazine loaded Ar-5% H<sub>2</sub> gas flow for 12 h. (b) Bi nanowires after chemical etching of the silica template in 1 mol/L NaOH solution for 3 h. (c) TEM images of 12 v% Bi replicated from KIT-6. Herefore,  $Bi(NO_3)_3$  was dissolved in 10 w% HNO\_3, impregnated and subsequently reduced at 220 °C in a hydrazine loaded Ar-5% H<sub>2</sub> gas flow for 12 h. (d) TEM image of 30 v% Bi loaded in SBA-15. BiCl<sub>3</sub> was impregnated dissolved in a 10 w% HCl - MeOH solution and subsequently reduced at 220 °C in a hydrazine loaded Ar-5% H<sub>2</sub> gas flow for 12 h. (e) Bi nanowires after chemical etching of the silica template in 1 mol/L NaOH solution for 3 h. (f) TEM images of 30 v% Bi replicated from KIT-6. Herefore, BiCl<sub>3</sub> was dissolved in 10 w% HCl - MeOH solution and subsequently reduced at 220 °C in a hydrazine loaded Ar-5% H<sub>2</sub> gas flow for 12 h. (e) Bi nanowires after chemical etching of the silica template in 1 mol/L NaOH solution for 3 h. (f) TEM images of 30 v% Bi replicated from KIT-6. Herefore, BiCl<sub>3</sub> was dissolved in 10 w% HCl-MeOH, impregnated and subsequently reduced at 220 °C in a hydrazine loaded Ar-5%

12  $H_2$ flow for h. gas TEM imaging confirmed that both a 20 w% HNO<sub>3</sub> based bismuth precursor solution and a 10 w% HCI-MeOH precursor solution were effectively impregnated in SBA-15 as depicted in Figure 5.18 (a-d). However, there are some differences in the obtained nanowires depending which precursor solvent/bismuth salt was used. Firstly, more interconnections between the nanowires remained when a nitric acid based metal precursor solvent was used rather than a hydrochloric acid based solution. The interconnections are nanometre thin fibres which originate from the micropores in the template's pore wall which were filled with the precursor and connect the replicated mesopores once the template is removed. This indicates that the micropores, which have a diameter of less than 2 nm were filled easier with Bi(NO<sub>3</sub>)<sub>3</sub> than BiCl<sub>3</sub>. Secondly, the BiCl<sub>3</sub> precursor yields nanowires with more Bi particles outside the template. We believe that this was caused due to leaching of BiCl<sub>3</sub> outside the template's pores, since its melting point of 227 °C is close to the reduction temperature (220 - 230 °C). When KIT-6 mesoprous silica is used as template material, a selfsustaining network of nanowires is obtained as depicted in Figure 5.18 (e-f).

#### 5.5.4.7 Surface modification of mesoporous silica

The precursor salt and the precursor solvent's interaction with the template's pore walls are of major importance to successfully load the template's pore channels. The interactions can be modified either through surface modification of the template, or by changing the precursor solvent. In order to study the interaction between the precursor solvent and different modified silica surfaces, contact angle measurements were performed on a simplified system. Glass microscope plates were used to resemble the surface properties of the template. Although the surface properties of glass and mesoporous silica are very different, the experiment was performed to observe trends in the wetting behavior of the precursor on different modified silica templates. The glass plates were treated in a similar way as the mesoporous silica to obtain surface properties, as close as possible, to that of as the silica template material. Therefore, the glass was washed in isopropanol for 1 h in the ultrasonic bath and subsequently heated at 550 °C for 5 h. The modified glass substrates were prepared by dip coating the plates in a MeOH solution containing 0.01 mL of APTES or MPTMS and drying at 60 °C for 24 h.

	Si-OH	Si-(CH <sub>2</sub> ) <sub>3</sub> -NH <sub>2</sub>	Si-(CH <sub>2</sub> ) <sub>3</sub> -SH
МеОН	0	0	0
MeOH + 5 v% HCl	0	0	0
MeOH + 10 v% HCI	0	0	0
MeOH + 20 v% HCI	0	0	0
H₂O	41	35	40
H₂O + 5 v% HCI	52	36	46
H <sub>2</sub> O + 10 v% HCl	34	33	40
H <sub>2</sub> O + 20 v% HCl	33	28	44
H <sub>2</sub> O	41	35	40
H <sub>2</sub> O + 5 v% HNO <sub>3</sub>	51	38	45
H <sub>2</sub> O + 10 v% HNO <sub>3</sub>	48	36	40
H <sub>2</sub> O + 20 v% HNO <sub>3</sub>	31	32	36

Table 5.4. Contact angles of various precursors on regular glass -OH and  $-NH_2$  or -SH modified glass substrates.

Table 5.4 displays the average contact angles measured for different precursor solvents on regular glass substrates APTES and MPTMS modified glass (Figure 5.19). A methanol based solution with up to 20 v% HCl spread out instantaneously what explains the absence of the contact angle. When an acid precursor solution was used, the most suitable template was APTES modified silica as it possessed a lower contact angle than both unmodified silica and MPTMS modified silica. Generally speaking, the MPTMS modified silica has the worse wettability with an acidic precursor solution, except below approximately 5 v% acid content.

The low contact angles for methanol indicates its excellent wettability, therefore, it could be used to improve the impregnation.



Figure 5.19. (a) (3-aminopropyl)triethoxysilane and (b) (3-mercaptopropyl)trimethoxysilane precursors for the grafting of respectively -NH<sub>2</sub> and -SH functionalities onto the silica surface.

Since many precursor solutions are water or ethanol based, surface modification has been used to alter the hydrophilicity of the pore walls, which could enhance the interaction with the precursor and lead to a better impregnation. To investigate the extent to which surface modification with amine and thiol functionalities affects the impregnation process of an acidic precursor solution, (3-aminopropyl) triethoxysilane (APTES) and (3-mercaptopropyl) trimethoxysilane (MPTMS) were grafted onto the silica surface.



Figure 5.20. FTIR spectrum of SBA-15 mesoporous silica calcined at 700 °C and the APTES and MPTMS modified mesoporous silica samples. It can be seen that the silanol stretch vibration reduced drastically after both APTES or MPTMS modification. The two N-H and three C-H stretch vibrations confirm the grafting of APTES, while only the C-H stretch vibrations of MPTMS modified silica are observed.

Typically, the silica template was calcined at 700 °C to reduce the amount of silanols, as they cannot all be grafted if they are too close to each other. The functionalization was carried out by adding a 3:1 molar ratio between the number of surface silanols and APTES or MPTMS. The number of silanol groups was calculated based on the number of Si-OH groups/nm<sup>2</sup> for samples calcined at 700 °C (Table 5.1) and the BET surface area. APTES or MPTMS was added to the dried silica template dispersed in dry toluene. The mixture was refluxed for 24 h and subsequently filtered and washed with ethanol. FTIR measurements of the silica templates calcined at 700 °C and the amine and thiol functionalized samples are depicted in

Figure 5.20. FTIR shows that the Si-OH stretch vibration at 3750 cm<sup>-1</sup> mostly disappeared upon grafting SBA-15 with APTES and MPTMS.

CHNS elemental analysis were performed on a Thermo Flash 2000 elemental analyser, using  $V_2O_5$  as catalyst. Measurements were conducted on both APTES and MPTMS functionalized SBA-15 samples in order to confirm the presence of N and S, respectively (Table 5.5).

Table 5.5. CHNS data of APTES and MPTMS modified SBA-15.

	m% C	m% H	m% N	m% S	m% CHNS
SBA 15 – APTES	6.83	1.29	1.13	0	9.25
SBA 15 – MPTMS	5.48	0.87	0	1.38	7.72

The TEM images in Figure 5.21 depict the effect of the surface functionalities of the SBA-15 template on the morphology of formed Bi nanostructures. All impregnations were conducted with BiCl<sub>3</sub> salt dissolved in diluted HCl. It can be seen that leaching phenomena occur particularly when untreated silica is used. However, there is still significant leaching with the APTES modified silica templates. Nevertheless, we believe the basic functionality of the -NH<sub>2</sub> moieties may facilitate the impregnation of the acid solution. In case a small amount of bismuth precursor was impregnated in the thiol modified template (Figure 5.21e), well dispersed bismuth nanoparticles appear to be stabilized within the pores without growing to larger particles. Even after a high loading of precursor, leaching phenomena and the growth of bismuth large bismuth particles seems to be suppressed. We anticipate this is due to the



Figure 5.21. TEM images of functionalised SBA-15, impregnated with BiCl<sub>3</sub> dissolved in a 10 w% HCl - MeOH and reduced at 220 °C for 10 h in a flow of Ar, 5% H<sub>2</sub> gas enriched with hydrazine. (a,b) Templated nanocasting of Bi nanowires in unmodified SBA-15 template. (c,d) Templated nanocasting of Bi nanowires in  $-NH_2$  modified SBA-15 template. (e,f) Templated nanocasting of Bi nanowires in -SH modified SBA-15 template.

favourable soft-soft interaction of bismuth and sulphur. When the template was removed, well defined nanowires can be observed (Figure 5.21f).

However, it must be noted that the grafting with APTES and MPTMS makes the template more hydrophobic. In addition, the propyl chain of the grafting agents contributes to the reduction of the hydrophilicity. The reduction of the hydrophilicity of the surface is particularly the case for MPTMS, since the  $-NH_2$  functionality can still carry a charge in an aqueous media. It was also observed that MPTMS modified silica templates cannot be impregnated easily with an aqueous precursor solution, but instead a methanol based precursor is preferred. However, methanol as co-solvent is not compatible with APTES modified silica's since the alcohol could react with the amine functionality of APTES.

#### 5.5.4.8 Polar precursor solvent vs non-polar solvent compatibility

The choice of non-polar solvent depends on the precursor solvent requirements. Table 5.6 shows the compatibility of several precursor solvents and non-polar solvents which were studied. The formation of a low boiling azeotrope of the non-polar solvent with the precursor solvent is advantageous to remove the latter. An example of this is the low boiling azeotrope of water and toluene at 84.1 °C resulting in a vapour mixture of approximately 55.6 % toluene and 44.4 % water [30], which leads to an efficient elimination of water from the precursor solvent.

Table 5.6. Compatibility chart for double solvent impregnation method of some common polar precursor solutions and nonpolar solvents. The temperatures in brackets shows the boiling point of the pure solvents or the azeotropic boiling point of the mixture. The term "Immiscible" indicates the precursor solvent and nonpolar solvent are compatible for the double solvent impregnation method, or simply that they are sufficiently immiscible.

Solvent compatibility chart	n-Hexane (68.5 °C)	n-Heptane (98.5 °C)	n-Octane (± 126 °C)	Toluene (110.7 °C)	Xylene (± 138 °C)
Methanol	Immiscible	Immiscible	Immiscible	-	-
(64.7 °C)	(50.6 °C)	(59.1 °C)	(63.0 °C)	(63.6 °C)	(64 °C)
Formic acid	-	-	Immiscible	Immiscible	Immiscible
(100 - 101 °C)	(60.6 °C)	(78.2 °C)	(90.5 °C)	(85.8 °C)	
Dil. Hydrochloric acid (61 - 108 °C)	-	-	Immiscible	Immiscible (84.1 °C)	Immiscible
Dil. nitric acid (83 - 121 °C)	-	-	Immiscible	Immiscible (84.1 °C)	Immiscible
Water (100 °C)	-	-	Immiscible	Immiscible (84.1 °C)	Immiscible

# 5.5.5 Post treatment and reduction of precursor material – silica nanocomposite

Various post treatments can be performed after the impregnation of the precursor salt. Such as the oxidation, reduction or chemical modification of the metal salt. Mesoporous metal oxides can be prepared by calcination of an impregnated metal nitrate salt for instance. Mesoporous metals, on the other hand, are either synthesized by thermal decomposition of its precursor, which is the case for AgNO<sub>3</sub> [31] or by reducing the impregnated precursor in a flow of argon – hydrogen gas (Ar – 5% H<sub>2</sub>). Here we also tested the use of reactive reducing agents such as hydrazine monohydrate or formic acid in order to lower the reduction temperature. This was particularly important for the reduction of bismuth salts since metallic bismuth melts already at 271.5 °C.

Alternatively, the impregnated metal salt within the template's channels could also be converted through the reaction with a CVD precursor. The treatment with a CVD precursor can be used to passivate the material's surface to avoid oxidation when exposed to air, to dope the material, to alter the composition or to enhance the pore loading. As an example,  $BiCl_3$  and  $Bi(NO_3)_3$  were treated with hydrogen selenide ( $H_2Se$ ) and trimethylstibine ( $Me_3Sb$ ) to convert the precursor salt to  $Bi_2Se_3$ ,  $Bi_{1-x}Sb_x$  or  $(Bi_{1-x}Sb_x)_2Se_3$ . Both precursor salts reacted with the reactive gas at a temperature between 100 and 200 °C. The same principle can be used for the synthesis of materials.

The treatment of the impregnated material with a volatile reactive metal precursor may also increase the amount of impregnated material, creating extra percolation paths, and/or strengthen the nanowire network. For example, when a mesoporous silica template is completely impregnated with BiCl<sub>3</sub>, upon treatment with any volatile chemical vapour deposition (CVD) precursor of Bi, such as Me<sub>3</sub>Sb, the volatile antimony source can react with BiCl<sub>3</sub> and form BiSb<sub>(s)</sub> and 3 CH<sub>3</sub>Cl<sub>(g)</sub>. Consequently, due to the reaction of the gaseous precursor with the metal salt inside the pores, the pores are extra filled.

Experimental results concerning the post-treatments of metal precursor – silica nanocomposite samples are provided in Chapter 8.

# 5.6 Conclusions

It was shown that the nanocasting method is a very powerful technique to synthesize mesoporous materials. Nevertheless, there are also many limitations coherent with this method. The possibility to successfully replicate the template material depends on many factors, such as the mobility of the precursor salt on the pore surface, the tendency of the precursor salt to aggregate, the wettability of the precursor solvent, the used nanocasting technique, the thermal treatment, etc.

The nanocasting method described here enables us to force the precursor inside the template's pore channels through capillary action and decompose the salt upon removal of the precursor solvent by means of a dean stark separator. As the precursor is added in a dropwise manner, little material is deposited onto the outside of the mesoporous silica grains. An important achievement in the nanocasting process was the ability to decompose the precursor salt during impregnation and deposit a denser precursor, what enabled us to achieve extremely high pore loading efficiencies compared to state of the art nanocasting techniques. In addition, the ability to use higher boiling solvents or work at higher pressures could possibly lead to further enhancement of the pore filling degree and a better replicated structure.

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# 6

### Nanostructured SrTiO<sub>3</sub> thermoelectrics

This chapter is dedicated to the development of a sol-gel based nanocasting synthesis route of  $SrTiO_3$ . Different strategies to adapt the impregnation rate of a mixed precursor solution are discussed to control the stoichiometry of the impregnated material. The impregnation of a double salt precursor, which provides greater control of the stoichiometry is discussed. It is also shown how the material could be doped by La.

#### 6.1 Introduction

Parallel with the study on nanostructured metallic TEs, much effort has been devoted to seek oxide materials exhibiting good TE properties since they are thermally and chemically more stable than their metallic counterparts [1]. Furthermore, they contain no toxic elements, consist of cheaper materials than conventional tellurium based TEs and they can operate at high temperature. Promising oxide TE materials, exhibiting a metallic behaviour, are the cobalt oxides,  $Na_xCoO_2$  and  $Ca_3Co_4O_9$  [2-6] as p-type TE material and  $SrTiO_3$ ,  $CaMnO_3$  [7] and ZnO [8, 9] as n-type TE material. One of the best n-type TE oxides is the perovskite-type material  $SrTiO_3$ . Also, it is an environmentally friendly, relatively cheap, chemically and thermally stable material. Interestingly, it has been shown that low dimensional  $SrTiO_3/SrTi_{0.8}Nb_{0.2}O_3$  superlattices resulted in a drastic enhancement of the Seebeck coefficient [10], which we intended to exploit in this research.

#### 6.2 Thermoelectric properties of SrTiO<sub>3</sub>

The 3d transition-metal oxide SrTiO<sub>3</sub> is of great interest for thermoelectric applications due to its high Seebeck coefficient and the ability to control the carrier concentration over a wide range up to  $10^{22}$  cm<sup>-3</sup> [3]. A large power factor PF was observed in La<sup>3+</sup> doped SrTiO<sub>3</sub> with a metallic carrier density in the range of 0.2-2 x  $10^{21}$  cm<sup>-3</sup> at room temperature, which is comparable with that of Bi<sub>2</sub>Te<sub>3</sub> compounds. Nevertheless, the zT value of doped SrTiO<sub>3</sub> is only

about 0.09 at room temperature, which is about one order of magnitude less than that of optimized Bi<sub>2</sub>Te<sub>3</sub> compounds. The lower zT of SrTiO<sub>3</sub> compared to heavy metal alloys as Bi<sub>2</sub>Te<sub>3</sub> can be attributed to the large thermal conductivity (respectively, 12 W/mK compared to 0.5-2 W/mK). Below room temperature SrTiO<sub>3</sub> is a nonmagnetic band insulator in which the valence band originates from the oxygen 2*p* state and the conduction band from the Ti 3*d*-*t*2*g* state with threefold orbital degeneracy. It is believed that the large entropy term arises from the sixfold degeneracy of the Ti 3*d*-*t*<sub>2*g*</sub> conduction bands, while the large density of states (DOS) effective mass (m<sub>d\*</sub>  $\approx$  6-10 m<sub>0</sub>) gives the material a large Seebeck coefficient. [10, 11]

#### 6.3 Synthesis of mesoporous and nanowire composite SrTiO<sub>3</sub>

Mesoporous SrTiO<sub>3</sub> has never been made before and for that reason several synthesis routes were explored to make this material. As mentioned earlier, two general methods are available for the synthesis of mesoporous materials. Firstly, one could use a soft template synthesis or secondly, a hard templating approach. In summary, in the soft templating method, a structural directing agent, such as CTAB, Pluronics P123, F127, etc., forms a liquid crystal lattice in solution, which acts as scaffold around which the inorganic precursor "polymerizes". The synthesis of mesoporous materials via this method is ideal when the inorganic precursor forms an amorphous network at temperatures below the decomposition temperature of the structural directing agent. However, when the inorganic precursor crystallizes during the synthesis, it destroys the "soft" liquid crystal lattice leading to structural collapse. Since a temperature exceeding 700 °C is required to form SrTiO<sub>3</sub>, the soft templating approach is not suitable for this material. Alternatively, a hard templating method, which provides a more rigid template and possesses a better thermal stability, was required to form mesoporous SrTiO<sub>3</sub> within the template's pore channels.

The loading of SrTiO<sub>3</sub> precursor into the template was tested by two approaches. Firstly, a diluted precursor solution containing both strontium ions and titanium ions stabilized with complexing agents was impregnated into a mesoporous silica template. A second approach was based on the direct impregnation of Sr(NO<sub>3</sub>)<sub>2</sub> or SrCl<sub>2</sub> salts without any complexing agents and various titanium oxalate Ti(OXA)<sub>2</sub> complexes in order to obtain a Sr(OXA)<sub>2</sub>Ti.xH<sub>2</sub>O molecular precursor within the pores, leading to a higher efficiency of pore loading of SrTiO<sub>3</sub> and better control of the stoichiometry.

#### 6.4 Experimental section

#### 6.4.1 Materials

Oxalic acid dihydrate ( $\geq$  99 %) (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>.2H<sub>2</sub>O), 30 % hydrogen peroxide, Sr(NO<sub>3</sub>)<sub>2</sub>, 97 % titanium(IV) isopropoxide (TTIP), 98 % iminodiacetic acid (IDA), 99 % DL-tartaric acid (TTA),  $\geq$  99 % mono ethanol amine (EA),  $\geq$  99 % triethanolamine (TEA), 99 % citric acid (CA), 99 % malonic acid (MAL) and anhydrous  $\geq$  99 % ethylenediaminetetraacetic acid (EDTA) were purchased from Sigma Aldrich. All chemicals were used as received.

#### 6.4.2 Synthesis

#### 6.4.2.1 Mixed Sr-Ti metal precursor solution

Various Sr-Ti precursor solutions were synthesized based on  $Sr(NO_3)_2$  complexated with iminodiacetic acid (IDA), while Ti-peroxo complexes were formed with citric acid (CA), tartaric

acid (TTA), malonic acid (MAL), triethanolamine (TEA) and IDA as complexing agent. The structure and the  $pK_a$  values of the complexing agents are depicted in Figure 6.1.



Figure 6.1. Chemical structures of the used complexing agents with their pK<sub>a</sub> values obtained from literature.

Typically, the mixed precursor solution was synthesized by dissolving  $Sr(NO_3)_2$  in water and adding 2.1 equivalents IDA. In order to dissolve the complexing agent, the base EA was added until a pH of 6 was reached. After stirring for 30 min, a clear and stable precursor solution with a metal concentration of 1 mol/L could be obtained. An equimolar amount of titanium precursor was prepared by hydrolysing titanium(IV) isopropoxide in water, which yielded a Ti(OH)<sub>4</sub> precipitate that could be dissolved in a mixture of 2 eq.  $H_2O_2$  and 2.1 eq. complexing agent and EA to bring to pH to 6. After 30 min stirring at 60°C a clear solution was obtained with a metal concentration of 1 mol/L. Both solutions were mixed together at 60 °C and subsequently filtered to remove any possible precipitate. The precursor could be used as such and remained stable for several months in a pH range of typically 4 to 8 depending on the used complexing agents.

Mixed complexing agent precursor solutions for Ti were prepared by dissolving the required amount of  $Ti(OH)_4$  precipitate in a mixture of 2 eq.  $H_2O_2$  and 1.05 eq. of each of the complexing agents. The remaining synthesis steps were identical as those mentioned above.

#### 6.4.2.2 Impregnation of SrTiO<sub>3</sub> mixed metal precursor solution into mesoporous silica

Typically, a vacuum impregnation method assisted by ultrasonic sonication was used to infiltrate the mesoporous silica template with the aqueous metal precursor solution. This hybrid impregnation technique was based on ref. [19] and was further optimized for our purpose. Namely, Kong *et al.* reported the use of a high vacuum to infiltrate a liquid metal precursor solution into the pores of an ordered mesoporous silica template. In addition to that, we placed the samples in the ultrasonic bath for the duration of the impregnation to facilitate the impregnation. Prior to the impregnation, the template was degassed for 12 h at 130 °C under high vacuum to evaporate all physisorbed water inside the template's pores. In a typical synthesis, 2 mL 0.5 mol/L Sr-Ti mixed precursor solution was added under vacuum to 0.2 g template and subsequently placed in the ultrasonic bath, which facilitated the impregnation. The silica template was sonicated for 30 min to 5 h and subsequently separated through filtration. The sample was not washed to avoid leaching of the precursor impregnated from the pore channels.

### 6.4.2.3 Synthesis and impregnation of Sr(OXA)<sub>2</sub>Ti.2H<sub>2</sub>O double salt into mesoporous silica

Bulk  $Sr(OXA)_2Ti.2H_2O$  double salt was synthesized by dissolving  $SrCl_2$  in water, adding a solution containing 1.1 eq. oxalic acid and subsequently adding a solution of 0.5 mol/L  $Ti(OXA)_2$  complex at a temperature of 80 °C. The double salt formed instantaneously and the obtained precipitate was collected through filtration, washed three times with water and subsequently dried at 60 °C overnight. The  $Ti(OXA)_2$  solution was prepared by hydrolyzing TTIP in water, filtering the  $Ti(OH)_4$  precipitate and immediately dissolving the powder in 2.2 eq. OXA in a minimal amount of water, such that a high concentration of oxalic acid is obtained. Once all precipitate was dissolved, the solution was diluted to obtain a metal concentration of 0.5 mol/L.

The impregnation of this double salt within the pores of a mesoporous silica template was performed by impregnating 20 v% of the pores with SrCl<sub>2</sub> or Sr(NO<sub>3</sub>)<sub>2</sub>. Therefore, the "bubble" impregnation method was used to load the salt into the template's pores. More details concerning this impregnation method will be given in §7.2.2. Typically, for 1 g SBA-15 silica template with a pore volume of 1 mL/g, 0.6 g Sr(NO<sub>3</sub>)<sub>2</sub> and 8 mL water were added to the template in a perfluoroalkoxyalkane polymer (PFA) 250 mL round bottom flask. Next, 100 mL toluene was added, forming a two-phase system of water,  $Sr(NO_3)_2$  and SBA-15 on one hand and toluene on the other hand. A Dean Stark separator was attached to the round bottom flask and the solution was refluxed, using a bath temperature of 140 °C. By means of a Dean Stark separator, the aqueous phase was removed in a continuous manner. Since the silica template preferentially migrated to the aqueous phase, the  $Sr(NO_3)_2$  salt was "pushed" into the pores as all water was removed from the system. Typically, the mixture was refluxed for approximately 5 h until all aqueous precursor was removed and a loosely dispersed powder was obtained in the toluene phase. The impregnated material was subsequently filtered, washed with toluene and dried overnight at 60 °C. Next, the powder was stirred with a titanium oxalate precursor forming the double salt Sr(OXA)<sub>2</sub>Ti.2H<sub>2</sub>O. Herefore, 0.84 mL TTIP was hydrolyzed in water, filtered and immediately dissolved in 0.584 g OXA with 5 mL water. Once all Ti(OH)<sub>4</sub> precipitate was dissolved, the solution was diluted to 11.3 mL. The dried silica-Sr(NO<sub>3</sub>)<sub>2</sub> composite powder was stirred for 30 min with the 0.5 mol/L Ti(OXA)<sub>2</sub> solution, yielding a Sr(OXA)<sub>2</sub>Ti.2H<sub>2</sub>O precipitate. Depending on the solvent nature, the precipitate leached out or remained inside the pores. Typically, the higher the water content the more difficult it was to prevent leaching phenomena. 0.5 mol/L Ti(OXA)\_2 precursor solutions were prepared in water, 35 v% water in MeOH and 35 v% water in IPA.

Alternatively, when the pores were impregnated with  $SrCl_2$  instead of  $Sr(NO_3)_2$ , an extra modification step was required to remove all chlorides. Namely, the silica-  $SrCl_2$  composite powder was stirred for 10 min with a 0.5 mol/L aqueous solution of 1.2 eq. oxalic acid dihydrate (OXA), forming strontium oxalate (SrOXA). The following steps involved the treatment with  $Ti(OXA)_2$  as described above, drying and calcination.

#### 6.4.2.4 Synthesis of crystalline SrTiO<sub>3</sub>

Any of the aforementioned Sr-Ti precursor solution, either as gel or impregnated in a mesoporous silica template, were thermally treated between 700 and 850 °C to form crystalline SrTiO<sub>3</sub>. The calcination was performed in air in a box furnace, using a heating rate of 2 °C/min and a dwell time of 2 h.

#### 6.4.3 Characterization

See paragraph 5.5.3.

#### 6.5 Results and discussion

#### 6.5.1 Nanocasting using a mixed Sr-Ti metal precursor

Firstly, a mixed Sr-Ti precursor was prepared to impregnate the silica template and subsequently subjected to a thermal treatment to obtain  $SrTiO_3$ . The precursor solution optimization concerned the selection of the metal salt source, the choice of complexing agents, the pH regulator and the solvent and/or co-solvent with the aim to obtain a precursor solution with high metal ion concentration and good wetting behaviour of the template. However, there are also some restrictions concerning the precursor solution chemistry which have to be considered. Namely, the metal complexes have to be sufficiently small to access the mesopores of the template material easily and the infiltration rate of both Sr and Ti complexes should be the same to obtain a 1:1 ratio between both ions resulting in phase pure  $SrTiO_3$  after the thermal treatment.

A water based precursor solution was chosen as it enabled us to prepare a highly concentrated precursor solution, since we wanted to obtain a high loading of precursor in the pores during the impregnation. In order to synthesize a stable water based precursor solution of both strontium and titanium, hydrolysis of the metal ions had to be avoided. Sr(NO<sub>3</sub>)<sub>2</sub> could be easily dissolved in water and remained stable under acidic conditions. However, the titanium precursor used, titanium tetraisopropoxide (TTIP), hydrolysed immediately upon contact with water. Therefore, strong complexing agents were required to obtain a stable precursor solution of both Sr and Ti. The base ethanolamine (EA) was used since it does not evaporate during drying of the precursor solution.

Drying the solution yielded a clear gel without any precipitates. The thermal decomposition of the Sr-IDA/Ti-TEA mixed precursor in air is shown in Figure 6.2. The profile of the weight loss as a function of the temperature shows that most precursor decomposes below 550 °C. The weight loss of the precursor occurs gradually. Any weight loss below 100 °C can be assigned to vaporization of water since it is the only volatile component. EA evaporates at 170 °C, but does not show a distinct signal in the TGA. Further, a gradual decomposition of the organic complexing agents takes place. However, a temperature of approximately 650 °C is required

to remove all organics, since no further weight loss occurs above that temperature. The DTA signal in Figure 6.2 indicates that the most exothermic decomposition of the precursor occurs around 550 °C. Subsequently, the precursor gel was calcined in air at a temperature of 850 °C for 2 h. It can be seen in the XRD diffractogram in Figure 6.3 that crystalline SrTiO<sub>3</sub> was obtained.



Figure 6.2. TGA analysis (left axis) and DTA analysis (right axis) of Sr-IDA/Ti-TEA precursor solution in air.



Figure 6.3. XRD diffractogram of SrTiO<sub>3</sub> after the calcination of the Sr-IDA/Ti-TEA precursor solution at 850 °C for 2h in air. The reference pattern of SrTiO<sub>3</sub> was obtained from Ref.

To understand the influence of the complexing agent and the pH on the impregnation kinetics of the mixed Sr-Ti precursor solution inside a mesoporous silica template, we impregnated a Sr-Ti mixed precursor with different complexing agents in a pH range from about 4 to 9 and measured the impregnated Ti/Sr ratio by means of X-ray fluorescence spectroscopy (XRF) as depicted in Figure 6.4. It is observed that the impregnation efficiency of the Sr complex and the Ti complex were pH dependent and changed for the different complexing agents used.

The influence of the complexing agent and the pH on the impregnation kinetics of the mixed Sr-Ti precursor solution was investigated by impregnation of a Sr-Ti mixed precursor with different complexing agents in a pH range from about 4 to 9 and measuring the impregnated Ti/Sr ratio by means of X-ray fluorescence spectroscopy (XRF) (see Figure 4). It can be observed that the impregnation efficiency of the Sr complex and the Ti complex were pH dependent and changed for the different complexing agents used.



Figure 6.4. Impregnated Ti/Sr ratios inside a SBA-15 mesoporous silica template analysed by XRF of several Sr-Ti precursor solutions as a function of pH during impregnation.

Figure 6.4 indicates that the impregnated Ti/Sr ratio can be controlled by changing the combination of complexing agents. This influences the interaction of the Sr and Ti complex with the silica surface and so the impregnation efficiency for both metal complexes. The interactions of the precursor and the template are influenced by the  $pK_a$  values of the specific carboxylic groups present in the complexing agent, the number of amine and carboxylic groups, the size of the complex and the charge density of the cation. IDA was used as complexing agent for Sr(NO<sub>3</sub>)<sub>2</sub>. If we consider the number of carboxylic acid functionalities present in the complexing agent used to chelate the titanium ions, then we can notice that the Ti/Sr ratio reduced significantly when the acidity of the complexing agent increased. In the case of Ti ions chelated with citric acid, more Sr precursor was impregnated than Ti precursor above a pH of approximately 5.

	TEA	IDA	MAL	TTA	CA	SILICA
pH<1.85	+1	+1	0	0	0	-OH
1.85 < pH < 2	+1	0	0	0	0	-OH
2 < pH < 2.84	+1					-0-
2.84 < pH < 3.09	+1	-1	-1	0	0	-0
3.09 < pH < 3.22	+1					-0-
3.22 < pH < ±4	+1	-1	-1	-1	-1	-0
±4 < pH < 4.75	+1					-0-
4.75 < pH < 4.85	+1	-1	-1	-1	-2	-0-
4.85 < pH < 5.41	+1			-2	-2	-0-
5.41 < pH < 5.69	+1	-1	-1	-2	-3	-0-
5.69 < pH < 7.74	+1		-2	-2	-3	-0-
7.74 < pH < 9.79	0	-1	-2	-2	-3	-0
9.79 < pH		-2	-2	-2	-3	-0-

Table 6.1. Charge on the individual complexing agents and on silica as a function of the pH.

For a successful impregnation of the Sr-Ti precursor solution into the pores of the template, the affinity of the solvent and the interaction of the metal complexes with the template material is crucial. Based on the data shown in Figure 6.4, we can see that the ratio of Sr/Ti impregnated in the silica template changes depending on the pH and depending on the used complexing

agents. If we compare the used complexing agents shown in Table 6.1, we see a difference in number of carboxylic acid and amine groups. Since the charge of the complexing agent changes with pH, we can expect that this affects the charge on the entire metal complex and its interaction with the silica surface. We anticipate that the difference in charge of the metal complexes affects the impregnation kinetics. Therefore, we want to form a  $SrTiO_3$  precursor solution in which Sr-ions and Ti-ions are chelated with different complexing agents, such that the total charge of each of the complexes is similar. Consequently, we expect that a more uniform impregnation of both metal complexes would be obtained. The isoelectric point of silica is at approximately pH 2. Below that pH the silica surface is neutral, while the silanol moieties becomes negatively charged above pH 2. An empirical evaluation of the net charges on the complexing agents, based on their pKa values is reported in Table 6.1. The charge on the silica surface as a function of the pH is also provided. Note that this is an over simplification of a complex process that would require further research to fully understand. The data in Table 6.1 shows the net charge on one molecule of the respective complexing agent as a function of the pH. Since we do not know the exact number of complexing agents interacting with the metal ions in solution, we cannot determine the charge of the entire metal-chelate complex. Nevertheless, we can order the complexing agents from the positively to most negatively charged as: TEA > IDA > MAL > TTA > CA. The experiment data shown in Figure 6.4 were obtained by impregnating 0.2 g mesoporous silica template with a mixed precursor solution of 2 mL 0.5 mol/L Sr-IDA complex and 0.5 mL Ti-TEA, Ti-IDA, Ti-TTA and Ti-CA for the same time at different pH's. It appears from Figure 6.4 that the Ti/Sr ratio impregnated in the template follows the same trend as the charge on the complexing agent. Namely, the highest to lowest Ti/Sr ratio impregnated can be ordered as: TEA > IDA > TTA > CA. From this observation, we can conclude that the charge of the metal-chelate complex may affect the electrostatic interaction with the silica surface and influence the impregnation rate of the individual metalchelate complexes.

Based on the aforementioned reasoning, we investigated the Ti/Sr impregnated ratio when two different complexing agents were used for the Ti-complex. The impregnated Ti/Sr ratio as a function of the pH for the mixed precursor solutions of Sr-IDA and Ti-TEA, Ti-IDA-TTA and Ti-MAL-CA were determined by XRF analysis and shown Figure 6.5.



Figure 6.5. Impregnated Ti/Sr ratios analysed by XRF of several Sr-Ti precursor solutions as a function of pH during impregnation.

The data in Figure 6.5, show that the only impregnated mixed precursor solution yielding a Ti/Sr ratio = 1 was obtained for the Sr-IDA and Ti-MAL-CA precursor impregnated at a pH of

approximately 5.5. Below that pH, the Ti/Sr exceeded 1, while more Sr-IDA was impregnated above that value.



Figure 6.6. Impregnated Ti/Sr ratios analysed by XRF of a Sr-IDA/Ti-MAI-CA precursor solution as a function of the pH during impregnation for several impregnation times: 20 min, 1 h and 5 h.

It can be seen in Figure 6.6 that also the impregnation time affects the impregnated Ti/Sr ratio. After optimizing the impregnation conditions (Figure 6.5) we could successfully impregnate a water based Sr-Ti mixed precursor solution and control the Ti/Sr ratio that effectively infiltrates the template's pore channels by controlling the impregnation time which seems optimal after 5h.

After impregnating the mesoporous silica powder a thermal treatment transformed the mixed Sr-Ti precursor into crystalline SrTiO<sub>3</sub> inside the template's pore system. Figure 6.7a shows the X-ray diffraction pattern of a silica template impregnated with a 1 mol/L Sr-IDA/Ti-MAI-CA precursor solution for 5 h and subsequently calcined at 850 °C. Note that TiO<sub>2</sub> was present as secondary phase due to an off stoichiometry of the impregnated precursor. Generally, there was insufficient control of the impregnation kinetics of both precursors to obtain phase pure SrTiO<sub>3</sub>. Nitrogen sorption measurements of the original template and after impregnation and decomposition of the precursor indicate a reduction of the pore diameter with 0.8 nm as shown in Figure 6.7b.



Figure 6.7. (a) XRD pattern of  $SrTiO_3$  -  $SiO_2$  composite powder after impregnation and calcination of mixed precursor solution. (b) Pore size distribution of SBA-15 and impregnated SBA-15 calculated on the desorption branch.

#### 6.5.2 Problems concerning the optimization of the impregnation procedure

Although we managed to fill the pores successfully with the Sr-Ti precursor solution, we encountered some problems with the applicability of the aforementioned impregnation technique. Firstly, the experimental reproducibility in terms of the impregnated Ti/Sr ratio was insufficient. Namely, the pH, the metal concentration of the precursor solution and the impregnation time influenced the amount of Sr and Ti that effectively entered the pores, which made the aforementioned optimization unreliable. Secondly, the impregnation method did not allow a sufficiently high filling of the pores. Since the pores were impregnated with a solution and subsequently dried and calcined, a drastic volume reduction of material inside the pores occurred. Namely, after drying the precursor solution becomes a rigid transparent gel that mainly comprises of organic material (complexing agents), which prevents the metal ions to precipitate. As can be seen in the TGA results of a dried Sr-Ti precursor solution in Figure 6.2, only 20 m% of the gel was converted to SrTiO<sub>3</sub>. The mass of SrTiO<sub>3</sub> present in pores was estimated assuming that the pores were completely filled with a 1 mol/L Sr-Ti precursor solution, which was typically used. Taking into account that ceramic SrTiO<sub>3</sub> has a density of 5.11 g/cm<sup>3</sup>, it was derived that 3.5 v% of the pores could be filled with SrTiO<sub>3</sub> during one impregnation. A higher filling degree could only be obtained if multiple impregnation steps were performed.

Although the developed technique was not suitable to fill the pores sufficiently for our purpose, it could be used to synthesize complex metal oxide nanoparticles inside mesoporous silica, provided that there is sufficient control of the stoichiometry of the impregnated metal oxide precursors or if similar metal ions/metal ion complexes with a similar charge density and ligands are impregnated.

#### 6.6 Impregnation of double salt precursor solutions

A completely new technique was developed to impregnate a water based precursor solution of a strontium salt without any complexing agent together with a titanium oxalate complex inside the silica template. Namely,  $SrCl_2$  or  $Sr(NO_3)_2$  salt was used since they lead to a higher loading than in the case they were stabilized by complexing agents. The titanium precursor, on the other hand, required a complexing agent to avoid hydrolysis in an aqueous medium. In this case, oxalic acid was used as a chelating agent since it is a very small molecule and it decomposes at a relatively low temperature. Namely, its main decomposition step is between 190 and 220 °C (TGA, 50 ml/min air flow, 10 °C /min heating rate). Rather than forming a gel, the combination of both solutions resulted in the formation of  $Sr(OXA)_2Ti.2H_2O$  double salt yielding crystalline  $SrTiO_3$  after calcination without any secondary phases.

The impregnation method of the strontium salt was based on a double solvent system where the silica was dispersed in toluene as nonpolar solvent, while an aqueous phase containing the metal salt was added. The water phase, containing  $Sr(NO_3)_2$ , impregnated in the pores and became more concentrated by heating the solution at 140°C while removing the water via a Dean Stark setup. This process was continued until all water was removed and the silica template loaded with strontium salt in the pores remained. Presumably, the nonpolar solvent prevented the salt to deposit outside the pores. (S)TEM imaging and EDX analysis showed that  $Sr(NO_3)_2$  was successfully impregnated in the pores and homogeneously distributed. Typically, a mass loading of 15-25% was obtained. TEM images of SBA-15 with  $Sr(NO_3)_2$  impregnated in its pore system are shown in Figure 6.8. Note that this impregnation method was the successor of the impregnation method described in Chapter 5.



Figure 6.8. TEM images of SBA-15 impregnated with  $Sr(NO_3)_2$  without any heat treatment, note there is hardly external  $Sr(NO_3)_2$  deposited.



Figure 6.9. STEM images of SBA-15 impregnated with  $Sr(NO_3)_2$ . Point EDX indicates the presence of Sr rich (light coloured) and Si rich (dark coloured) regions.

After filling the pores partially with  $Sr(NO_3)_2$ , the composite was treated with a titanium oxalate solution in water, water/methanol or water/isopropanol, which formed the  $Sr(OXA)_2Ti.2H_2O$  double salt upon contact with  $Sr(NO_3)_2$ . After drying and calcination, crystalline  $SrTiO_3$  was formed. Note that the mechanism of this reaction has been studied intensively for the synthesis of bulk  $SrTiO_3$  [20]. However, it required more care to form the double salt inside the template's pores without letting the material leach out of the template's pore system. Namely, the impregnated  $Sr(NO_3)_2$  tended to dissolve when the  $Ti(OXA)_2$  precursor was added, causing the double salt to precipitate outside the pores rather than inside. The leaching phenomena can be seen in Figure 6.10. In order to reduce the solubility of  $Sr(NO_3)_2$  while the composite powder was treated with the  $Ti(OXA)_2$  precursor solution, methanol and isopropanol were added since it reduces the solubility of the salt. However, an increasing amount of methanol or isopropanol also destabilized the precursor causing precipitation of  $Ti(OXA)_2$  when the volume fraction of alcohol exceeded 65 v%. Also, sufficient water was required to be able to form the double salt. Consequently, two solutions were tested, namely, a mixture of 35 v% water with methanol and 35 v% water with isopropanol.

Implementing the aforementioned handlings helped us to reduce the amount of leaching as shown in Figure 6.10. It can be seen that the amount of externally deposited  $SrTiO_3$  was significantly reduced by using a solvent with a poor solubility for  $Sr(NO_3)_2$ . The effect is the most noticeable when a solution of  $Ti(OXA)_2$  in 35 v% water in isopropanol was used. However, adding isopropanol also destabilized the precursor leading to precipitation of the titanium oxalate precursor and deterioration of the phase purity of the formed  $SrTiO_3$ .



Figure 6.10. TEM images of external SrTiO<sub>3</sub> after the reaction of Sr(NO<sub>3</sub>)<sub>2</sub> impregnated SBA-15 with Ti(OXA)<sub>2</sub> dissolved in water (a,b), Ti(OXA)<sub>2</sub> dissolved in 35 v% water and methanol (c,d) Ti(OXA)<sub>2</sub> dissolved in 35 v% water and isopropanol, followed by a thermal treatment at 850 °C.



Figure 6.11. STEM image of SBA-15 impregnated with  $SrTiO_3$ , by the impregnation of  $Sr(NO_3)_2$  and the reaction with  $Ti(OXA)_2$  dissolved in 35 v% water and isopropanol, calcined at 850 °C. Note that the dark regions are  $SrTiO_3$  poor while the light ones are  $SrTiO_3$  rich. Inset: SAED pattern of  $SrTiO_3$ .

The STEM image and SAED shown in Figure 6.11 indicated that crystalline  $SrTiO_3$  is present in the material. However, it is not completely obvious from the image whether  $SrTiO_3$  nanowires were contained within the pores or not. The white zones are  $SrTiO_3$  rich while the dark zones are Si rich. It is noticeable that the sides of both silica templates are whiter what indicates the presence of external  $SrTiO_3$ . EDX data confirmed those observations. The colour contrast in the right figure indicates that the  $SrTiO_3$  rich zones are present as clusters rather than wires, which should be the case when  $SrTiO_3$  is present in the pores.

#### 6.6.1 Synthesis of La doped nanostructured SrTiO<sub>3</sub>

An effective way to enhance the zT value of SrTiO<sub>3</sub> is by electron doping the material with rare earths to enhance its carrier concentration. SrTiO<sub>3</sub> doped with lanthanum (III) or niobium (V),

for instance, causes a drastic increase of the electrical conductivity  $\sigma$ , a slight decrease of the thermal conductivity  $\kappa$  and a moderate reduction of the Seebeck coefficient *S*, which results in an increase of the figure of merit between approximately 140 % [21] and 170 % [22] at 773 K by increasing the La/Sr ratio from 2 % to 10 %. Therefore, Sr<sup>2+</sup> was substituted with 8 % La<sup>3+</sup>, which was reported to give rise to the highest *zT* for single doped SrTiO<sub>3</sub> with La<sup>3+</sup> [3]. In order to synthesized doped SrTiO<sub>3</sub> nanowires, we mixed lanthanum as La(NO<sub>3</sub>)<sub>3</sub> salt with Sr(NO<sub>3</sub>)<sub>2</sub> and impregnated it together. Upon addition of the Ti(OXA)<sub>2</sub> complex, a lanthanum containing double salt precipitate was formed which was also confirmed via XRF spectroscopy and XRD analysis.

#### 6.7 Conclusions

It can be concluded that the impregnation of metal ion species chelated with complexing agents is possible in a mesoporous silica template, however, we could not achieve sufficient control of the impregnation rate of dissimilar metal complexes. In addition, the loading efficiency was too small to form a percolating path of nanowires within the pore system after calcination and densification of the nanocomposite powders.

A higher pore loading could be obtained when the double salt  $Sr(OXA)_2Ti.2H_2O$  was formed in the templates pore system. Also, it gave us the possibility to synthesize La doped  $SrTiO_3$ . On the down side, we did not manage to completely avoid leaching of the double salt out of the pores during the synthesis. Consequently, we never managed to make pure  $SrTiO_3$  nanowires after template removal and the work was discontinued because of the lack of reproducibility to make  $SrTiO_3$  nanostructures embedded in mesoporous silica templates.

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# 7

### Mesoporous materials synthesized via nanocasting

This chapter is dedicated to the synthesis of mesoporous materials made via the nanocasting procedure developed for the synthesis of nanostructured bismuth materials. In order to study the applicability of this new nanocasting process, several classes of materials were synthesized. Namely, mesoporous oxides, such as  $TiO_2$ , mesoporous chalcogenides, for example  $TiS_2$  and mesoporous metals, such as silver. Note that the synthesis was not optimized for these materials. Nevertheless, it is shown which parameters during the synthesis affect the replication process and how it could be improved.

#### 7.1 General introduction

Micro/mesoporous materials or simply "nanoporous" materials are best known for their use in catalyst supports or catalysis itself as they possess a high surface area, high fluid permeability and molecular sieving and shape-selective effects. [1-3] However, numerous other applications where nanoporous materials are important include absorbents [4, 5], separation [6, 7], gas storage [8], carrier material for medical applications [9, 10], electro and photo catalysis [11-13], sensors [14, 15], electrode materials in fuel cells and batteries [16-20], etc. Lately, a lot of research effort has been devoted to the development of porous electrode materials for batteries since they could potentially have better rate capabilities, better cycle lives and greater gravimetric capacities. [19]

For these reasons, the continuous feed nanocasting method described in Chapter 5 was tested for its ability to impregnate the hydrolysis sensitive acidic metal precursor solution Ti-HCl and normal metal nitrate salts, such as  $AgNO_3$ . In addition, the chemical conversion of TiO<sub>2</sub> confined in the mesoporous silica template to TiS<sub>2</sub>, using a gas phase reaction with CS<sub>2</sub> was tested. To ensure the formation of a self-sustaining structure after template removal, KIT-6 mesoporous silica was used in all cases.

#### 7.2 Mesoporous TiO<sub>2</sub>

#### 7.2.1 Introduction

Mesoporous titanium dioxide or titania has been investigated thoroughly for its unique electronic and optical properties, such as its photocatalytic ability to decompose organic pollutants, for its use in lithium-ion batteries, solar cells, catalyst supports etc. [11] For any of these applications, a high surface area is desired to enhance its active surface. Therefore, much effort has been dedicated to the fabrication of mesoporous titania, which is either synthesized via a soft templating method or via hard templating. A commonly used soft templating approach for titania is the EISA technique, which is discussed in Chapter 4. [21] During the soft templating synthesis of mesoporous materials, there are two competing processes which prevent obtaining simultaneously a high surface area and a high crystallinity. Namely, as the material starts to crystallize, the soft template supporting the framework tends to collapse. Also, when the calcination temperature is increased to form a crystalline material, the template can thermally decompose. As an example, the commonly used structural directing agent P123 or [PEO]<sub>20</sub> [PPO]<sub>70</sub> [PEO]<sub>20</sub> thermally decomposes already at temperatures from approximately 300 °C onwards. [22] To avoid this problem thermally stable surfactants must be used such as cetyltrimethylammonium bromide (CTAB) or noncommercial block copolymers of polystyrene and poly(ethylene oxide). [11, 23, 24]

Since we were interested in mesoporous titania with simultaneously a high surface area and high crystallinity, we used the nanocasting method to synthesize mesoporous  $TiO_2$  confined in the pore channels of a mesoporous silica template. The different parameters affecting the synthesis of mesoporous  $TiO_2$  via the nanocasting process are the template surface chemistry, the polar precursor solvent, the metal salt and the impregnation temperature/ pressure and the thermal treatment conditions.

It was reported by Yue *et al.* that the titanium precursor chemistry affects the formed crystal phase and influences the morphology of the titania nanograins. [25] Namely, Ti-HCl yielded anatase titania, which tends to form sphericle nanograins, while Ti-HNO<sub>3</sub> yielded a higher fraction of rutile titania and replicated the pores better, as schematically shown in Figure 7.1.





(b) SBA-15 – TiO<sub>2</sub>

(c) Replicated TiO<sub>2</sub>



Data replicated from Yue *et al.* (Table 7.1) shows that Ti-HCl precursors yield mesoporous  $TiO_2$  with the highest pore volume and surface area, whereas the surface area reduced significantly as the calcination temperature was increased. [25] The precursor was impregnated into SBA-15 mesoporous silica by stirring the template with an appropriate

amount of precursor solution for 2 h and letting the solvent evaporate. The data provided here is used later on to evaluate our results.

Table 7.1.  $N_2$  sorption data of SBA-15 and replicated TIO<sub>2</sub> using different Ti precursor solutions and calcination temperatures. Data replicated from [25].

Sample	Calc. temp. (°C)	S <sub>BET</sub> (m²/g)	Vp (cm³/g)	D (nm)
SBA-15	550	736	1.13	10.2
TiO <sub>2</sub> (Ti-HNO <sub>3</sub> )	100	110	0.1	4.9
TiO <sub>2</sub> (Ti-HNO <sub>3</sub> )	200	163	0.14	5.2
TiO <sub>2</sub> (Ti-HNO <sub>3</sub> )	300	84	0.15	6.8
TiO <sub>2</sub> (Ti-HNO <sub>3</sub> )	600	30	0.14	7.6
TiO <sub>2</sub> (Ti-HCI)	100	247	0.23	2.9
TiO <sub>2</sub> (Ti-HCl)	200	317	0.33	4.1
TiO2 (Ti-HCI)	300	256	0.3	4.1
TiO2 (Ti-HCI)	600	166	0.24	6

#### 7.2.2 Experimental

All impregnations were performed in a similar manner as described in detail in Chapter 5 for the impregnation of BiCl<sub>3</sub> in a mesoporous silica template. However, they differed in the way the precursor solution was added to the non-polar solvent. Whereas the BiCl<sub>3</sub> precursor was added dropwise, in this example, all precursor solution was added at once. Mesoporous titania was synthesized via the impregnation of a diluted titanium chloride or nitrate solution in KIT-6 mesoporous silica, followed by a calcination treatment and a template removal step. Typically, 1 g KIT-6 template material was used, which has a pore volume of approximately 1 mL/g as determined by N<sub>2</sub> physisorption measurements. The mesoporous silica template was dispersed in 150 mL toluene or xylene and brought into a 250 mL PFA round bottom flask equipped with a Dean Stark separator and reflux cooler. The entire system was connected to a vacuum pump with pressure controller to adjust the boiling temperature of the solvent. Prior to the addition of the precursor solution, the recipient was heated to 120 °C while the pressure was reduced to 50 mbar. Since the solvent refluxed and all water was removed, this process was used to eliminate all water within the template's pores. The titania precursor solution was prepared by hydrolysing 6.3 mL titanium tetraisopropoxide (TTIP) in distilled water, washing the Ti(OH)<sub>4</sub> precipitate with excess water on a glass filter and dissolving the white powder in 36 % hydrochloric acid or 68 % nitric acid until a metal concentration of 1 mol/L was obtained. Next, the metal precursor solution was added all at once. The process from the dispersion of the silica template to the addition of the polar precursor solution, impregnation and removal of all precursor solvent is schematically depicted in Figure 7.2. Specifically, when the polar precursor phase was added, the mesoporous silica template migrated from the non-polar phase to the polar phase. This kind of impregnation is denoted here as the "bubble" impregnation since the mesoporous silica and the polar metal precursor solution formed a bubble within the non-polar toluene phase. It was expected that the metal precursor would migrate in the pores while the acid boiled off. As the impregnation proceeded, the volume of the polar phase shrank until a solid sphere of compressed mesoporous silica remained. The impregnation was continued until all polar solvent was removed and the sphere of compressed mesoporous silica template broke down and a dispersion of mesoporous silica particles in toluene was formed.



Figure 7.2. Schematic of the postulated impregnation procedure when all precursor was added at once, also called "bubble" impregnation. (a) Representation of mesoporous silica particles dispersed in a non-polar solvent, such as toluene. (b) When the polar precursor solution was added to the mesoporous silica material migrated to the polar phase. (c) It is believed that the metal precursor migrates within the silica's pores. As the polar phase was systematically removed, the metal concentration increased, while the volume of the polar phase reduced, causing a compressive force on the mesoporous silica particles. (d) Once most of the polar solvent was removed, a hard sphere of compressed mesoporous silica particles in toluene, the impregnation was considered finished as all liquid holding the mesoporous grains together was removed.

The temperature of the reaction mixture was set at 40 °C above the boiling point of the solvent at the applied pressure. For example, when the impregnation was performed at a pressure of 100 mbar, the temperature mantle was set at 40 °C above the boiling point of the solvent at that pressure. The impregnation was continued until all precursor solvent was removed from the reaction mixture by means of the Dean Stark separator. The amount of titania precursor impregnated was the amount of precursor necessary to fill 25 - 95 v% of the template's pores with anatase TiO<sub>2</sub> after calcination. Such high pore loading efficiencies could be obtained since the titanium precursor underwent condensation reactions within the pores while it was impregnated, yielding amorphous titania upon removal of the polar precursor solvent. The composite powder (silica + titania) was filtered off, heated at a rate of 2 °C/min, calcined at 450 °C for 4 h in air and chemically etched with 0.5 mol/L NaOH solution for 4 h to yield mesoporous titania. The obtained powder was washed 3 times with water and collected via centrifugation.

#### 7.2.3 Results and discussion

Firstly, a set of experiments in which the loading of titania precursor was altered using the "bubble" impregnation method is discussed. The N<sub>2</sub> physisorption isotherms of TiO<sub>2</sub> replicated from KIT-6 mesoporous silica with different filling degrees of the template are shown in Figure 7.3, while the BET surface area and pore volume and diameter are reported in Table 7.2. The silica template was impregnated with different amounts of Ti-HCl precursor, namely an amount required to yield 25, 50, 75 and 95 % pore filling with anatase TiO<sub>2</sub> after calcination at 450 °C for 4 h.

It can be seen in Table 7.2 that the pore volume is hardly affected by the amount of Tiprecursor impregnated in the template's pores. Also, there is no clear correlation between the BET surface area and the filling degree. However, narrow pores of approximately 5-8 nm were obtained when the pore leading was 25 and 50 %, while the spread on the pore size distribution increased upon filling the pores with more precursor solution. It is not clear form the observed trends in BET surface area, pore volume and pore diameter whether the porosity was created by the release of gas during the impregnation or by the nanocasting process

itself. Firstly, it is unlikely that the pores could contain the amount of Ti-precursor to yield 95 v% pore filling with anatase titania after calcination. As the Ti-precursor hydrolyses during the impregnation we believe that amorphous titania with a low density was obtained, which formed crystalline anatase  $TiO_2$  at 450 °C. Secondly, we presume that the "bubble" impregnation method does not prevent the deposition of material on the external surface of the silica template material, particularly when an excess of precursor solution was added. Therefore, advancements on the impregnation method were tested, while reducing the amount of precursor impregnated.

Table 7.2. Summary of BET surface area, BJH pore volume and pore diameter obtained from the BJH pore size distribution plot calculated on the desorption isotherm of mesoporous TiO<sub>2</sub> synthesized by the "bubble" impregnation method.

Sample no.	Pore filling degree (%)	Impreg.	Precursor	Solvent	Temp. (°C) / pressure (bar)	BET Surface Area (m²/g)	Vp (cm³/g)	D (nm)
A	25	All at once	Ti-HCl in 36% HCl	Toluene	110 / 0.05	117	0.27	7
В	50	All at once	Ti-HCl in 36% HCl	Toluene	110 / 0.05	64	0.20	5 - 8
С	75	All at once	Ti-HCl in 36% HCl	Toluene	110 / 0.05	82	0.19	~ 15
D	95	All at once	Ti-HCl in 36% HCl	Toluene	110 / 0.05	57	0.2	5 - 15

Considering the N<sub>2</sub> sorption isotherms in Figure 7.3, H3 hysteresis loops (see §4.4) are observed for all samples, indicating inter particle adsorption with split-shaped pores. Nevertheless, it is clear that the pore volume of the  $TiO_2$  sample prepared by impregnating 25 % of KIT-6's pores with anatase titania is the largest, while there are no clear distinctions between the other samples.



Figure 7.3. N<sub>2</sub> physisorption isotherms of mesoporous TiO<sub>2</sub> replicated from KIT-6 filled with different amounts of amorphous TiO<sub>2</sub>. Note that the isotherms of 50, 75 and 95 % are shifted along the vertical axis by 50, 100 and 150 cm<sup>3</sup>/g STP, respectively.

In order to investigate how the impregnation procedure could be improved, two different impregnation techniques were compared. In the first case, all precursor was added at once (sample A in Table 7.3), while in the second case, the precursor was added in a dropwise manner (sample B in Table 7.3). Both precursors were Ti-HNO<sub>3</sub> based, which involves that the precursor condensated both due to hydrolysis and due to the oxidation with HNO<sub>3</sub>. A lower

surface area and pore volume was obtained when the precursor was added all at once compared to drop by drop addition for a comparable pore filling degree. Although not specifically confirmed with TEM imaging, we presume that the latter impregnation technique resulted in a reduced amount of externally deposited material. Comparable results were obtained for the impregnation of a Ti-HCI based precursor solution added either all at once or approximately 0.4 mL every 15 min (sample C and D of Table 7.3, respectively). The latter case can also be considered as a combination of the "double solvent" impregnation and incipient wetness as the amount of precursor solution added was always lower than the total pore volume of the silica template. Note that the amount of precursor added was reduced in time since the pore volume occupied by previously impregnated precursor had to be taken into account. We believe the pore volume of the last sample in Table 7.3 had a low surface area and pore volume because an excess of precursor was added.

One complication which occurred during the impregnation of a 36 w% HCl titania precursor solution in a dropwise manner was the fact that a lot of gas was created when the metal precursor was added to boiling toluene. Namely, the boiling point of 36 w% hydrochloric acid is only 61 °C, while the boiling point of toluene under standard conditions is approximately 110 °C. The foaming due to HCl release during the impregnation occurred particularly when the pressure during the impregnation was reduced below 0.2 bar. This problem could be overcome by impregnating a diluted HCl based metal precursor solution since the boiling point increases above 100 °C when the concentration of HCl drops below approximately 20 w%.

Table 7.3. BET surface area, BJH pore volume and pore diameter obtained from the BJH pore size distribution p	olot
calculated on the desorption isotherm of TiO <sub>2</sub> nanocasted from KIT-6 impregnated under different conditions. T	he
letters A – E in the first column denote the sample name.	

Pore filling degree (%)	Impreg.	Precursor	Solvent	Temp. (°C) / pressure (bar)	BET Surface Area (m²/g)	Vp (cm³/g)	D (nm)
A_50	all at once	Ti-HNO₃	toluene	110 / 0.05	23	0.06	± 7
B_45	drop by drop	Ti-HNO₃	xylene	170 / 0.05	142	0.22	5.5
C_50	all at once	Ti-HCI	toluene	110 / 0.05	64	0.20	5 - 8
D_40	0.4 mL/ addition	Ti-HCI	toluene	110 / 0.2	153	0.24	~ 5

It was observed from TEM images depicted in Figure 7.4 and low angle XRD measurements in Figure 7.5 that no ordered mesoporous titania was obtained. Indeed, neither pore channels, nor pore walls can be observed in the TEM images. If we recall Figure 7.1, it was show that a Ti-HCI based precursor solution leads to a nanograin type morphology, which is observed here too.

It can be seen from the low angle XRD patterns depicted in Figure 7.5a that no significant reflections were copied from KIT-6 to the nanocasted  $TiO_2$ . Consequently, no long-range ordering of the pore system of the KIT-6 mesoporous template was transferred to the  $TiO_2$  replica. This was the case for the impregnation of both concentrated acid solutions of Ti-HNO<sub>3</sub> and Ti-HCI.



Figure 7.4. TEM images of mesoporous  $TiO_2$ , replicated from KIT-6 mesoporous silica template impregnated with Ti-HCI based precursor solution in toluene by dropwise addition and calcined at 450 °C for 4 h.

Although the long-range ordering of the pores of the replicated  $TiO_2$  samples were not preserved, mesoporous  $TiO_2$  with a pure anatase phase was obtained using a Ti-HCl based precursor solution and calcining the sample at 450 °C for 4 h (Figure 7.5b). The silica template was removed in 0.5 mol/L NaOH for 4 h, followed by washing with water and isolation via centrifugation.



Figure 7.5. (a) Low angle XRD pattern of KIT-6 mesoporous silica template and its  $TiO_2$  replicated structure.  $TiO_2$  was synthesized using a Ti-HCl based precursor solution, added in a dropwise manner to KIT-6 dispersed in toluene heated and calcined at 450 °C for 4 h.(b) XRD pattern of anatase mesoporous  $TiO_2$ , replicated from KIT-6 silica impregnated with a Ti-HCl precursor solution, calcined at 450 °C for 4 h and template removal in 0.5 mol/L NaOH solution for 4 h.

#### 7.2.4 Conclusions

The different impregnation techniques: the "bubble" impregnation and the double solvent / incipient wetness impregnation with a dean stark separator were compared. The continuous feed impregnation resulted in replicated  $TiO_2$  with the highest surface area. Nevertheless, we believe that the precursor solution could still be improved by impregnating a diluted acid precursor with methanol or formic acid as co-solvents to improve the wettability of the template. Also, more attention should be given to the surface chemistry as the interaction of the precursor salt and the silanol moieties play a crucial role in the aggregation of material within the pores (see Chapter 5).

Considering our recorded data compared to Table 7.1, we can suggest that the calcination temperature of  $TiO_2$  should be reduced from 450 to approximately 300 °C to enhance the surface area. It is expected that this could also improve the ordering of the replicated  $TiO_2$ .

#### 7.3 Mesoporous TiS<sub>2</sub>

#### 7.3.1 Introduction

Titanium disulphide is of interest both as thermoelectric material and as electrode material in batteries. [26-29] It has a high electrical conductivity and relatively large power factor, while the layered TiS<sub>2</sub> structure enables the intercalation of electropositive elements. [27, 30] A general synthesis route of mesoporous metal sulphides was proposed by Yonemoto *et al.* by converting metal precursors to their oxide and subsequently reacting the composite material with H<sub>2</sub>S gas [31]. However, as far as our knowledge is concerned, no studies have been reported on mesoporous TiS<sub>2</sub>. The work performed here on the synthesis of TiS<sub>2</sub> was a preliminary study for its use as nanocomposite thermoelectric material. It differs from Yonemoto's work as we used the less toxic CS<sub>2</sub> rather than H<sub>2</sub>S.

#### 7.3.2 Experimental

Firstly, KIT-6 – TiO<sub>2</sub> nanocomposite powder was prepared by impregnating the mesoporous template with a solution of TiCl<sub>4</sub> in 36 v% HCl. The precursor solution was prepared by hydrolysing 2.51 mL TTIP in excess water, the white TiOH<sub>4</sub> powder was filtered off and dissolved in 8 mL HCl. The Ti-HCl precursor was added at a rate of 4 mL/h to KIT-6 dispersed in xylene. A dean-stark separator was used to remove the aqueous phase, while the temperature was set at 140 °C and the pressure reduced to 0.2 bar. Next, the powder was separated through filtration and subjected to a thermal treatment in CS<sub>2 (g)</sub> between 750 and 800 °C for 4 h. Herefore, approximately 1 g of KIT-6 – TiO<sub>2</sub> nanocomposite powder was placed in an alumina crucible and placed in a horizontal flow tube furnace. The sample was heated to 750 °C at a rate of 2 °C/min under an argon flow bubbled through a CS<sub>2 (l)</sub> container before entering the furnace. During this gas phase reaction TiS<sub>2</sub> was obtained according to the reaction shown in 1.

$$TiO_{2(s)} + CS_{2(g)} \xrightarrow{750^{\circ}C} TiS_{2(s)} + CO_{2(g)}$$
 1

Mesoporous TiS<sub>2</sub> was obtained by dissolving the silica template in a 14 mol/L NaOH solution for 15 min. The powder was washed three times with isopropanol and isolated by centrifugation. Note that a strong basic solution was used to avoid the hydrolysis of TiS<sub>2</sub> followed by the generation of toxic H<sub>2</sub>S gas and TiO<sub>2</sub> according to Reaction 2.

$$TiS_{2(s)} + H_2O_{(l)} \longrightarrow TiO_{2(s)} + H_2S_{(g)}$$
 2

To avoid hydrolysis by air the samples were stored under inert atmosphere.

#### 7.3.3 Results and discussion

Prior to template removal, X-ray diffraction analysis was performed on the KIT-6 –  $TiS_2$  nanocomposite powder (Figure 7.6). The broad hump between 20 ° and 30 ° originates from the amorphous silica template, while the sharp reflections at 32.98 ° and 56.34 ° arise from the silicon substrate on which the sample was placed during XRD measurements. All other reflections could be assigned to  $TiS_2$ . After template removal, N<sub>2</sub> sorption measurements were performed and shown in Figure 7.7.



Figure 7.6. X-ray diffraction pattern of KIT-6 –  $TiS_2$ . The silicon single crystal substrate reflections are marked with a red star, while the broad hump between 20 ° and 30 ° originate from the amorphous silica template. The reference pattern of  $TiS_2$  was obtained from Ref. [32]



Figure 7.7  $N_2$  sorption isotherms of TiS<sub>2</sub>.

The H3 type hysteresis loop of the isotherm in Figure 7.7 indicates the presence of aggregations of plate-like particles forming split-shaped pores. The measured BET surface area of the material was  $95 \text{ m}^2/\text{g}$ , while a pore volume of 0.2 mL/g was obtained.



Figure 7.8. TEM images of mesoporous TiS<sub>2</sub> replicated from KIT-6 mesoporous silica.

A porous structure, apparently consisting of fibrous and plate-like material, could be seen on the TEM images of  $TiS_2$  shown in Figure 7.8. Nevertheless, no pore structures or any ordering could be observed. This could be explained by the fact that the parent nanocasted  $TiO_2$  did not show any ordering in low angle XRD or on TEM images either. Note that the creation of porosity in the material may also be affected by the chemical reaction of  $TiO_2$  with CS<sub>2</sub> as shown in Reaction 1.

#### 7.3.4 Conclusions

Although further research is required to optimize the synthesis and properties of this material, it is shown here that mesoporous  $TiS_2$  could be synthesized by means of a high temperature reaction of a KIT-6 –  $TiO_2$  nanocomposite structure and  $CS_2$  gas to obtain KIT-6 –  $TiS_2$  and subsequently  $TiS_2$  after template removal in concentrated NaOH. Furthermore, any advancement in the synthesis of mesoporous  $TiO_2$  would also benefit the properties of  $TiS_2$ . It is also recommended to use a mesoporous silica template with better thermal stability than KIT-6, as was shown in Chapter 5. No thermoelectric measurements were performed on the aforementioned samples since the samples were too resistive.

#### 7.4 Mesoporous Ag

#### 7.4.1 Introduction

Shortly after the development of the MCM type molecular sieves [33], and large pore mesoporous silica materials [34], it was reported that the pore channels could be used as template material to synthesize noble metals in their channels. [35-37] Although various metals have been made in their mesoporous form, the conventional replication processes are very inefficient in terms of pore filling. Namely, the volume contraction between a 1 mol/L metal precursor solution and the reduced metal itself is typically about 100:1. Therefore any effort to enhance the loading is beneficial making the nanocasting synthesis more efficient/interesting.

#### 7.4.2 Experimental

0.5 g KIT-6 mesoporous silica was impregnated with 1.38 g AgNO<sub>3</sub> dissolved in 8 mL distilled water and 12 mL methanol. The AgNO<sub>3</sub> precursor solution was added at a rate of 4 mL/hr to 0.5 g KIT-6 mesoporous silica template dispersed in a mixture of 70 mL heptane and 30 mL toluene. The temperature was set at 170 °C and the pressure reduced to 0.8 bar. Heptane was used here as nonpolar solvent to slow down the removal of water as its boiling point is at approximately 98.5 °C. Consequently, water was only removed by the formation of a low boiling azeotrope of water with toluene at 84 °C. The powder was collected through filtration, washed with toluene and dried overnight at 60 °C, heated at a rate of 2 °C/min to 350 °C and calcined for 2 h in air. The silica template was removed using 1 mol/L NaOH. The powder was washed 3 times with distilled water and isolated by centrifugation.

#### 7.4.3 Results and discussion

Reviewing the TEM images of mesoporous silver replicated from KIT-6 in Figure 7.9, it can be seen that the pore walls consist of spherical nanograins. This observation was also reported by Shon et al. [38] Namely, silver nitrate was impregnated via the double solvent method in untreated KIT-6 and methylated KIT-6. It was shown that Ag replicated from untreated KIT-6 templates yielded dispersed small silver nanoparticles within the template, while highly ordered mesoporous Ag was obtained using methylated KIT-6. It was suggested that the

silanol groups on the silica surface interacted strongly with the silver, preventing aggregation of the salt within the pores. Since the polar interactions between the precursor salt and the template were absent in the methylated silica, the precursor could migrate in the pores and form larger clusters.

Nevertheless, large mesoporous agglomerates with sizes up to 1  $\mu$ m were prepared by us as can be observed in the TEM images in Figure 7.9. We believe that the formation of dispersed nanoparticles is less obvious in our work since the loading of salt within the pores was much higher than in the aforementioned case. However, Shon's findings provide a possible explanation for the absence of long range ordering of the pores as can be seen in the low angle XRD data in Figure 7.10.



Figure 7.9. TEM images of mesoporous Ag replicated from KIT-6, using  $AgNO_3$  precursor salt dissolved in a 60 % methanol- water solution and impregnated in the template dispersed in 70 mL heptane and 30 mL toluene. Silver metal was obtained after a calcination of 2 h at 350 °C. Subsequently, the silica template was removed using an etching solution of 1 mol/L NaOH.



Figure 7.10. Low angle XRD pattern of KIT-6 mesoporous silica template and replicated mesoporous Ag.

#### 7.5 Conclusions

It can be concluded from the different case studies described here that the continuous feed nanocasting method developed throughout this research could be used for the synthesis of mesoporous oxides, chalcogenides and metals. Although any of the cases were optimized, relatively high surface areas could be obtained using unmodified KIT-6 as template material, water (or  $H_2O - MeOH$ ) based polar precursor solvents and toluene/xylene (heptane or noctane) as nonpolar solvent. However, no mesopore ordered structures were obtained for any of the tested materials. It was reported that too strong interactions between the precursor salt and the polar silica surface prevented aggregation of the precursor salt leading to the

formation of spherical nanograins and the absence of ordered replicas, as observed in  $TiO_2$  and Ag. Therefore, further optimization of the surface chemistry of the mesoporous template for the impregnation of specific salts is recommended.

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# 8

## Bismuth based nanowire composite thermoelectrics

While previous chapters have introduced the synthesis of mesoporous silica materials and their use in the nanocasting principle, this chapter discusses the synthesis and analysis of  $Bi_{1-x}Sb_x$  nanocomposite thermoelectrics. Specifically, the template characteristics, the impregnation of the mesoporous silica with the  $Bi_{1-x}Sb_x$  precursor solution, the reduction treatment of the impregnated salts, the sintering process and the characterization of the transport properties are discussed. Furthermore, various issues encountered when  $Bi_{1-x}Sb_x$  nanowires are used in a bulk nanocomposite are tackled. Ultimately, the thermoelectric performance in bulk  $Bi_{1-x}Sb_x$  nanowire composites is investigated in this chapter in order to examine if nanostructuring does provide the predicted enhancement.

#### 8.1 Introduction

Since the pioneering paper of Hicks and Dresselhaus [1], attempts at making Bi nanowire thermoelectrics have resulted in large thermopowers but not large zT's [2, 3]. One issue has been that no  $Bi_{1-x}Sb_x$  nanowires could be prepared by conventional methods, whereas theory predicted superior performance in these alloy wires [4]. Therefore, the continuous feed impregnation method was developed in order to synthesize  $Bi_{1-x}Sb_x$  nanowire structures. Since the intention of this work is to use the nanowires while they are still embedded in the silica template, it is desirable to have a 3D pore system rather than a 1D pore system, since the former can lead to electrical percolation paths. Consequently, the 3D ordered silica templates KIT-6 and FDU-12 were used here.

#### 8.2 Experimental

#### 8.2.1 Materials

99.5 % selenium powder, 98% hydrazine monohydrate and 99% tetrahydrofuran stabilized with 250-350 ppm BHT, 36 % hydrochloric acid, 99.999 % antimony(III) oxide and 99,9998 % bismuth(III) oxide were supplied by Alfa Aesar. 98.5 % xylenes, 99% toluene and 98 %

methanol were supplied by Fiers. 97% n-octane was supplied by TCI Europe N.V. > 95 % sulfuric acid, 30 % hydrogen peroxide, 98 % sodiumborohydride and methylmagnesiumbromide 3 M solution in diethylether were purchased from Sigma Aldrich. All reagents were used as received.

#### 8.2.2 Synthesis

#### 8.2.2.1 Mesoporous silica

The detailed syntheses of all mesoporous silica templates are described in Chapter 4.

#### 8.2.2.2 Impregnation of Bi<sub>1-x</sub>Sb<sub>x</sub> precursor into silica template

All of the aforementioned silica template materials were impregnated in the same manner. The template was loaded with bismuth or a mixture of bismuth and antimony salt by impregnating it with a solution of  $Bi_2O_3$  and  $Sb_2O_3$  dissolved in diluted hydrochloric acid. Taking the mixed "Bi<sub>0.94</sub>Sb<sub>0.06</sub>" precursor as example, 1 g silica template material with a BJH pore volume of 1 mL/g was dispersed in 100 mL octane and brought into a 250 mL PFA round bottom flask equipped with a dean stark separator and reflux cooler. The recipient was heated to 160 °C to enable the solvent to reflux gently while the pressure in the vessel was reduced to 0.8 bar to facilitate evaporation of the solvent. Next, 3.3118 g  $Bi_2O_3$  (7.107 mmol) and 0.1323 g Sb<sub>2</sub>O<sub>3</sub> (0.457 mmol) were dissolved in 15 mL 20 w% hydrochloric acid and 30 mL MeOH and brought into an addition funnel or syringe pump placed above the reaction vessel. Subsequently, the precursor was added dropwise to the PFA flask at a rate of 4 mL/h. Since the volume of the precursor solution was lower than the total pore volume at any single moment during the impregnation, the precursor infiltrates the pores through capillary action and decomposes inside the template's pore channels upon removal of the acidic precursor solvent. The procedure was continued until all bismuth precursor solution was added to the suspended template solution, while the diluted acid mixture was collected in a continuous manner with the dean stark setup.

#### 8.2.2.3 Reduction treatment

Approximately 0.5 g BiCl<sub>3</sub>/BiOCI - SiO<sub>2</sub> nanocomposite powder was spread out in a ceramic crucible and placed in the middle of a horizontal flow furnace. The Ar - 5 % H<sub>2</sub> reducing gas bubbled through a solution of formic acid or 98 % hydrazine monohydrate before entering the tube furnace. The vapour of either of these chemicals was carried by the gas flow with a flow rate of 20 mL/min, enabling a lower reduction temperature of the bismuth salts. A heating rate of 2 °C/min was used and typically, the samples were reduced between 220 and 265 °C for 10 h. The sample was cooled down in an uncontrolled manner under an Ar - 5 % H<sub>2</sub> flow until the temperature dropped below approximately 50 °C. Consequently, the reactor tube was sealed and transferred to glovebox where the powder was collected and stored.



Figure 8.1. Reaction tube for treating air sensitive samples.



Figure 8.2. Horizontal split flow furnace for the reduction of bismuth precursor to bismuth nanowire composite powder.

#### 8.2.2.4 Sintering

The reduced  $Bi_{1-x}Sb_x - SiO_2$  powder was transferred into a graphite die with Ø 10 mm. The powder was sandwiched between the graphite punches and sealed with rubber cement to avoid any contact with the air when the die was transferred from the glovebox to a Dr. Sinterlab spark plasma sintering (SPS) machine. The SPS chamber was flushed 3 times with argon and the sintering was carried out under vacuum. Typically, the sintering was performed using the profile shown in Figure 8.3, unless otherwise stated. Other variations of sintering time, pressure and temperature were used for Bi – SiO<sub>2</sub> nanowire composites, whereas the same heating rate and pressure profile was used. All nanocomposite powders were sintered between 180 and 250 °C at a pressure between 30 and 50 MPa.



Figure 8.3. (a) SPS die in sintering device with thermocouple inserted. (b) SPS sintering profile for  $Bi_{1-x}Sb_x$  - SiO<sub>2</sub> nanowire composite samples. The temperature was increased at a rate of 10 °C/min to 230 °C and at 2 °C/min to 245 °C, with a dwell time of 90 min. The maximum pressure of 3.9 kN (50 MPa for  $\emptyset$  10 mm die) was applied in 15 min.

Typically, disks of 10 mm diameter and approximately 4 mm thick were obtained after sintering and were stored in the glovebox to avoid oxidation.

#### 8.2.3 Characterization

#### 8.2.3.1 Material analysis

X-Ray powder diffraction (XRD) patterns were recorded on a Thermo ARL X'tra diffractometer with the Bragg–Brentano theta-2 theta configuration using Cu K<sub> $\alpha$ </sub> = 1.5405 Å radiation and a solid-state Si-Li detector. All measurements on Bi1-xSbx alloys were performed at the OSU on a Rigaku MiniFlex Diffractometer with Cu-K<sub> $\alpha$ </sub> radiation. Rietveld refinement was used for crystal-structure refinement using TOPAS Academic V4.1 software [5]. The Rietveld refinement method was used here for the determination of the percentage crystallinity of the sample and to quantify the secondary phases. Herefore, 10 w% of ZnO (zincite phase) with a known crystallinity and phase was added as internal standard and grinded together with the sample. XRD patterns were recorded using a sample holder with fixed height. Nitrogen sorption experiments were performed at 77 K with a Micromeritics TriStar 3000 device. Samples were vacuum dried at 120 °C for 12 h prior to analysis. The surface area was calculated using the BET method while the pore size distribution was determined by analysis of the adsorption branch of the isotherms using the BJH method [6, 7]. Thermogravimetric analysis (TGA) were performed on a NETZSCH STA 449-F3 Jupiter device. Transmission Electron Microscopy images were recorded on a JEOL JEM-2200FS instrument with Cs correction. Specimens for were prepared on a 200 mesh carbon copper grid.

#### 8.2.3.2 Thermoelectric characterization

TE samples were prepared by consolidating TE powder using Spark Plasma Sintering (SPS). Typically disks with a diameter of 10 mm and 3 - 4 mm thick were prepared. Bars of approximately 1 x 2 x 6 mm were cut out of the disks with a wire saw and polished to obtain smooth and parallel surfaces. The measurement assembly consisted of an alumina base plate, with a rectangular brass plate mounted in the middle with silver epoxy. The brass plates were used to provide a good thermal and electrical contact with the sample. The contacts were made as shown Figure 8.4.



Figure 8.4. Schematic representation of sample assembly.

The thermocouples were prepared using a copper – constantan junction. All wires were 2  $\mu$ m thin to minimize heat dissipation through the contacts and were connected to the sample by silver epoxy or through spot welding. Silver epoxy was hardened thermally at 120 °C for 30 min. The sample was sandwiched between two brass plates using silver epoxy as glue, and mounted on the alumina base. A resistive heater of 120  $\Omega$  was placed on top of the sample to create a temperature gradient in the material.

The applied magnetic field, the induced Hall voltage, Seebeck voltage, temperature gradient and resistive voltage difference are indicated in Figure 8.5. Firstly, the sample temperature was stabilized, while a temperature gradient was applied by means of the heater on the top of the sample. A temperature gradient was measured between the top and bottom thermocouple. The sample resistivity was measured via the four-probe method by measuring the voltage drop between both cupper wires of the thermocouples when electric current is flowing through the sample. Upon applying an external field B, the Nernst effect was measured in the absence of the sample current. The induced electric field was measured between the top thermocouple and the top Hall contact, and performed likewise at the bottom. Under the influence of an external field, the sample current gives rise to a Hall voltage, measured in the same manner as described for the Nernst effect.



Figure 8.5. Schematic representation of the measurement assembly with the indication of the measured properties.

Due to the oxygen sensitivity of bismuth nanowires, all nanocomposite samples were handled under inert atmosphere. This involved the reduction of the nanocomposite powder (Figure 8.1), the sintering of the powder (Figure 8.3a) and the mounting of the sample onto the cryostat (Figure 8.6). The sample was mounted onto the cryostat inside the glovebox. Next, the head of the cryostat was fitted with a copper radiation shield and sealed from the environment with a metal shield. The measurements were performed under vacuum in a custom build cryostat (Figure 8.6 and Figure 8.7), which allows simultaneous analysis of the electrical conductivity,

thermal conductivity and the Seebeck coefficient. The measurements ran on an in-house build LabVIEW program, while all data were recorded with Keithley 2182A nanovoltmeters.



Figure 8.6. Sample mounted onto the cryostat.

Samples were measured in a configuration shown in Figure 8.7, positioned in the magnetic field of the electromagnet. Measurements were performed under vacuum, while the sample was cooled with liquid nitrogen. Data were recorded from 77 K to 420 K with increments of 20 K. At every temperature, the magnetic field was scanned from - 1.4 to 1.4 T. All measurements ran under LabVIEW software and data analysis was performed with Mathcad software.



Figure 8.7. Measurement of transport properties from 80 K to 420 K.

High temperature Seebeck coefficient and electrical resistivity data were performed on a LSR -3 Linseis - Seebeck coefficient and electric resistivity unit, allowing measurements from room

temperature up to 1500 °C. Herefore, a bar of approximately  $2 \times 2 \times 10$  mm was cut and sandwiched vertically between two adjustable contacts, while the contacts for the electrical resistivity measurements were translated until contact was made with the sample. The measurements were performed under He atmosphere.

#### 8.2.3.3 Error analysis

An error analysis of the used cryostats system for the thermoelectric and thermomagnetic measurements was reported by Jovovic and Heremans [8] and is reviewed here. The main source of experimental inaccuracy were the errors on the sample dimensions and the longitudinal distance between the thermocouples on the sample. Consequently, the relative error on the electrical resistivity is on the order of 10%. The Hall coefficient depends only on the transverse dimension, which is the thickness of the sample, and can be measured with an accuracy of 2%. The two-carrier analysis, reflecting the properties of the majority carriers, depends on both longitudinal and transversal magneto-conductances and thus carries through both errors on the longitudinal data, for a total of 10%. A similar inaccuracy was determined for the density of the minority carriers electrons which dominate the Hall coefficient. Since the Seebeck coefficient does not depend on the sample geometry, it can be measured more accurately. Due to the sample uniformity, which is the main source of inaccuracy, the error of the Seebeck coefficient measurement is limited to 3%. The Nernst data are afflicted by the 10% inaccuracy in the longitudinal distance between the temperature probes. The accuracy on the thermal conductivity is again limited by the geometry and the inaccuracy of the longitudinal distance between the thermocouples, which is approximately 10 %.

#### 8.3 Results and discussion

#### 8.3.1 Mesoporous silica templates

Although it is preferred to use a silica template with a 3D pore structure to enhance the number of percolation paths through the replicated nanowires, SBA-15 is used as well since the 2D ordered cylindrical pores are easy to characterize and provide the most information when their impregnation is studied by means of N<sub>2</sub> sorption measurements. However, they are not suitable as nanocomposite template due to the fact that they create too few electrical percolation paths with adjacent nanocomposite particles when they are sintered. The pore network of KIT-6 also consists of 2 sets of 3D structured cylindrical channels (also called bicontinuous), which enables easier impregnation than linear pores. In addition, the replicated structures of SBA-15. FDU-12 also possesses a 3D pore system, but in contrast to KIT-6 it consists of cages that are connected through smaller channels. Also, the pores are completely interconnected which should benefit the formation of percolation paths.

In summary, SBA-15 and KIT-6 both have a pore diameter of approximately 7 nm, while the BET surface area ranged from 600 to 1000 m<sup>2</sup>/g and 700 to 900 m<sup>2</sup>/g and the pore volume from 0.6 to 1 mL/g and 0.6 to 1.3 mL/g, respectively. This corresponded with a porosity between 60 and 75 %. FDU-12 possesses cages with a diameter from 5 to 30 nm, while the windows are approximately 1 - 15 nm and strongly dependent on the synthesis conditions as shown in Chapter 4.



Figure 8.8.  $N_2$  sorption isotherms and BJH pore size distribution plot of SBA-15, KIT-6 and FDU-12. The large pore (LP) equivalents of KIT-6 and FDU-12 are shown in bold, denoted LP-KIT-6 and LP-FDU-12, respectively. The isotherms of ultra large pore (ULP) FDU-12 are depicted with the thickest lines.

Typical  $N_2$  sorption isotherms and BJH pore size distribution plots of SBA-15, KIT-6 and FDU-12 synthesized under standard conditions and with enlarged pores are presented in Figure 8.8. All synthesis conditions of the silica templates are shown in table:

Table 8.1. N <sub>2</sub> sorption data of SBA-15 and replicate	∋d TIO₂ using	ı different 7	Ti precursor	solutions a	nd cal	cination
temperatures. Data replicated from [9].						

Sample	Pore expander / (pore expander : P123)	Stirring temp. (°C) / time (h)	Ageing temp. (°C) / time (h)	Calcination temp. (°C) / time (h)
SBA-15	-	45 / 5	90 / 18	550 / 5
KIT-6	-	35 / 24	100 / 24	550 / 5
FDU-12	-	30 / 24	100 / 24	550 / 5
LP-KIT-6	-	35 / 24	150 / 24	550 / 5
LP-FDU-12	Xylene / 4.5 : 1	35 / 24	120 / 48	550 / 5
ULP-FDU-12	Xylene / 4.5 : 1	35 / 24	150 / 48	550 / 5

Note that standard synthesis conditions consist of a stirring step at 35 - 45 °C, an ageing step at 90 - 100 °C and then calcining at 550 °C. Pore expanded silica templates were prepared by performing the ageing treatment between 120 - 150 °C and/or by using xylene or trimethylbenzene (TMB) as pore expanders. Further study is required to enhance the pore volume and pore diameter of FDU-12. See Chapter 4 for more details.

#### 8.3.2 Impregnation of BiCl<sub>3</sub> into mesoporous silica templates

During the impregnation of a diluted  $BiCl_3$  solution, the salt decomposed to BiOCl during the impregnation since  $BiCl_3$  hydrolyses:

$$BiCl_{3(aq)} + H_2O \rightarrow BiOCl_{(s)} + 2HCl_{(aq)}$$
 Eq. 8.1

A similar hydrolysis occurred for SbCl<sub>3</sub> salt, but it could not be identified through X-ray diffraction measurements, which may be due to the low content of Sb (< 12 at%) or because it remained amorphous. Focussing on the main constituent BiCl<sub>3</sub>, it was confirmed through XRD that the chloride salt decomposed during the impregnation. Consequently, due to the higher density and lower molecular weight of the decomposition product, the theoretical loading of Bi after reduction of the precursor salt are 32 v% and 60 v% for respectively, BiCl<sub>3</sub> and BiOCl. Here we considered the complete pore filling with either BiCl<sub>3</sub> or BiOCl. Typically,
the pores were filled with the amount of precursor necessary to fill the pores with 45 v% bismuth metal after reduction. Although higher loadings were achieved, it is important to mention that more material was deposited outside the template as we tried to get closer to the theoretical maximum loading.

In case Bi and Sb salts were simultaneously impregnated,  $HNO_3$  could not be used as acid since  $Sb(NO_3)_3$  is unstable and oxidizes to  $Sb_2O_3$ , forming a white precipitate in solution. In addition,  $HNO_3$  is incompatible with the co-solvents methanol and formic acid as they undergo an exothermic reaction resulting in the formation of toxic  $NO_x$  gas. As discussed more detailed in chapter 5, when the pores are impregnated with  $Bi(NO_3)_3$ , the maximum pore filling with metallic Bi after reducing the composite is much smaller compared to  $BiCl_3$ . Therefore, mainly  $BiCl_3$  was used.

### 8.3.3 Heat treatment

### 8.3.3.1 Reduction of bismuth and bismuth – antimony salts

Different reducing agents were tested to reduce Bi(NO<sub>3</sub>)<sub>3</sub>, BiCl<sub>3</sub>, SbCl<sub>3</sub>, BiOCl and/or SbOCl to metallic bismuth and/or antimony. However, the low melting point of metallic Bi, 271 °C, was a major limitation on the applicability of conventional reducing agents, such as H<sub>2</sub> gas, since it did not reduce the precursor salts below 271 °C. Bulk Bi<sub>2</sub>O<sub>3</sub> and BiCl<sub>3</sub> powder were used to investigate the influence of different atmospheres on their reduction capacity. ZnO was used as internal standard since it has sufficient diffraction peaks which do not overlap with diffraction peaks from the sample. Rietveld refinement was used to calculate the fraction of crystalline vs amorphous Bi, as well as the amount of secondary phases. Hydrazine was used here as reducing agent since it is powerful and clean. In other words, all decomposition products are gaseous and no solid residues remain. Typically, it is used as reducing agent under basic conditions, following the reaction mechanism [10-12]:

$$N_2H_{4(aq)} + 40H^- \rightarrow N_{2(q)} + 4H_2O + 4e^-$$
, with  $E^o = 0.33V$  Eq. 8.2

Hydrazine should be handled with care since it is a toxic and explosive liquid, particularly in its anhydrous form. Hydrazine hydrate, on the other hand, is more stable and was used here. The auto-ignition temperature of anhydrous hydrazine is 270 °C and 310 °C for 55 % hydrazine hydrate. The lower explosion limit of anhydrous hydrazine is 2.9 % and the upper explosion limit 98 %, while its vapour pressure at room temperature is approximately 12 mbar. Consequently, any concentration of hydrazine solution can be used in a safe manner as long as reductions are performed below 270 °C and the bubbler temperature is not higher than room temperature, so that the vapour pressure is always below the explosion limit. It was necessary to use a minimum concentration of 64 % hydrazine solution to obtain sufficient reducing power. Namely, the reducing capacity reduces quickly as the solution becomes more diluted. Although anhydrous hydrazine was not used in this research, it may be beneficial to lower the reduction time and temperature.

Formic acid vapour could be used without any problem since experiments were performed well below the auto-ignition temperature of 540 °C, while the lower explosion limit of 18 % is much higher than the vapour pressure of approximately 43 mbar. It is reported that formic acid thermally decomposes according to the following reaction pathways [13]:

$$HCOOH \rightarrow CO_2 + H_2$$
 Eq. 8.3

$$HCOOH \rightarrow CO + H_2O$$
 Eq. 8.4

$$2HCOOH \rightarrow CO_2 + H_2O + HCHO \qquad \qquad Eq. 8.5$$

According to literature, the decomposition of formic acid became evident above 250 °C in a Pyrex glass tube, which is approximately the temperature region of interest for our applications. [13] It can be seen from reaction mechanism 3 and 4 that  $H_2$  or CO are created, which are both affective reducing agents. Due to the in-situ generation of CO gas and the use of a chemical scrubber of the outlet gas, the hazards were minimized.



Figure 8.9. X-ray diffraction patterns of  $Bi_2O_3$  reduced at different temperatures in Ar - 5% H<sub>2</sub> and in the presence of  $N_2H_4$  vapour. ZnO was used as internal standard to quantify the amount of crystalline and amorphous phases through Rietveld refinement.

X-ray diffraction patterns of  $Bi_2O_3$  reduced at different temperatures in a flow of Ar - 5% H<sub>2</sub> and in the presence of N<sub>2</sub>H<sub>4</sub> vapour are depicted in Figure 8.9. It can be seen from the XRD patterns of samples reduced at 220 °C, 250 °C and 265 °C in N<sub>2</sub>H<sub>4</sub> vapour that all Bi<sub>2</sub>O<sub>3</sub> phase had completely disappeared at 265 °C. In contrast, Bi<sub>2</sub>O<sub>3</sub> reduced in an Ar - 5% H<sub>2</sub> gas flow was predominantly unchanged, with hardly any Bi phase formed. XRD data of the reduction of BiCl<sub>3</sub> at different temperatures in an Ar - 5% H<sub>2</sub> flow and in the presence of N<sub>2</sub>H<sub>4</sub> vapour are depicted in Figure 8.10. It can be seen that at 220 °C the sample was partly reduced to bismuth with the presence of BiOCl secondary phase. BiOCl is formed by the hydrolysis of BiCl<sub>3</sub> in humid air. No apparent differences are observed between the sample reduced at 250 and 265 °C. In the case Ar - 5% H<sub>2</sub> gas was used at 265 °C, no reduction of the Bi salt occurred.



Figure 8.10. X-ray diffraction patterns of BiCl<sub>3</sub> reduced at different temperatures in Ar,5%H<sub>2</sub> and in the presence of  $N_2H_4$  vapour. ZnO was used as internal standard to quantify the amount of crystalline and amorphous phases through Rietveld refinement.

The Rietveld refining data calculated from the recorded XRD patterns in Figure 8.9 and Figure 8.10 is shown in Table 8.2. In the case of  $Bi_2O_3$ , a minimum temperature of 265 °C for 10 h in hydrazine vapour was required to reduce all material to Bi, while BiCl<sub>3</sub> was completely reduced to Bi at 250 °C. The importance of hydrazine vapour to reduce both  $Bi_2O_3$  and BiCl<sub>3</sub> is clear when the reductions are compared to the reduction in Ar - 5% H<sub>2</sub> only, which shows that less than 5 % Bi was formed at 265 °C.

Material	Red. Temp.	Atmosphere	Bi	Bi <sub>2</sub> O <sub>3</sub>	BiOCI	Amorphous
Bi <sub>2</sub> O <sub>3</sub>	220 °C	5 % H <sub>2</sub> + N <sub>2</sub> H <sub>4</sub>	36 %	13 %	0,0%	51 %
BiCl <sub>3</sub>	220 °C	5 % H <sub>2</sub> + N <sub>2</sub> H <sub>4</sub>	32 %	0 %	17 %	51 %
Bi <sub>2</sub> O <sub>3</sub>	250 °C	5 % H <sub>2</sub> + N <sub>2</sub> H <sub>4</sub>	48 %	4 %	0 %	48 %
BiCl <sub>3</sub>	250 °C	5 % H <sub>2</sub> + N <sub>2</sub> H <sub>4</sub>	34 %	0 %	0 %	66 %
Bi <sub>2</sub> O <sub>3</sub>	265 °C	5 % H <sub>2</sub> + N <sub>2</sub> H <sub>4</sub>	38 %	0 %	0 %	62 %
BiCl <sub>3</sub>	265 °C	5 % H <sub>2</sub> + N <sub>2</sub> H <sub>4</sub>	26 %	0 %	0 %	74 %
Bi <sub>2</sub> O <sub>3</sub>	265 °C	5 % H <sub>2</sub>	3 %	63 %	0 %	34 %
BiCl₃	265 °C	5 % H <sub>2</sub>	1 %	0 %	44 %	55 %

Table 8.2. Rietveld refinement data of  $Bi_2O_3$  and  $BiCl_3$  powder reduced at different temperatures and atmospheres for 10 h. Note that the error on the fractions is approximately 5-10%.

Although a minimum temperature of 250 °C and 265 °C was required to reduce respectively bulk BiCl<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub> powder with N<sub>2</sub>H<sub>4</sub>, the nanocomposite powders were typically reduced at 220 °C (see Figure 8.11). We believe that the high exposed surface area facilitated the reduction of BiCl<sub>3</sub> – silica nanocomposite powder. Also, it was observed through TEM analysis that bismuth leached out of the pore channels upon increasing reduction temperatures as shown in Figure 8.13b. For that reason, it was important to perform the reduction at a temperature as low as possible and for the shortest necessary time.

The reduction of BiOCI impregnated in SBA-15 in formic acid vapour was conducted by bubbling Ar - 5%  $H_2$  through a formic acid container before entering the furnace. The heat treatment was performed for 10 h with a flow rate of 20 mL/min. It can be seen from the XRD patterns in Figure 8.12 that formic acid vapour also reduced to Bi precursor salt to metallic Bi. At 250 °C, all precursor was reduced completely without the presence of any secondary phases. Consequently, both formic acid and  $N_2H_4$  was used to reduction of BiOCI – silica

nanocomposites. In addition, also  $Bi(NO_3)_3$  precursor salt was reduced under the same conditions.



Figure 8.11. X-ray diffractogram of BiOCI loaded silica template (denoted BiOCI – SiO<sub>2</sub>) before and after reduction in  $N_2H_4$  vapour for 10 h at 220 °C.



Figure 8.12. X-ray diffraction patterns of BiCl<sub>3</sub> reduced in formic acid vapour at different temperatures for 10 h.

As mentioned before, the low melting temperature of Bi prevents the use of a long reduction time or a high reduction temperature. The influence of the reduction temperature on the leaching of Bi outside the pores during the thermal treatment in a flow of Ar - 5% H<sub>2</sub> containing N<sub>2</sub>H<sub>4</sub> vapour is shown in Figure 8.13a and in Figure 8.13b. However, we need to bear in mind that the bismuth spheres formed outside the template can be caused by the incomplete impregnation of the precursor inside the pore or due to leaching during the thermal treatment itself. For example, BiOCI salt could be deposited outside the pores leading the bulk Bi sphere after reduction of the nanocomposite, or the impregnated precursor or bismuth metal could leach out the pores during the thermal treatment. The TEM images in Figure 8.13 show that bulk bismuth particles were formed when the samples were reduced both at 220 as at 265 °C However, as the Bi salt is reduced closer to the melting point of Bi (271 °C), larger particles appear to be formed.



Figure 8.13. (a) TEM image of 30 v% Bi loaded in SBA-15. BiCl<sub>3</sub> was impregnated dissolved in a 10% HCl - MeOH solution and subsequently reduced at 220 °C in a hydrazine loaded Ar - 5% H<sub>2</sub> gas flow for 10h. The template was chemically etched with a 1 mol/L NaOH - 0.5 mol/L hydrazine solution for 3 h. (b) TEM image of 30 v% Bi loaded in SBA-15. BiCl<sub>3</sub> was impregnated dissolved in a 10% HCl - MeOH solution and subsequently reduced at 265 °C in a hydrazine loaded Ar - 5% H<sub>2</sub> gas flow for 10h. The template was are bismuth. Note that the material partially oxidizes during TEM sample preparation.



Figure 8.14. (a) TEM image of 12 v% Bi loaded in SBA-15.  $Bi(NO_3)_3$  was dissolved in 20 w% HNO\_3, impregnated and subsequently reduced at 220 °C in a hydrazine loaded Ar - 5% H<sub>2</sub> gas flow for 12 h. Inset: Bi nanowires after chemical etching of the silica template in 1 mol/L NaOH solution for 3 h. (b) TEM image of 32 v% Bi loaded in SBA-15.  $BiCl_3$  was impregnated dissolved in a 10 w% HCl - MeOH solution and subsequently reduced at 220 °C in a hydrazine loaded Ar - 5% H<sub>2</sub> gas flow for 12 h. Inset: Bi nanowires after chemical etching of the silica template in 1 mol/L NaOH solution for 3 h. Note that the material partially oxidizes during TEM sample preparation.

If we compare the effect of the precursor salts on the obtained nanowires, it was observed that a 20 w% HNO<sub>3</sub> based bismuth precursor solution was effectively impregnated in SBA-15 as depicted in Figure 8.14a. It can be seen that no material was deposited on the exterior surface of the template. The obtained nanowires after silica removal by etching were interconnected via ultra-thin fibres that originated from the micro pores in the template's pore wall. When BiCl<sub>3</sub> was used as precursor source, smooth nanowires were obtained (Figure 8.14b). Also, the

nanowires are less interconnected when BiCl<sub>3</sub> was used as precursor salt compared to  $Bi(NO_3)_3$ . Nevertheless, BiCl<sub>3</sub> was used as precursor salt since the higher density and the lower molecular weight of BiCl<sub>3</sub> compared to  $Bi(NO_3)_3.5H_2O$  enabled a 2.5 times higher loading of metallic bismuth after the reduction of both salts. Namely, when  $Bi(NO_3)_3.5H_2O$  is used as precursor salt and no decomposition of the precursor salt is considered, then the maximum fraction of the template's pores filled with metallic bismuth after reducing the precursor salt is 12 v%, whereas the pore loading becomes 32 v% when BiCl<sub>3</sub> is impregnated. The expected mass loading was confirmed by means of XRF analysis. It can be understood that a higher loading of the template increases the aspect ratio of the nanowires, which is also more desirable to obtain a good electrical percolation path through the sintered nanocomposite sample.

### 8.3.3.2 Gas phase alloying of Bi nanowires

Since bismuth nanowires oxidize spontaneously upon contact with air, two routes were explored to avoid this problem. Firstly, methods to obtain completely filled pores were investigated, such as the synthesis of  $Bi_{1-x}Sb_x$  alloys through the reaction with Me<sub>3</sub>Sb and secondly, we aimed to find a way to seal the pore entrances through the reaction with H<sub>2</sub>Se, forming  $Bi_2Se_3$ . The use of reactive gasses to alloy or dope bismuth nanowires is demonstrated here. Firstly, bismuth salt was impregnated in a mesoporous silica template and subsequently subjected to a treatment with trimethylantimony vapour or hydrogen selenide gas yielding  $Bi_{1-x}Sb_x$  alloys and  $Bi_xSe_y$ , respectively.



Figure 8.15. Setup for the synthesis of  $Me_3Sb$  and  $H_2Se$  and reaction with  $BiCI_3$  – silica nanocomposite powder.

The organometallic compound trimethylstibine acted both as a reducing agent and alloy compound when exposed to the bismuth precursor salt within the template's pores. The reactive liquid was generated by adding the Grignard reagent MeMgBr to a solution of SbCl<sub>3</sub> dissolved in tetrahydrofuran (THF) with a syringe pump or addition funnel in a three-neck flask as depicted in Figure 8.15. The reaction mechanism of the in situ generation of Me<sub>3</sub>Sb is shown in *Eq.* 8.6. [14] The alloying of Bi(NO<sub>3</sub>)<sub>3</sub> or BiCl<sub>3</sub> loaded silica template was performed by heating the composite powder at 120 °C in a tubular furnace while carrying the Me<sub>3</sub>Sb vapour in an argon gas flow. The amount of antimony that reacted with the impregnated Bi(NO<sub>3</sub>)<sub>3</sub> was controlled by varying the duration of the exposure to Me<sub>3</sub>Sb. The alloy composition was semi quantitatively determined by means of XRF analysis and ranged from Bi<sub>0.99</sub> Sb<sub>0.01</sub> to Bi<sub>0.4</sub>Sb<sub>0.6</sub>. The chloride salt of bismuth showed the lowest reactivity towards Me<sub>3</sub>Sb, while the impregnated Bi(NO<sub>3</sub>)<sub>3</sub> reacted easily with the gas. Note that Me<sub>3</sub>Sb is a pyrophoric and toxic liquid. Therefore, it was prepared in situ, carried by argon gas into the tube furnace, while the outlet was chemically oxidized.

$$SbCl_{3(THF)} + 3MeMgBr_{(THF)} \xrightarrow{THF} SbCl_{3(l)} + 3MgBrCl_{(s)}$$
 Eq. 8.6

Figure 8.16 depicts the XRD patterns of the bismuth nanocomposite samples treated with trimethylstibine gas for different durations, followed by a reduction treatment at 220 °C in  $N_2H_4$  vapour. Upon reaction with Me<sub>3</sub>Sb, the XRD reflections of the bismuth – silica nanocomposite samples shifted to higher 20 values, indicating the increase in antimony content. It can be seen from the broad diffraction peaks that a range of alloy compositions were formed rather than a homogeneous alloy composition throughout the sample. Consequently, we cannot calculate the  $Bi_xSb_{1-x}$  composition based on the shift in diffraction pattern. In order to improve the homogeneity of the composition in the sample, an additional annealing procedure is required. It must be noted that there is a limited controllability of the alloying level with Sb in the sample, since no in situ measurements were performed.



Figure 8.16. X-ray diffractogram of  $Bi_{1-x}Sb_x$  silica nanocomposite reduced at 220 °C for 12h in a hydrazine loaded Ar - 5% H<sub>2</sub> atmosphere. The composition of the alloys was determined by XRF analysis. In case single phase alloys are obtained, the composition could also be derived from the position of the diffraction peaks and the known dependence of the lattice parameter on x.



Figure 8.17. TEM images of mesoporous  $Bi_{0.88}Sb_{0.12}$  synthesized using KIT-6 mesoporous silica. The template was impregnated with a BiCl<sub>3</sub> precursor solution and exposed to Me<sub>3</sub>Sb vapour at 120°C in a tubular furnace. The sample was completely reduced at 220 °C in N<sub>2</sub>H<sub>4</sub> vapour and subsequently subjected to 1 mol/L NaOH etching solution to remove the silica template. Note that the material partially oxidizes during TEM sample preparation.

TEM images of  $Bi_{1-x}Sb_x$  nanowire composite alloys synthesized through the gas phase reaction of Me<sub>3</sub>Sb with BiOCI – silica nanocomposite powder are shown in Figure 8.17 and

Figure 8.18. It can be seen that  $Bi_{0.88}Sb_{0.12}$  was successfully replicated from the KIT-6 template with a limited amount of bulk nanoparticles. This implies that during the reaction no crystal growth or leaching of the material outside the pores occurred. In the latter case, mesoporous  $Bi_{0.4}Sb_{0.6}$  consisting of nanowire arrays replicated from SBA-15 were obtained. It can be noticed from Figure 8.18 that the nanowires formed dense bundles and uninterrupted wires. This means that the concept to form  $Bi_{1-x}Sb_x$  alloys and enhance the pore loading through gas phase reaction of  $Me_3Sb$  with a  $BiOCI - SiO_2$  could be effectively achieved while there are no indications that leaching of material out of the template occurred.



Figure 8.18. TEM images mesoporous  $Bi_{0.4}Sb_{0.6}$  replicated from SBA-15 mesoporous silica. The template was impregnated with a BiCl<sub>3</sub> precursor solution and exposed to Me<sub>3</sub>Sb vapour at 120°C in a tubular furnace. The sample was completely reduced at 220 °C in N<sub>2</sub>H<sub>4</sub> vapour and subsequently subjected to 1 mol/L NaOH etching solution to remove the silica template. Note that the material partially oxidizes during TEM sample preparation.

Doping with selenium or the synthesis of  $Bi_2Se_3$  was achieved by reducing Se powder to  $Na_2Se$  in an aqueous sodiumborohydride solution at pH 14 and adding diluted sulphuric acid by means of a syringe pump according to Equation 7. [15, 16] The setup to synthesize the gas was similar with the scheme depicted in Figure 8.15.

$$4NaBH_{4(aq)} + 2Se_{(s)} + 7H_2O + 2NaOH_{(aq)} \xrightarrow{T^1} 2Na_2Se_{(aq)} + Na_2B_4O_{7(aq)} + 14H_{2(g)} + 2H_2O \quad Eq.8.7$$

The released H<sub>2</sub>Se gas was carried by an argon gas flow through a tubular furnace heated to 220 - 250 °C at a rate of 2 °C/min for 2h. The sample readily reacted with the gas yielding Bi<sub>2</sub>Se<sub>3</sub>. Note that H<sub>2</sub>Se is flammable and toxic. Both bismuth as bismuth antimony alloy composite materials were selenized, obtaining Bi<sub>2-x</sub>Sb<sub>x</sub>Se<sub>3</sub> thermoelectric material. Due to the reducing properties of the H<sub>2</sub>Se gas, both Bi(NO<sub>3</sub>)<sub>3</sub> and BiCl<sub>3</sub> reacted easily, with the formation of Bi<sub>2</sub>Se<sub>3</sub> at a temperature of approximately 220 °C. Noteworthy is the fact the pore loading could be easily enhanced due to the reaction of the bismuth salt with the reactive gas. For instance, when the pores were for 100 v% filled with BiCl<sub>3</sub>, the occupied fraction would reduce to 32 v% upon reduction to metallic bismuth. However, upon reaction with H<sub>2</sub>Se, a theoretical pore loading of 73 v% could be reached for Bi<sub>2</sub>Se<sub>3</sub>. Since it is desirable to obtain completely filled pores, the BiCl<sub>3</sub> salt was decomposed during the impregnation to BiOCl enabling a higher loading of bismuth inside the pore channels and subsequently a higher pore filling with Bi<sub>2</sub>Se<sub>3</sub> upon reaction with H<sub>2</sub>Se.

The TEM images of  $Bi_xSe_y$  shown in Figure 8.19 were obtained by exposing the same BiOCI –  $SiO_2$  nanocomposite sample to  $H_2Se$  gas at 200 and 220 °C, respectively. It can be noticed from the images that larger and more crystallites outside the template were formed when the reaction temperature was enhanced. However, the formation of large  $Bi_xSe_y$  grains was

minimized by performing the reduction treatment first, followed by the reaction with  $H_2Se$ . A sample prepared in that way is presented in Figure 8.20.

The measurement of the composition across a nanocomposite particle was performed by means of STEM-EDX and is presented in Figure 8.21. Several  $Bi_xSe_y$  flake-like structures can be observed on the template's surface. The Se/Bi ratio was relatively stable and varied between 2 and 2.3, which is an excess of Se compared to the desired 1.5 ratio in  $Bi_2Se_3$ . On the other hand, the loading of  $Bi_xSe_y$  was slightly higher at the edges of the nanocomposite particle than in the centre. Although  $Bi_xSe_y$  was formed throughout the entire sample, we lacked the ability to control the Se level.



Figure 8.19. (a) TEM images of  $Bi_xSe_y$  within the pores of SBA-15 mesoporous silica after exposure to  $H_2Se$  at 200 °C. (b)  $Bi_xSe_y$  within the pores of SBA-15 mesoporous silica after exposure to  $H_2Se$  at 220 °C.



Figure 8.20. TEM images of  $Bi_xSe_y$  replicated from SBA-15 mesoporous silica, synthesized by reducing the nanocomposite powder at 220 °C in N<sub>2</sub>H<sub>4</sub> and followed by a treatment in H<sub>2</sub>Se at the same temperature.



Figure 8.21. STEM dark field image of bismuth salt reduced at 240 °C for 2h in a hydrazine loaded Ar-5% H<sub>2</sub> gas flow and subsequently treated at 260 °C for 30 min in a flow of H<sub>2</sub>Se loaded Ar gas. The bright zone of the image

depicts the heavy  $Bi_xSe_y$ . The composition of the sample measured across the nanocomposite particle is shown in the right graph.

In order to improve the crystallinity of the material, the  $Bi_xSe_y - SiO_2$  nanocomposite powders were annealed for 5 h between 400 and 475 °C. It can be seen from the increase in intensity of the diffraction patterns in Figure 8.23 that the crystallinity improved after annealing the sample above 400 °C. Also, excess of selenium sublimed out of the sample and condensed on the cold part of the vacuum tube as shown in Figure 8.22.



Figure 8.22. Schematic representation vacuum tube for the annealing of Bi<sub>x</sub>Se<sub>y</sub> nanocomposite powder.



Figure 8.23. X-ray diffractogram of BiOCI – SiO<sub>2</sub> nanocomposite samples heat treated at 220 and 260 °C in a flow of H<sub>2</sub>Se and annealed at 400 and 475 °C under vacuum.

Although the crystallinity improved after the annealing of the sample, it was observed via TEM imaging and EDX measurements that  $Bi_xSe_y$  leached completely out of the pores and formed large grains. EDX data showed that less than 2 at% Si (originating from the SiO<sub>2</sub> template) remained in the  $Bi_xSe_y$  grains, while the overall at% Si was about 50%. Notice that there was also limited control of the obtained stoichiometry during the treatment with H<sub>2</sub>Se, since  $Bi_xSe_y$  forms solid solutions over almost the entire composition range. Furthermore, the Se depletion of the sample during the annealing treatment was uncontrollable.

It can be concluded from the described experiments that alloying with Sb and Se does not yield samples with a well-defined stoichiometry. As both materials form solid solutions with Bi, we were unsuccessful to form  $Bi_2Se_3$  thermoelectric alloys within the pore channels. However, it was possible to form both  $Bi_{1-x}Sb_x$  alloys or  $Bi_xSe_y$  within the pores of the silica template with a limited amount of bulk material formed outside the pores. It is suggested to perform hot pressing rather than vacuum annealing to enhance the crystallinity without changing the composition. Namely, it was shown that  $Bi_xSe_y$ , for instance, leached completely out of the pores during the annealing process. The same was observed when  $Bi_{1-x}Sb_x$  alloys were

annealed close to their melting point to improve the homogeneity and phase purity of  $Bi_{1-x}Sb_x$ . We propose an alternative route to synthesize  $Bi_{1-x}Sb_x$  nanostructured alloys consisting of the simultaneous impregnation of Bi and Sb salts, which provides precise control of their stoichiometry. The impregnation is considered as the coprecipitation of both metal salts inside the pores, which can be reduced in a subsequent step. Since this approach is easy to execute, it was used to make  $Bi_{1-x}Sb_x$  nanowire arrays.

In order to obtain fully loaded pores while controlling the  $Bi_{1-x}Sb_x$  stoichiometry, a mixture of Bi and Sb salt could be simultaneously impregnated with control of the stoichiometry and followed by a treatment with Me<sub>3</sub>Bi. In this manner, both the pore loading could be enhanced while the Sb content could be diluted in a controlled manner. So far, these experiments were not performed due to the high reactivity of Me<sub>3</sub>Bi. Specifically, the liquid ignites spontaneously upon contact with air and decomposes above 110 °C. [17]

### 8.3.3.3 Impregnation of mixed Bi – Sb precursor solution into silica template

As mentioned in previous section, the only way the Sb stoichiometry was controlled is by the impregnation of a mixed Bi - Sb precursor solution. Namely, both chloride salts were dissolved in diluted hydrochloric acid, methanol or formic acid for the preparation of the precursor solution. XRD patterns of the obtained powder after impregnation in n-octane showed only the presence of BiOCI phase, while no SbCl<sub>3</sub> or SbOCI were detected. Neither peak shift occurred which indicates that no BiOCI – SbOCI solid solution was formed with a difference in lattice parameter.

In order to enhance the thermoelectric properties of Bi through alloying with Sb, it is important that Sb is incorporated in the crystal lattice. If that is not the case, the positive Seebeck coefficient of Sb metal would reduce the negative Seebeck coefficient of Bi as can be seen from the reference data of polycrystalline Sb and Bi shown in Figure 8.24. As mentioned above, bismuth and antimony possess a Seebeck coefficient with opposite sign, what leads to the cancellation of the overall Seebeck coefficient if a mixture of elemental Bi and Sb is measured. From this, it can be understood that a change in Seebeck coefficient should occur when a mixture of Bi and Sb would be heated near its alloying temperature.



Figure 8.24. Seebeck coefficients of polycrystalline Sb, Bi,  $Bi_{0.95}Sb_{0.05}$  and  $Bi_{0.88}Sb_{0.12}$ . Data calculated from the Seebeck coefficients of single crystal Sb, Bi,  $Bi_{0.95}Sb_{0.05}$  and  $Bi_{0.88}Sb_{0.12}$  along the 11 and 33 crystal axes. Reference data replicated from [18].

In order to find the temperature at which  $Bi_{1-x}Sb_x$  phase forms, XRD patterns were recorded from  $Bi_{1-x}Sb_x - SiO_2$  nanowire composite samples reduced at different temperatures. In

addition, Seebeck coefficient measurements were performed in the temperature range that Bi and Sb alloy. In the first case, it was already shown in Table 3.1 that the lattice parameter of Bi changes linearly with the Sb content. Consequently, a shift of the reflection peak should be observed in XRD measurements. Secondly, a change in Seebeck coefficient as a function of temperature and time should give an increase of the absolute Seebeck coefficient upon alloying during an isothermal measurement.

Since both BiCl<sub>3</sub> and SbCl<sub>3</sub> were impregnated in the templates' pores, it was necessary to reduce both salts under the same conditions to form  $Bi_{1-x}Sb_x$  alloys. The conditions for the reduction of BiCl<sub>3</sub> were discussed earlier, whereas the reduction of  $Sb_2O_3$  and SbOCl are studied here. The same reducing agents were used for  $Bi_2O_3$  and BiOCl as for SbCl<sub>3</sub>.



Figure 8.25. X-ray diffraction patterns of (a)  $Sb_2O_3$ , (b) the material reduced in Ar - 5% H<sub>2</sub> loaded with formic acid (FA) vapour and (c) in hydrazine (N<sub>2</sub>H<sub>4</sub>) vapour for 10 h at 240 °C. The bottom reference pattern shows Sb.



Figure 8.26. X-ray diffraction patterns of  $Bi_{1-x}Sb_x - SiO_2$  nanowire composite samples reduced at different temperatures for 10 h in Ar - 5% H<sub>2</sub> bubbled through a 65% hydrazine solution.

The samples were heated at 240 °C for 10 h in Ar - 5% H<sub>2</sub> loaded with the vapour of a 50% hydrazine solution. XRD patterns of Sb<sub>2</sub>O<sub>3</sub> reduced with formic acid and hydrazine are shown in Figure 8.25. It can be seen that bulk Sb<sub>2</sub>O<sub>3</sub> powder was completely reduced to metallic Sb at 240 °C using FA vapour as reducing agent. Note the slight shift in peak position compared to the reference pattern. Apart from a possible offset of the sample height, no explanation can be given for the shift in peak position. N<sub>2</sub>H<sub>4</sub>, on the other hand, was unsuccessful to reduce antimony oxide at that temperature. It was earlier mentioned that the concentration of hydrazine hydrate affects its reactivity. Typically, 98 % hydrazine hydrate was used, which consist of approximately 65 % hydrazine. The hydrazine solution used here was a 50 % hydrazine solution. The absence of any Sb phase shows the effect of the concentration of hydrazine on its reducing power. When a 65 % hydrazine solution was used, Sb<sub>2</sub>O<sub>3</sub> was reduced to metallic Sb. The latter can also be seen in the XRD data presented on the reduction of Bi<sub>x</sub>Sb<sub>1-x</sub>OCl in N<sub>2</sub>H<sub>4</sub> vapour shown in Figure 8.26.

The reduction of  $Bi_{1-x}Sb_x - SiO_2$  nanowire composite powder in hydrazine vapour was conducted in a temperature range from 230 °C to 270 °C. A higher temperature range was necessary to allow alloying of Sb into Bi. All XRD measurements were performed under argon atmosphere since any peak shift observed in  $Bi_{1-x}Sb_x$  nanowire composite powders disappeared when the samples were exposed to air. It can be seen from the XRD data shown in Figure 8.26 that both BiOCI and SbOCI were reduced at a temperature as low as 230 °C. Nevertheless, the broad reflection of Sb at a 2  $\theta$  value of approximately 28.3 ° shows that no single alloy phase was formed in the temperature range between 230 and 265 °C. Whereas SbCl<sub>3</sub> reduced to Sb, no alloying of Sb into Bi occurred below approximately 265 °C. However, the reflection at 28.3 °C suggests that some Bi alloyed into Sb, leading to an increase in d-spacing or lower 2  $\theta$  value. The two samples reduced at 270 °C were bulk  $Bi_{1-x}Sb_x$ OCI formed by coprecipitation of BiCl<sub>3</sub> and SbCl<sub>3</sub> under basic conditions and a mesoporous silica template



Figure 8.27. X-ray diffraction patterns of  $Bi_{1-x}Sb_x - SiO_2$  nanowire composite samples reduced at different temperatures for 10 h in Ar - 5% H<sub>2</sub> bubbled through a formic acid.

impregnated with both metal salts. Only a small peak shift occurred for the  $Bi_{0.88}Sb_{0.12}$  -  $SiO_2$  sample, whereas the bulk sample showed a single composition alloy phase. The reason for this difference may be the difficulty for the metal atoms to diffuse into each other when confined in the template's channels.

Similar results as in Figure 8.26 were obtained when  $Bi_{0.88}Sb_{0.12}$ - SiO<sub>2</sub> samples were reduced between 250 and 265 °C in a formic acid atmosphere. Namely, Figure 8.27 shows that there is no significant difference in crystallinity of the formed Sb phase at a 2  $\theta$  value of 28.3 ° as a result of the different reducing agent.

It can be concluded form the X-ray diffraction studies performed on the reduction and annealing of  $Bi_xSb_{1-x}OCI - SiO_2$  nanowire composite samples that Bi and Sb could be obtained using either hydrazine or formic acid as reducing agent at temperature at 230 and 240 °C, respectively. However, an annealing temperature of approximately 270 °C was required to form a homogeneous  $Bi_{1-x}Sb_x$  phase. Since the melting temperature of Bi is only 271.5 °C, the high annealing temperature would lead to complete leaching of the impregnated material. Consequently, an alternative sintering process consisting of a reduction treatment, SPS sintering and an annealing procedure was used to prepare  $Bi_{1-x}Sb_x$  samples. Firstly, the samples were reduced at 230 °C in a flow of hydrazine vapour and subsequently sintered into pellets by means of SPS under an inert atmosphere between 180 and 220 °C for 20 min and a pressure of 50 MPa. Finally, the samples were post annealed to form  $Bi_{1-x}Sb_x$  phase.

Further optimization of this procedure was obtained by determining the optimum temperature and time for the annealing of  $Bi_{1-x}Sb_x$ . Therefore, the following experiment was carried out: a BiOCI/SbOCI – SiO<sub>2</sub> nanocomposite sample with composition  $Bi_{0.94}Sb_{0.06}$  was prepared by impregnating a silica template with a mixed  $BiCl_3 - SbCl_3$  precursor solution. Subsequently, the sample was reduced at 230 °C for 10 h in a flow of Ar – 5% H<sub>2</sub> loaded with N<sub>2</sub>H<sub>4</sub> vapour. The nanocomposite powder was handled under inert atmosphere and sintered at 180 °C for 20 min under a pressure of 50 MPa using SPS. A sample with dimensions 2 x 2 x 10 mm was cut from the obtained disk and mounted in a Linseis high temperature Seebeck coefficient



Figure 8.28. Measurements of the Seebeck coefficient as a function of the temperature and time of a  $Bi_{0.92}Sb_{0.08}$  -  $SiO_2$  nanocomposite sample. Due to alloying of Bi and Sb, the Seebeck coefficient was both temperature and time dependent. The Seebeck coefficient as a function of the temperature and time is depicted on the right y-axis, while the temperature as function of time is depicted on the left y-axis.

measurement device. The annealing was carried out while the Seebeck coefficient was monitored. Measurements were performed under helium atmosphere while the sample was heated from RT to 250 °C. The temperature was kept at 250 °C to see whether alloying occurred and its effect on the Seebeck coefficient as a function of time. It can be seen on the right axis from the data presented in Figure 8.28 that the absolute value of the Seebeck coefficient decreases as the temperature increases until approximately 248 °C. The temperature remained more or less stable at 249.7 °C, what involved that the Seebeck coefficient was measured under isothermal conditions. It can be seen that the |S| increased for 150 min, subsequently decreased (300 to 400 min), and increased again. Note that only small changed were observed. We decided to use a sintering time of approximately 90 min, based on the local maximum Seebeck coefficient after about 250 min. However, no peak shift was observed in XRD data when the samples were annealed at that temperature for 10 h. Consequently, further optimization, both for the reduction conditions of BiSb and the sintering is still required to form better quality Bi<sub>1-x</sub>Sb<sub>x</sub> nanocomposite samples.

### 8.3.4 Thermoelectric property measurements

In this section, the thermoelectric properties of bismuth antimony nanowire composites with different pore loadings, pore structure, pore diameter and composition of the nanowires were studied. A pore loading of approximately 40 v% Bi was typically obtained, with tuneable pore symmetry and pore diameter. The samples were reduced at a temperature as low as 230 °C with limited leaching. In the case of Bi<sub>1-x</sub>Sb<sub>x</sub> samples, the nanowire composites generally consisted of Bi and Sb rather than Bi<sub>1-x</sub>Sb<sub>x</sub> alloy. Bi<sub>1-x</sub>Sb<sub>x</sub> alloy nanostructures were only obtained by simultaneous sintering and annealing using the SPS equipment.

### 8.3.4.1 Influence of pore loading on TE properties

KIT-6 mesoporous silica with a pore volume of 0.6 mL/g or porosity of 61 % and 6.5 nm pore diameter was used as template material. The pores were loaded with approximately 32, 44 and 58 v% bismuth metal. The nanowire composite powder was sintered into pellets at 230 °C for 20 min at a pressure of 50 MPa using SPS. Note that the sample prepared by impregnating the template with 32 v% Bi was not conducting. Consequent, only the results of 44 and 58 v% loaded templates are discussed.



Figure 8.29. Electrical resistivity of sintered Bi - KIT-6 mesoporous silica nanowire composite powder with different pore loading fractions of the template. Reference reproduced from [18].

As mentioned earlier, the theoretical maximum pore loading that can be obtained when the  $BiCl_3$  precursor solution is decomposed to BiOCI during the impregnation is approximately 60 v%. However, the closer the pore loading approached the theoretical limit, the more material is deposited on the external surface of the template rather than inside the pores. Therefore, the TE properties for samples with a different pore loading were measured. Namely, it was expected that the formation of external deposited material would be noticeable from an increase of the electrical conductivity. Also, the higher the pore loading the more electrical percolation paths are formed within the template. Note that the occurrence of leaching during the reduction and the sintering conditions affect the TE properties significantly.



Figure 8.30. Electrical resistivity of (a) polycrystalline bulk Bi, (b) KIT-6 loaded with 44 v% Bi and (c) KIT-6 loaded with 51 v% Bi. Reference reproduced from [18].

It can be seen from the electrical resistivity measurements shown in Figure 8.29 that the electrical resistivity was several orders of magnitude higher in the composite samples compared to the reference. In addition, the resistivity changed drastically depending on the pore loading. Figure 8.30a shows that the resistivity reduces linearly with the temperature, which is what we expect for a metallic behaviour. However, the fact that the resistivity increased with reducing temperature in Bi - KIT-6 nanowire composites indicates a semiconducting behaviour of the material. The occurrence of such semiconducting behaviour of the resistivity with decreasing temperature was particularly the case for KIT-6 loaded with 44 v% Bi. Consequently, the resistivity behaviour confirms a semiconducting behaviour of the nanowire composite samples due to size quantization. Note that an infinite resistivity was measured when the pores were filled with 32 v% Bi, which is most likely due to the lack of electrical percolation paths between the electrical contacts on the sample or due to complete localization of the carriers. When 58 v% Bi was



Figure 8.31. Seebeck coefficient measurements of KIT-6 - Bi nanowire composites with different pore loading of the template. Reference reproduced from [18].

loaded within the template, the increase in resistivity below 150 K was less noticeable than for 44 v% Bi. Presumably, the lower resistivity of the sample could be allocated to the deposition of Bi on the template's pore surface when the pores were attempted to fill with 58 v% Bi, leading to a more metallic character of the resistivity vs temperature data.

The Seebeck coefficient for different pore fillings are shown in Figure 8.31. Due to size quantization, an increase in Seebeck coefficient of the nanowire composites was expected. However, the absolute values of the Seebeck coefficient was lower than that of bulk Bi. Also, the absolute Seebeck value is slightly lower when the template's pores were filled with 58 %.



Figure 8.32. Thermal conductivity data of KIT-6 - Bi nanowire composites prepared by impregnating the template with different loadings of Bi. Reference reproduced from [18].

The thermal conductivity of bismuth nanowire composites shown in Figure 8.32 are significantly lower than the thermal conductivity of bulk bismuth. A low thermal conductivity was expected, as the nanostructured architecture of the composite scatter phonons very effectively. Since silica has a low thermal conductivity, of approximately 0.2 W/mK, parasitic losses through the scaffold are limited. However, any increase in porosity of the template material reduces the contribution of heat losses through the matrix. Striking in Figure 8.32 is the fact that the thermal conductivity of 58 v% filled template is lower than the 42 v% filled template. The positive slope of the change of conductivity with temperature suggests either an electronic or a radiative contribution to the thermal conductivity. Since the resistivity of the 58 v% sample is lower than that of the 44 v% sample, the electronic thermal conductivity is



Figure 8.33. Carrier concentration of 51 v% and 44 v% Bi - KIT-6 nanowire composites. References reproduced from [18, 19].

probably not at the origin of the observation. One possible but speculative explanation is that because the matrix is optically clear, heat may have radiated through the matrix (radiative contribution to the thermal conductivity). With increasing filling, the material becomes opaquer and the radiative channel conducts less heat. Unfortunately, we have no experimental evidence for this explanation.

The carrier concentration derived from Hall effect measurements in Figure 8.33 is consistent with the observations from the resistivity and Seebeck measurements. It can be seen that KIT-6 impregnated with 44 v% Bi has a 10-fold lower carrier density than the bulk Bi reference. However, there is a distinct difference in carrier concentration with the 51 v% Bi sample, which is very similar with that of metallic bismuth (see Bi <sub>REF</sub>). We know that more leaching phenomena occur as we try to fill the pores with more precursor. Consequently, it is expected that we only measured the properties of bulk bismuth present at the exterior of the template.



Figure 8.34. Carrier concentration of bulk bismuth and 29 v% Bi – SiO<sub>2</sub> (KIT-6) nanowire composite sample as function of 1/2kT. The lower carrier concentration of the nanocomposite sample compared to bulk Bi can be attributed to size-quantization effects in the nanowires. The carrier concentration for the intrinsic semiconductor was derived by  $n_i=n_0 e^{-Eg/2kT}$ . The band gap obtained by the fit through the data points yields: Eg = 45 meV, which corresponds to Bi nanowires with diameter 20 nm according to Lin et al. [20] Note that all sample preparations and measurements were performed under inert atmosphere.

Evidence of size quantization in the bismuth nanowire composites was obtained from measurements of the Hall effect (Figure 8.33 and Figure 8.34) of the sintered samples. The inverse of the low-field (< 1 Tesla) Hall slope  $R_H$  was interpreted to give the charge-carrier concentration via  $n = (e R_H)^{-1}$  with *e* the electron charge.  $R_H$  was positive, so the dominant carriers are holes. Figure 8.34 shows the temperature dependence of *n* measured on the sample (29 v% Bi – SiO<sub>2</sub>), in an Arrhenius plot. A very clean, activated behaviour is observed, following a law  $n(T) = n_0 e^{-Eg/2kBT}$  valid for intrinsic semiconductors, where  $E_g$  is the band gap of the semiconductor. A mixture of very narrow nanowires with bulk-like Bi (which displays a metal-like conductivity) will not generate such a simple temperature-dependence. Furthermore, the charge-carrier concentration measured on the nanowire sample is an order of magnitude smaller than that (also shown in Figure 8.34) of bulk Bi. Finally, the value of  $E_g$  = 45 meV obtained from the Arrhenius plot in Figure 4 corresponds very well to the theoretical value of the band gap opened by size-quantization effects in Bi nanowires of about 20 nm diameter, providing evidence of size quantization effects in the nanowire composites.

At first sight, the 20 nm diameter measured by electrical measurements appears to contradict the observation that the template's pores were 7 nm, which should correspond to a bandgap exceeding 100 meV. However, it has been observed experimentally [3] that conduction in nanowires of diameter smaller than 9 nm becomes localized. In contrast, no localization is observed in the sample measured here, as is illustrated by the resistivity data in Figure 8.30b. These data show a temperature dependence consistent with the decrease in carrier concentration, very different from bulk Bi. Because there is always a statistical distribution of nanowire diameter, these observations lead to the conclusion that the conduction is dominated by nanowires with diameters near 20 nm with conduction in all the narrower wires simply localized.



8.3.4.2 Influence of annealing on TE properties of Bi<sub>0.94</sub>Sb<sub>0.06</sub> – KIT-6

Figure 8.35. Electrical resistivity of 58 v% Bi<sub>0.94</sub>Sb<sub>0.06</sub> - KIT-6 mesoporous silica. Reference reproduced from [18].

Since no enhancement of the Seebeck coefficient was observed in Bi nanowire composites, the material was alloyed with 6 at% Sb. Samples were prepared by impregnating KIT-6 mesoporous silica with a mixed precursor of BiCl<sub>3</sub> and SbCl<sub>3</sub> in HCl, MeOH or FA. The pore diameter and pore volume of the template were 6.5 nm and 0.6 mL/g, respectively. The reduction of the impregnated powder was performed at 230 °C in a flow of Ar - 5% H<sub>2</sub> loaded hydrazine vapour for 10 h, leading to a pore volume of 58 v% with Bi<sub>0.94</sub>Sb<sub>0.06</sub>. Subsequently, the powders were pressed into pellets at 180 °C for 20 min using SPS. All steps were performed under argon atmosphere to avoid oxidation. The first sample was measured without any further treatment, whereas a second sample was measured after annealing the sintered sample at 250 °C for 12 h. Note that the sintered sample was exposed to air before the



Figure 8.36. Electrical resistivity of  $Bi_{0.095}Sb_{0.05 REF}$ , 58 v%  $Bi_{0.094}Sb_{0.06}$  – KIT-6 sintered at 180 °C and subsequently annealed at 250 °C for 12 h.

annealing procedure, but since that step was also performed under reducing conditions, it should not affect any of the presented data.

The data for 58 v%  $Bi_{0.094}Sb_{0.06}$  – KIT-6 reported in Figure 8.35 and Figure 8.36b,c show a semiconducting behaviour of the electrical resistivity. A similar trend is observed for the sample before and after annealing. It can be seen in Figure 8.36c that the resistivity increased significantly after annealing the sample under reducing conditions for 12 h, which is most likely due to the alloying of Bi with Sb. Namely, we see a contribution of size quantization effects (similar as shown in Figure 8.34 for Bi nanowire composites) and a semiconducting behaviour of the resistivity of  $Bi_{0.094}Sb_{0.06}$ .

The Seebeck coefficient data reported in Figure 8.37 shows that no enhancement in thermopower was obtained upon alloying the nanowires with 6 at% Sb. Presumably, because of shortcuts through bulk material around the mesoporous silica grains and poor quality of the formed  $Bi_{1-x}Sb_x$  phase was formed with the used thermal treatment. Namely, the least we would expect is a Seebeck coefficient that resembles the value of bulk  $Bi_{0.94}Sb_{0.06}$ .



Figure 8.37. Temperature dependence of the Seebeck coefficient of 58 v% Bi<sub>0.094</sub>Sb<sub>0.06</sub> – KIT-6 before and after annealing. Reference reproduced from [18].



Figure 8.38. Carrier concentration of 58 v% Bi<sub>0.094</sub>Sb<sub>0.06</sub> – KIT-6 before and after annealing at 250 °C. References reproduced from [18, 21].

According to literature reports on the carrier concentration of  $Bi_xSb_{1-x}$  alloys [18, 19], only a slight reduction in carrier density occurs with increasing Sb content. Consequently, the drop in carrier density in the annealed sample shown in Figure 8.38 is either caused by oxidation

of the sample or due to size quantization effects. Since the carrier concentration is lower than its bulk alloy in both cases, this could be by quantization in the sample. However, since no enhancement in Seebeck coefficient was observed it is likely that any oxide formed between the sintering and annealing process was not completely removed.

The thermal conductivity data depicted in Figure 8.39 shows a slight reduction in  $\kappa$  after annealing the sample at 250 °C. However, no clarification can be given for the lower thermal conductivity. Since the thermal conductivity is so low already, we believe that the thermal conductivity measurements are extra sensitive towards any variations caused during the synthesis, sintering or annealing of the sample.



Figure 8.39. Thermal conductivity of 58 v%  $Bi_{0.094}Sb_{0.06}$  – KIT-6 before and after annealing at 250 °C. References reproduced from [18].

#### 8.3.4.3 TE properties of Bi<sub>0.88</sub>Sb<sub>0.12</sub> – KIT-6

 $Bi_{1-x}Sb_x$  nanowire composites with a composition of 12 at% Sb were synthesized in the channels of KIT-6 with a pore diameter of 13 nm. Due to the higher resistivity of bulk  $Bi_{0.88}Sb_{0.12}$  compared to bismuth, a higher pore diameter was required to avoid complete localization of the charge carriers. Namely, pores with a smaller diameter yielded nanocomposite samples with an infinite resistivity. The reduction of the impregnated powder was performed at 230 °C in a flow of Ar - 5% H<sub>2</sub> loaded hydrazine vapour for 10 h, leading to a pore volume of 32 v% with  $Bi_{0.88}Sb_{0.12}$ . Sample was annealed under reducing conditions at 250 °C for 12 h before measuring.



Figure 8.40. Electrical resistivity of 32 v% Bi<sub>0.88</sub>Sb<sub>0.12</sub> – KIT-6 - Ø 13 nm nanowire composite. References reproduced from [18].

The electrical resistivity data in Figure 8.40c,b shows that the resistivity increases with reducing temperatures. A minimum in resistivity was observed at 170 K for the bulk  $Bi_{0.88}Sb_{0.12}$  reference, which is a typical behaviour for a semiconducting compound.  $Bi_{0.88}Sb_{0.12} - KIT-6$ ,

on the other hand, shows a continuous increase of the resistivity. As in previous samples, the semiconductor behaviour of the electrical resistivity can be allocated to size quantization in the nanowires.



Figure 8.41. Seebeck coefficient of 32 v%  $Bi_{0.88}Sb_{0.12} - KIT-6 - \emptyset$  13 nm bulk nanowire composite compared with  $\alpha$  for different  $Bi_{1-x}Sb_x$  alloy compositions. References reproduced from [18].

The Seebeck coefficient reported in Figure 8.41 does not show any enhancement of  $\alpha$  in the nanowire composite structure. We believe the sample was not completely alloyed and therefore did not show any enhancement of  $\alpha$ . Namely, regardless whether Bi<sub>0.88</sub>Sb<sub>0.12</sub> would be deposited on the template's surface or within the pores, the Seebeck coefficient should be higher for Bi<sub>1-x</sub>Sb<sub>x</sub> alloys compared to Bi as can be seen from the bulk reference samples.

The carrier concentration in Figure 8.42 shows an unexpected trend for *n* as a function of temperature. Namely, the  $Bi_{0.88}Sb_{0.12} - KIT-6$  sample showed a similar value to that of bulk Bi, while bulk  $Bi_{0.88}Sb_{0.12}$  possesses a carrier density of  $1.1 \times 10^{17}$  cm<sup>-3</sup>. This data is also in contrast to the observations in Figure 8.38. We expect that the high carrier concentration of the  $Bi_{0.88}Sb_{0.12} - KIT-6$  sample is due to incomplete alloying with Sb. This can be understood from the fact that metallic Sb has a carrier concentration of approximately two orders of magnitude higher than Bi, which may have led to an increase of the carrier concentration compared to  $Bi_{0.88}Sb_{0.12}$  alloy.



Figure 8.42. Carrier concentration as function of temperature of for different  $Bi_{1-x}Sb_x$  alloys. References reproduced from [18, 21].



Figure 8.43. Temperature dependence of the thermal conductivity for different  $Bi_{1-x}Sb_x$  alloys. References reproduced from [18].

The thermal conductivity of all reference  $Bi_{1-x}Sb_x$  samples are shown in Figure 8.43. It can be seen that  $\kappa$  drops significantly when the Sb fraction in the reference alloy was enhanced.  $\kappa$  of bulk  $Bi_{1-x}Sb_x$  dropped about with a factor 4 at liquid N<sub>2</sub> temperatures when alloyed with 12 at% Sb and halved near 200 K. Note that we did not observe a significant dependence of the alloy concentration of the  $Bi_xSb_{1-x} - KIT-6$  samples on the thermal conductivity.

### 8.3.4.4 Effect of leaching on transport properties

It is clear from the aforementioned cases that no enhancement of the Seebeck coefficient was achieved. Regardless of the alloy composition or pore diameter of the template, a value for *S* comparable with bulk bismuth was obtained. Nevertheless, it was clear from the resistivity data and the carrier concentrations of the nanowire composites that size quantization occurred. We predicted that the reason for the absence of any enhancement of the Seebeck coefficient could be due short circuits within the nanowire composites.



Figure 8.44. (a) TEM image of Bi - SBA-15 nanowire composite. The arrows show bulk Bi particles on the template's surface. (b) Schematic showing electrical short circuits formed bypassing the nanowires due to bulk material around the silica template.

This idea can be understood better by the help of Figure 8.44a and Figure 8.44b. It can be seen in the TEM image that some spherical bulk bismuth nanoparticles were formed around the template, either due to incomplete impregnation or due to leaching during the reduction treatment. It was expected that those nanoparticles around the silica template caused a short circuit of the nanowires. Namely, due to size quantization, the resistivity of the nanowires was relatively large. Since the current passes through the sample via the least resistive path, it would flow through bulk bismuth around the silica grains in case there is external deposited material present. The red arrows indicate bulk bismuth particles outside the template, whereas



the green arrow indicates the nanowires itself. The aforementioned date suggests that the current flows through bulk Bi around the silica grains, rather than through the nanowires.

Figure 8.45. (a) TEM image of Bi - SBA-15 nanowire composite. It is suggested to fill the pores with Bi or  $Bi_{0,94}Sb_{0,06}$ , which is well conducting, and add an excess of precursor causing externally deposited material of  $Bi_{0,88}Sb_{0,12}$ , which is more resistive than the former. (b) Schematic of nanowire composite consisting of conductive nanowires and more resistive matrix. The green arrows indicate preferential conduction through the nanowires while the red arrows are more resistive.

A mechanism to overcome this problem is by alloying the nanowires and the matrix (which we refer to as the bulk material deposited outside the template) in such way that the nanowires are better conductors than the matrix as shown in Figure 8.45b. Consequently, any bulk material present around the silica template would no longer bypass the nanowires. Specifically, the template could be loaded with Bi or Bi<sub>0.94</sub>Sb<sub>0.06</sub>, while an excess of precursor could be added with 12 at% Sb. Due to the difference in resistivity of Bi or Bi<sub>0.94</sub>Sb<sub>0.06</sub> and Bi<sub>0.88</sub>Sb<sub>0.12</sub>, as shown in Figure 8.46, the current should go preferentially through the nanowires even if there would be an electrical path available through the bulk material around the template grains.



Figure 8.46. Electrical resistivity of bulk  $Bi_xSb_{1-x}$  alloys as a function of temperature. References reproduced from [18].

In addition, the presence of a  $Bi_{1-x}Sb_x$  matrix may also help to enhance the contacts between two adjacent template grains, which can be considered as a binder as shown in Figure 8.47. Namely, if all material were contained within the mesoporous template, the only electrical connections which would be made upon sintering are those where the silica particles touch each other. From this scenario, it can be understood that a 3D interconnected pore system, for example in KIT-6 and FDU-12, is preferred over a 2D ordered pore system, such as for SBA-15. Consequently, upon the addition of a  $Bi_{0.88}Sb_{0.12}$  "binder" between the  $Bi_{0.94}Sb_{0.06}$  –  $SiO_2$  grains, more nanowires should be included in the electrical conduction of the composite. However, it is important to mention that external material is only beneficial if its resistivity is higher than that of the nanowires. If this criterion is not met, the matrix will short circuit the nanowires and exclude their contribution to the thermoelectric properties of the bulk nanowire composite.



Figure 8.47. Schematic representation of the effect a matrix material could have on the number of nanowires included in the electrical transport. (a) In the absence of any matrix, contacts between the nanowires are only made where the template particles touch each other. (b) In the case a matrix material is deliberately added, extra contacts between adjacent template particles can be made.

### 8.3.4.5 TE properties of Bi<sub>0.94</sub>Sb<sub>0.06</sub> – FDU-12 nanowire composite in Bi<sub>0.88</sub>Sb<sub>0.12</sub> matrix

In order to overcome short circuits of the nanowires within the bulk nanowire composite, the aforementioned strategy was tested. Ultra large pore FDU-12 with pore diameters ranging from 10 to 30 nm and a pore volume of 0.9 mL/g was used as template material. The porosity of the template derived from the pore volume was 70 v%. As previously mentioned, the maximum pore loading with bismuth metal is 60 v% of the pores. Herefore, the pores must be completely filled with BiOCI. Firstly, the amount of precursor solution to fill the template's pore with 100 v% Bi<sub>0.94</sub>Sb<sub>0.06</sub>OCI (or 60 v% Bi<sub>0.94</sub>Sb<sub>0.06</sub> metal) was impregnated. Secondly, a precursor solution with 12 at% Sb was added to form the matrix material. The amount of matrix accounted for 15 v% of the silica template. Since the silica template was filled completely with Bi<sub>0.94</sub>Sb<sub>0.06</sub>OCI, it was assumed that the excess of precursor would not impregnated the pores and form the matrix material with composition Bi<sub>0.88</sub>Sb<sub>0.12</sub>. Consequently, for 1 g of mesoporous silica template, the pore volume was 0.9 cm<sup>3</sup>, while the volume of SiO<sub>2</sub> occupied 0.39 cm<sup>3</sup>. It could be derived that the volume of Bi<sub>0.94</sub>Sb<sub>0.06</sub> nanowires in the pores was 0.54 cm<sup>3</sup>. The volume of unoccupied pores was 0.36 cm<sup>3</sup> and the added Bi<sub>0.88</sub>Sb<sub>0.12</sub> matrix accounted for 0.2 cm<sup>3</sup>. In summary, the overall composition of the nanowire composite consisted of 26 v% SiO<sub>2</sub>, 36 v% Bi<sub>0.94</sub>Sb<sub>0.06</sub> nanowires, 13 v% Bi<sub>0.88</sub>Sb<sub>0.12</sub> matrix and 24 v% empty pore. Note that it is considered that no material leached out of the template.

The composite powder was reduced at 230 °C for 24 h in Ar – 5% H<sub>2</sub> gas loaded with N<sub>2</sub>H<sub>4</sub> vapour. The long reduction time was required since there was still BiOCI secondary phase present after 12 h. Next, the reduced powder was sintered at 245 °C for 90 min at a pressure of 50 MPa using SPS. It was expected that the annealing under pressure would limit further leaching of bismuth out of the template's pores. According to the isothermal Seebeck coefficient measurements discussed in Figure 8.28, it was shown that the maximum absolute Seebeck value was obtained after sintering 150 min at 250 °C. Nevertheless, the set temperature of 245 °C was selected since there is a temperature offset between the actual sample temperature and the set value.

In comparison to the aforementioned data, the electrical resistivity of the nanowire composite samples was drastically reduced. We believe this is due to a combination of the larger number of nanowires contributing to the electrical conductions as a result of the matrix and due to the

higher loading of the pores compared to previous samples. Namely, a pore loading of 64 v% bismuth alloy compared to 58 v% for the sample discussed in Figure 8.35.



Figure 8.48. Electrical resistivity measurement of  $Bi_{0.94}Sb_{0.06} - Bi_{0.88}Sb_{0.12} - FDU-12$  nanowire composite sample. References reproduced from [18].

The occurrence of a minimum in resistivity and subsequent increase when the temperature is reduced is typical for semiconductors, however, compared to the reference samples the relative increase is more pronounced. As observed in other samples, this indicates that size quantization occurred in the nanowire composite.



Figure 8.49. Seebeck coefficient of  $Bi_{0.94}Sb_{0.06} - Bi_{0.88}Sb_{0.12} - FDU-12$  nanowire composite sample compared to  $Bi_xSb_{1-x}$  reference samples for polycrystalline alloys and polycrystalline data derived from single crystal measurement data. References reproduced from [18, 21, 22, 23].

Figure 8.49 shows the Seebeck coefficient of the  $Bi_{0.94}Sb_{0.06} - Bi_{0.88}Sb_{0.12} - FDU-12$  sample compared to literature data. To the best of our knowledge, this is the first data reported on  $Bi_{1-x}Sb_x$  nanowires or nanowire composites. In addition, we show here that an enhancement of the Seebeck coefficient was obtained due to size quantization effects in the  $Bi_{0.94}Sb_{0.06}$  nanowires embedded in the silica template and a resistive  $Bi_{0.88}Sb_{0.12}$  matrix. Note that the

presented was measured on one sample only, therefore, the reproducibility of this experiment must be checked. Nevertheless, it can be seen that in the temperature region from 250 K up to 420 K, the absolute value of the measured Seebeck coefficient is higher than any data reported on  $Bi_{1-x}Sb_x$  alloys. Consequently, we can say with certainty that this is not a bulk effect due to alloying, but solely a result of nanostructuring. Further research is required to investigate the influence of the pore diameter on this effect, the ratio between the amount of matrix material and the nanowires, the doping level of the nanowires, the alloy composition of the nanowires and the matrix are the most important issues which still need to be addressed.



Figure 8.50. Carrier concentration of Bi<sub>0.94</sub>Sb<sub>0.06</sub> – Bi<sub>0.88</sub>Sb<sub>0.12</sub> – FDU-12 nanowire composite sample. References reproduced from [18, 21].

Although an enhancement in Seebeck coefficient was observed, we would expect a reduction of the carrier concentration in Figure 8.50 due to size quantization. The fact that the carrier concentration is in the same range as bulk Bi suggests that  $Bi_{1-x}Sb_x$  was not completely alloyed, or in other words, that the sample may still contain elemental Sb. However, further research is required to confirm this statement.



Figure 8.51. Thermal conductivity of  $Bi_{0.94}Sb_{0.06} - Bi_{0.88}Sb_{0.12} - FDU-12$  nanowire composite sample. References reproduced from [18].

The thermal conductivity reported in Figure 8.51 shows a relatively low value compared to the reference samples, however, values below 1 W/mK were also observed in other nanowire composite samples. It is believed that the thermal conductivity is affected by the pore volume of the template, diameter of the pores and the composition of the material. Also, the sintering temperature and pressure may affect the thermal conductivity. In general, we could not correlate the thermal conductivity to the synthesis or processing conditions.

The carrier mobilities of all discussed bismuth nanowire composites are given in Figure 8.52. Compared to reported values by Michenaud *et al.*, the carrier mobilities measured here are roughly 2 order of magnitude smaller. [24] The lower mobility may be caused by impurity scattering or quantization effects of the charges. Note that the highest mobility is obtained for  $Bi_{1-x}Sb_x$  alloys with 6 at% Sb.



Figure 8.52. Carrier mobilities of bismuth nanocomposite samples.

The Nernst coefficients of all samples are given in Figure 8.53. It can be seen that the highest absolute Nernst coefficient is obtained in samples consisting of Bi<sub>0.88</sub>Sb<sub>0.12</sub>. In the absence of quantization and in samples in which there are simultaneously electrons and holes, the Nernst coefficient is a measure of the difference between the partial electron and hole thermopowers. In semiconducting alloys, whether that semiconducting nature is brought about by Sb alloying or by size quantization, the conduction is by only electrons and the Nernst measures the energy dependence of the scattering mechanism. Assuming that all the Bi<sub>1-x</sub>Sb<sub>x</sub> nanowires are semiconducting, the change in sign between the Nernst coefficient of the 6 nm diameter wires and the 13 or 20 nm diameter wires is likely due to that. It would indicate that in the 6 nm wires, scattering is dominated by ionized impurities; whereas in the 20 nm wires it is dominated by



Figure 8.53. Nernst coefficient of all samples discussed in this section.

phonon scattering. Under the circumstances,  $20 \ \mu V/(K.T)$  is a very high value for the Nernst coefficient of a single-carrier system. To the best of our knowledge, the effect of size quantization on the Nernst coefficient has not been calculated because it is impossible to measure on single wires. The present work shows that it is possible to measure it on wire composites, and will hopefully inspire theoretical models.

# 8.4 Conclusions

Bismuth nanowire composite structures were synthesized by impregnating a mesoporous silica template with a precursor solution of BiCl<sub>3</sub> dissolved in diluted HCl, methanol and/or formic acid. BiCl<sub>3</sub> decomposed to BiOCl during the impregnation and was reduced in a flow of formic acid or hydrazine hydrate at 230 °C. Depending on the used silica template, linear nanowires or interconnected nanowire networks were obtained when the silica was chemically etched. However, due to oxidation of single Bi nanostructures in air, they were used embedded in a silica template and used as a thermoelectric nanowire composite. Bi<sub>1-x</sub>Sb<sub>x</sub> nanowire composites were synthesized by impregnating a precursor solution containing both BiCl<sub>3</sub> and SbCl<sub>3</sub>. Metallic Bi and Sb were obtained after reducing the salts in a flow of formic acid or hydrazine hydrate at 230 °C. However, Bi<sub>1-x</sub>Sb<sub>x</sub> alloys were only obtained after annealing the samples between 260 and 270 °C in a flow furnace or at 250 °C using SPS.

We were able to demonstrate size quantization in  $Bi_xSb_{1-x}$  nanowire composite powders based on electrical resistivity measurements and carrier concentration data in 6.5 nm Bi nanowire composites, but no enhancement of the Seebeck coefficient was observed. Provided, however, that the  $Bi_{0.94}Sb_{0.06} - SiO_2$  nanocomposite powder was mixed in a  $Bi_{0.88}Sb_{0.12}$  matrix, a very large enhancement of the Seebeck coefficient was observed at and above 300 K in the 20 nm diameter bismuth nanowire composite sample embedded in pore expanded FDU-12 mesoporous silica. In the absence of the  $Bi_{0.88}Sb_{0.12}$  matrix, no enhancement of the thermopower was obtained. The 20 nm sample shows size quantization, since such an enhancement in Seebeck is not observed by alloying only in any bulk  $Bi_xSb_{1-x}$  samples. Noteworthy is also the large Nernst coefficient.

Taken as a whole, it can be concluded from the data presented here that the Seebeck coefficient can be enhanced in nanowire composites, provided that a matrix is used of material with a higher resistivity than the nanowires.

# 8.5 References

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# 9

# Spin Seebeck effect in bulk nanocomposite Ni-Pt

In this chapter, we discuss the synthesis of Ni-Pt nanocomposites in which the contribution of the spin Seebeck effect to the transverse Nernst thermopower in bulk nanocomposite materials was demonstrated. The spin-Seebeck effect (SSE) is a new thermal-to-electrical energy conversion technology related to Nernst-Ettingshausen thermoelectrics. The electrical power produced by conventional SSE thin-film structures is limited by their reliance on interfacial spin transport between a ferromagnet and a normal metal. It was demonstrated experimentally that the SSE can be exploited in a bulk nanocomposite, with a geometry that is better suited for generating high power. The nanocomposites consist of a conducting ferromagnetic material, such as Ni, containing nanoparticles of a normal metal (NM) with strong spin-orbit interactions, for example Pt. The SSE contribution in Ni-Pt composites more than doubled the power factor of the reference material at every temperature studied, establishing proof-of-principle for this new approach. It was the first time that this effect was observed in a bulk nanocomposite material, what led to the publication of this work in Nature Communications [1].

# 9.1 Introduction

The spin Seebeck effect is observed as an interfacial effect between a ferromagnet and a nonmagnetic material. It refers to the generation of a spin voltage caused by a temperature gradient in a ferromagnet, which enables the thermal injection of spin currents from the ferromagnet into an attached nonmagnetic metal over a macroscopic scale. The inverse spin Hall effect converts the injected spin current into a transverse charge voltage, thereby producing electromotive force as in the conventional charge Seebeck device. The spin Seebeck effect [2] (SSE) offers an alternate approach to conventional thermoelectric effects for solid-state heat-to-electricity energy conversion. [3,4] SSE has been studied so far only in thin-film heterostructures, which are useful for understanding the physics of SSE, but not necessarily for energy conversion. The potential of this approach is demonstrated here in a Ni-Pt composite, where the addition of Pt nanoparticles results in a significant enhancement of the transverse thermopower due to combined contributions from both the Nernst effect and

SSE. Together with low bulk electrical resistivity, this resulted in a 2-5 times improvement in the transverse power factor compared to a sample without Pt, which is discussed in detail in Boona *et al.* [1] It was demonstrated that bulk nanocomposites can use the SSE to produce significantly more electrical power from the same temperature gradient relative to single phase magnetic materials. However, in order to allow spin pumping to enhance the transverse thermopower, the normal metal, which is Pt, must have a thickness smaller or comparable with its spin diffusion length. For Pt, this is approximately 1 – 10 nm. Larger particles would short circuit the generated transverse field near the ferromagnet's interface. Therefore, different synthesis routes were investigated to form Pt nanoparticles with sizes below 10 nm homogeneously distributed onto Ni particles. Since the SSE is an interfacial effect between Ni and Pt, no alloying of Ni and Pt could occur. Therefore, low temperature processes were required. The SSE data in Ref. [1] shows the opportunities of nanocomposites for thermal-to-electric energy conversion applications.

# 9.2 Experimental

# 9.2.1 Materials

Hydrogen hexachloroplatinate(IV) hydrate, ca. 40% Pt and sodium borohydride powder 99% were purchased from Acros Organics. Sodium citrate dihydrate >99%, nickel nitrate hexahydrate 99.99%, 64-65% hydrazine monohydrate and 99.8% ethylene glycol were supplied by Sigma Aldrich. 99% NaOH was purchased from Mallinckrodt Chemicals. All chemicals were used as received.

# 9.2.2 Synthesis

Several reducing agents and complexing agents were tested to form small Pt nanoparticles with a diameter below 10 nm on the surface of Ni particles. Two approaches were explored; firstly, Pt was deposited onto the surface of nickel powder and secondly, Pt nanoparticles were formed on Ni nanoparticles synthesized from solution. In order to have clean interfaces between the Ni particles and Pt nanoparticles, the use of organic surfactants was limited. NaBH<sub>4</sub>, hydrazine hydrate and formic acid were used as reducing agents, while citric acid was used as complexing agent. All samples were prepared with 2 m% Pt.

# 9.2.3 Characterization

Since it was required to form Pt nanoparticles with a diameter below 10 nm onto crystalline Ni particles, samples were analyzed on a Philips CM12T twin lens conventional TEM. XRD patterns were recorded on a Rigaku MiniFlex Diffractometer with  $Cu-K_{\alpha}$  radiation.

# 9.3 Results and discussion

# 9.3.1 Deposition of Pt nanoparticles on Ni powder

Nickel powder with particle sizes of approximately 2  $\mu$ m were used here. H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O was reduced with formic acid without any complexing agents upon heating to 80 °C for 5h while stirring. No complexing agent was used here. In a typical synthesis, 0.5 g Ni powder was dissolved in 50 mL 0.5 mol/L formic acid containing 0.0265 g H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O. The sample was heated for 5 h at 80 °C and subsequently isolated by centrifugation. The TEM images in Figure 9.1 show that small agglomerates at the edges of the particles. No EDX was performed on

this sample, but we believe that the particles on the surface are Pt nanoparticles (NPs). Features around 10 nm can be observed on the surface.



Figure 9.1. TEM images of Ni particles with NPs on the surface.

Upon the addition of citric acid as complexing agent, smaller nanoparticles were observed on the particle's surface as can be seen from the TEM images in Figure 9.2. Nevertheless, the formed nanoparticles tended to agglomerate.



Figure 9.2. TEM images of Ni particles with NPs on the surface, synthesized from Ni powder, citric acid as complexing agent and FA as reducing agent.

### 9.3.2 Solution based synthesis of Ni NPs

Platinum nanoparticles were deposited on nickel nanoparticles by reducing Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O with NaBH<sub>4</sub> or N<sub>2</sub>H<sub>4</sub>.2H<sub>2</sub>O in the presence of H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O and sodium citrate as complexing agent. In a typical synthesis, 2 g Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O salt and 0.0214 g H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O were dissolved in 250 mL water, stabilized by 4.87 g sodium citrate. Subsequently, the solution was heated to 80 °C and 0.2608 g NaBH<sub>4</sub> dissolved in 20 mL water and 3.3 g NaOH was added while stirring vigorously for 15 min. It can be seen from the TEM images shown in Figure 9.3 that nanoparticles with sizes below 10 nm were well distributed over the surface of larger particles.

In the case of hydrazine as reducing agent, 2 g Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O salt was dissolved in 20 mL EtOH and 10 mL ethyleneglycol (EG). 5.4 mL N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O was dissolved in 20 mL EG with 3.3 g NaOH and added to the Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O solution while stirring vigorously for 1 h at 80 °C. Note that ethanol and EG were added to avoid hydrolysis of Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O to Ni(OH)<sub>2</sub>. It can be seen from the TEM images in Figure 9.4 that hydrazine reduction did not result in small and distinctive nanoparticles on the surface. Also, the particle size appears larger than the maximum value of 10 nm.

When Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O complexated with citric acid was reduced with N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O in aqeous medium, the Ni particles were much larger compared to the previous case where the Ni salt was dissolved in a mixture of ethanol and EG. In addition, the NPs formed agglomerates on the surface which were larger than 10 nm.



Figure 9.3. TEM images of Pt NPs on surface of Ni particles. Simultaneous reduction of  $Ni(NO_3)_2$  and  $H_2PtCl_{6.}6H_2O$  in water in the precense of sodium citrate as complexing agent and  $NaBH_4$  dissolved in NaOH as reducing agent.



Figure 9.4. TEM images of Pt NPs on surface of Ni particles. Simultaneous reduction of Ni(NO<sub>3</sub>)<sub>2</sub> and H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in EG without any complexing agent and N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O as reducing agent.



Figure 9.5. TEM images of Pt NPs on surface of Ni particles. Simultaneous reduction of Ni(NO<sub>3</sub>)<sub>2</sub> and H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O in water with citric acid as complexing agent and N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O as reducing agent.

If we compare the crystallinity of the obtained Ni particles, reduced with either NaBH<sub>4</sub> or  $N_2H_4$ . $H_2O$ , then it can be seen from Figure 9.6 that the sample reduced with NaBH<sub>4</sub> remained amorphous, whereas crystalline Ni was obtained when the reduction was performed with hydrazine hydrate under basic conditions. Due to the broad reflection of the amorphous, no

information could be retreived from the crystallinity of Pt. In case of the reduction with hydrazine, a small reflection from the Pt nanoparticles can be seen, without any noticable peak shift of the Ni (111) reflection. Although Pt alloys with Ni at high temperatures, we did not expect alloying at room temperature.



Figure 9.6. XRD patterns of Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O reduced with N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O and NaBH<sub>4</sub> in the presence of 2m% Pt.

Well distributed NPs below 10 nm were formed when the Ni salt and  $H_2PtCl_6.6H_2O$  were reduced simultaneously with NaBH<sub>4</sub> and citric acid as complexing agent (Figure 9.3). However, no crystalline material was formed when NaBH<sub>4</sub> was used. Therefore, a second treatment was required to improve the crystallinity. It was shown in Figure 9.6 that hydrazine as reducing agent resulted in crystalline Ni and Pt without alloying. Consequently, the sample obtained in Figure 9.3 was treated with a basic solution of hydrazine in EG and heated for 1 h at 80 °C to improve the crystallinity. It can seen from the TEM images in Figure 9.7 that the particles which were initially deposited on the surface of the Ni particles dissapeared. Instead, it can be seen that small particles with a different contrast are present inside the material. EDX measurements of the sample confirmed the presence of Pt throughout the sample.



Figure 9.7. TEM image of  $Ni(NO_3)_2.6H_2O$  and  $H_2PtCI_6.6H_2O$  reduced with  $NaBH_4$  under basic conditions followed by a treatment with hydrazine to convert the amorphous nickel to crystalline nickel.

Samples for transport measurements were prepared by sintering the powder using SPS. It can be seen in Figure 9.8 that no alloying of the Ni and Pt occurred when sintered under 50 MPa of uniaxial pressure at a temperature of 200°C held for 5 minutes in a graphite die. Namely, no peak shift occurs between the Ni sample and Ni-Pt nanocomposite before and after sintering. In addition, crystalline Pt was observed around a  $2\theta$  value of 41°.



Figure 9.8. XRD patterns of Ni <sub>REF</sub>, Ni <sub>REF</sub> SPS 250 °C do not show a reflection of Pt around 41 °, while Pt does not alloy with Ni when sintered at 200 °C.

A TEM image of the sintered sample at 200 °C was reported by Boona *et al.* and confirms via EDX mapping that most Pt nanoparticles were homogenously distributed around the Ni particles.



Figure 9.9. High-angle annular dark-field (HAADF) image of NiNP-PtNP overlaid with false-colour elemental mapping of Pt (red), Ni (green) and O (blue) determined by X-ray energy-dispersive spectroscopy (XEDS) in a scanning transmission electron microscope (STEM). Figure reprinted from Ref. 1.

# 9.4 Conclusions

In order to exploit the advantages of SSE in composite materials, ultra-small Pt nanoparticles were required with a large interaction area with Ni. The smallest Ni particles were synthesized when a mixture of EtOH and EG were used as solvent and hydrazine as reducing agent. However, under the same conditions, large Pt NP agglomerates were formed. Small Pt NPs were only formed with NaBH<sub>4</sub> as reducing agent and citric acid as complexing agent. However, the reduction of Ni salt and the Pt precursor under these conditions resulted in amorphous samples. Crystalline Ni with Pt nanoparticles were only obtained when treated with hydrazine hydrate. Further enhancement of the observed results may be obtained if mesoporous Ni
would be used with Pt deposited on its surface as the SSE is an interface effect, which is the subject of future work.

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# A

# Conclusion remarks and future prospects

Mesoporous silica materials with linear and interconnected pore systems and tuneable pore diameters were synthesized for their use as template material for the nanocasting of thermoelectric materials, which allows us to synthesize nanowire network structures with a controllable diameter and interconnectivity. It was shown that the template's pore diameter could be easily enlarged by ageing them at a higher temperature or using hydrophobic swelling agents. Mesoporous silica with interconnected pores and a high pore volume, such as KIT-6 and FDU-12, were the most promising template materials for the synthesis of electrically conductive nanowire composite materials as they create more percolation paths than templates with linear pores, such as SBA-15. The surface of the silica template could be chemically modified to alter the interactions with the host molecules. Next, the mesoporous silica templates were used to synthesize SrTiO<sub>3</sub> and Bi<sub>1-x</sub>Sb<sub>x</sub> nanocomposites.

The A sol-gel precursor solution of Sr(NO<sub>3</sub>)<sub>2</sub> and Ti(OH)<sub>4</sub> complexated with chelating agents was impregnated in a mesoporous silica template. Since the charge density of both metal ions is very different, using the same complexing agent for both metal species favoured the impregnation of the Ti complex in the silica template. It was found that the use of complexing agents with more carboxylic acid functionalities for the Ti precursor slowed down its impregnation. Depending on the pH, impregnation time and the combination of complexing agents, Ti and Sr were impregnated at a similar rate into the template. However, the pore loading remained low, while the reproducibility to obtain a Ti/Sr 1:1 ratio inside the template was insufficient. A higher pore loading and better control of the impregnation kinetics of a mixed precursor solution could be achieved when the double salt Sr(OXA)<sub>2</sub>Ti.2H<sub>2</sub>O was formed in the template's pore system. Herefore, Sr(NO<sub>3</sub>)<sub>2</sub> was impregnated in the pore channels, treated with oxalic acid to form Sr oxalate and subsequently reacted with TiCl<sub>4</sub> to form the double salt Sr(OXA)<sub>2</sub>Ti.2H<sub>2</sub>O. However, we did not manage to completely avoid leaching of the double salt out of the pores during the synthesis. As a consequence, no SrTiO<sub>3</sub> nanowires were obtained in this way. Nevertheless, the impregnation of a mixed precursor solution of SrCl<sub>2</sub> and TiOCl<sub>2</sub> in diluted HCl may avoid the problem of leaching. Subsequently, a heat treated in an ammonia atmosphere at 400 °C may be used to remove all chlorides, followed by a thermal treatment under reducing conditions to form metallic oxygen deficient SrTiO<sub>3</sub>.

A new nanocasting method to impregnate an aqueous bismuth precursor solution into the pore channels of a mesoporous silica template was developed. The procedure consisted of two mechanisms to impregnate the pores and avoid deposition of material outside the template instead of inside. Namely, the two-solvent method and incipient method. Firstly, when the silica template was dispersed in a non-polar solvent, such as octane, and an aqueous precursor was added, due to their immiscibility, the precursor migrated into the pore channels. Secondly, by adding less precursor solution than the pore volume of the template, it was assumed that all precursor went inside the pores instead of being deposited on the template's exterior surface. Consequently, to fill the pores with metal salt instead of the precursor solution, the non-polar solvent was refluxed during the impregnation while the water was removed from the system using a Dean Stark separator. The method enabled us to synthesize mesoporous metal oxides and metalloids, such as TiO<sub>2</sub>, Bi<sub>1-x</sub>Sb<sub>x</sub>, Ni, TiS<sub>2</sub>, etc.

An unusually high pore loading of a Bi salt precursor enabled us to make bismuth nanowire composite materials. The samples were reduced at 230 °C in a flow of formic acid or hydrazine hydrate vapour and subsequently sintered using a SPS device. Evidence of size quantization in the bismuth nanowire composites was obtained from measurements of the Hall effect and resistivity of the sintered samples. An activated behaviour was observed, following a law n(T) =  $n_0 e^{-Eg/2kBT}$  valid for intrinsic semiconductors, with Eg the band gap of the semiconductor. A value of Eg = 45 meV corresponded very well to the theoretical value of the band gap opened by size-quantization effects in Bi nanowires of about 20 nm diameter. Furthermore, the charge-carrier concentration measured on the nanowire sample was an order of magnitude smaller than that of bulk Bi, which provides additional confirmation of size quantized nanostructures.

 $Bi_{1-x}Sb_x$  nanowire composites, on the other hand, were synthesized by impregnating a mixed precursor solution of BiCl<sub>3</sub> and SbCl<sub>3</sub>, followed by a reduction at 230 °C and sintering at 245 °C using SPS. We discovered that the short-circuits within the material could be avoided by synthesizing a nanocomposite embedded in a matrix with a resistivity higher than the nanowires, which lead to the enhancement of the Seebeck coefficient compared to bulk  $Bi_{1-x}Sb_x$  alloys due to size quantization.

Although we were able to prove that the Seebeck coefficient could be improved in a nanocomposite material, we believe that the further enhancement of the TE properties could be achieved. Firstly, the reduction time should be shortened to limit leaching. This could be achieved either by using a more reactive reducing agent, such as anhydrous hydrazine rather than hydrazine hydrate. Ideally, a vertical split tube furnace should be used to enhance the contact with the hydrazine vapour or any other reducing agent. Also, the temperature of the hydrazine hydrate bubbler could be increased to increase the reducing agent's vapour pressure, which might speed up the reduction. Secondly, we expect that the electrical resistivity could be further reduced by enhancing the pore loading through the reaction of the impregnated precursor with trimethylbismuth (Eq.1), as demonstrated in this research for trimethylantimony. By impregnating the pores with 50 v%  $Bi_{0.88}Sb_{0.12}$  and adding 10 v% Bi<sub>0.76</sub>Sb<sub>0.24</sub> matrix, for instance, a treatment of the composite powder with Me<sub>3</sub>Bi, would cause a complete filling of the pores with Bi<sub>0.94</sub>Sb<sub>0.06</sub> while the matrix would have a composition of Bi<sub>0.88</sub>Sb<sub>0.12</sub>. Since no voids would be present anymore and only a short reduction procedure would be required, it is expected that the resistivity would drop, while the amount of nanowires contributing to the TE efficiency enhancement would increase. Also, doping of the nanowires should be considered to control the carrier concentration. Since the latter is very dependent on the wire diameter and the temperature, the carrier density should be adjusted to 10<sup>18</sup> cm<sup>-1</sup>, which should lead to the highest thermopower of the nanowires. Namely, it is important that the resistivity of the nanowires remains lower than the matrix at all temperatures. Only under those circumstances short-circuits through the bulk matrix would be avoided.

$$BiCl_3 + 3MeMgBr \rightarrow BiMe_3 + 3MgBrCl$$
 Eq. 1

Thirdly, something which was not studied in this work was the morphology of the template. Namely, it is desirable to use spherical particles as they pack better than elongated or irregular particles, which is the case for respectively SBA-15 and KIT-6 mesoporous silica. This may also affect the electrical conductivity of the composite. It has been reported that the morphology of mesoporous silica materials can be tuned by the use ethanol as co-solvent and CTAB as co-surfactant or by changing the stirring conditions. [3-6] Moreover, any effort to enhance the pore volume and pore diameter of the template would also benefit the electrical conductivity. Specifically, localization of the charge carriers in  $Bi_{1-x}Sb_x$  nanowires must be avoided. Therefore, mesoporous silica with large pores (10-30 nm) is recommended. While FDU-12 is most suitable to synthesize a template material with large pores, its pore volume is generally lower than for KIT-6. Typically, a maximum porosity of 70 % can be obtained with FDU-12, whereas KIT-6 with a porosity up to 82 % and an average pore diameter of 13 nm was prepared. According to the classic effective medium theory for a binary thermoelectric system, the figure of merit of a composite cannot exceed the zT of any of its constituents. [7] In the most basic approximation, the volume fraction and their individual zT value will affect the macroscopic zT of the composite. It can be understood from this simplified situation that the occurrence of non-thermoelectric material in a composite will only reduce the overall performances. In the case studied here, the silica causes parasitic heat losses through the structure while it does not contribute to the thermoelectric effect. For this reason it is desirable to use mesoporous silica with the highest possible porosity.

In case KIT-6 with a pore volume of 1.8 mL/g or a porosity of 82 % is used as template material and the maximum pore loading of Bi of 60 v% is achieved, it was calculated that the composite consisted of 41 v% nanowires. This the highest amount that can be achieved for a fixed amount of 17 v% matrix in the composite. Only in case the pores would be completely filled by means of the gas phase impregnation of Me<sub>3</sub>Bi, a value as high as 69 v% may be achieved.

The thermopower enhancement through the spin Seebeck effect was demonstrated for the first time in a bulk nanocomposite sample of Ni-Pt. It is expected that the effect of nanostructuring could be further exploited by making smaller nanoparticles and higher surface areas of the magnetic material, for example depositing Pt nanoparticles onto mesoporous Ni to enhance the interaction area. Alternatively, individual nanowires of Ni and Pt could be mixed and compressed yielding a composite with a very high interaction surface.

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# B

# Nederlandstalige samenvatting

Thermo-elektrische (TE) materialen zijn in staat om warmte direct om te zetten in elektriciteit en kunnen ook gebruikt worden voor koelingstoepassingen wanneer een elektrische stroom door het materiaal vloeit. De omzetting van warmte naar elektrische stroom gebeurt door middel van een vaste stof proces. Dit houdt in dat deze omzetting doorgaat in het materiaal zelf en dat hiervoor geen mechanische onderdelen noodzakelijk zijn. Hierdoor zijn thermoelektrische materialen heel betrouwbaar en hebben ze een lange levensduur. Deze materialen zijn reeds een lange tijd gekend, maar door de relatief lage efficiëntie zijn de toepassingen beperkt tot niche toepassingen, zoals in de ruimtevaart en kleinschalige toepassingen, zoals koeling/verwarming in autozetels, koeling van elektronische apperatuur en mobiele koelsystemen.

De thermo-elektrische efficiëntie wordt uitgedrukt als zT en hangt af van de materiaaleigenschappen, deze zijn de thermische geleidbaarheid  $\kappa$  (W/mK), de elektrische geleidbaarheid  $\sigma$  ( $\Omega^{-1}m^{-1}$ ), de temperatuur T (K) en de Seebeck coëfficiënt S of  $\alpha$  ( $\mu$ V/K). De efficiëntie wordt bepaald als:

$$zT = \frac{\sigma \alpha^2 T}{\kappa}$$
 1

Aangezien deze materiaaleigenschappen onderling van elkaar afhangen, is het moeilijk om de efficiëntie te verhogen. Bijvoorbeeld, als de elektrische geleidbaarheid  $\sigma$  verhoogd wordt door dopering, dan daalt de Seebeck coëffiënt. Tegelijkertijd verhoogt de thermische geleidbaarheid door een hogere concentratie van de ladingdragers. In klassieke thermoelektrische materialen wordt gezocht naar de optimale ladingdrager concentratie, waarbij de "power factor" of het product van de elektrische geleidbaarheid en de Seebeck coefficiënt ( $\sigma \alpha^2$ ) een maximum bereikt. Tegelijkertijd wordt gezocht naar materialen met een lage thermische geleidbaarheid, zoals door het vormen van legeringen, composiet materialen of materialen met een complexe kristalstructuur.

In 1993 voorspelden Hicks en Dresselhaus door middel van hun theorie dat nanogestructureerde TE materialen betere eigenschappen kunnen bezitten dan hun bulk variant [1, 2], wat leidde tot de ontdekking van verschillende dunne laag nanogestructureerde materialen met betere TE eigenschappen in vergelijking met het bulk materiaal [3-6]. De dunne laag TE materialen zijn echter moeilijk te gebruiken voor toepassingen. Daarom werd

in dit onderzoek gezocht naar nieuwe synthesemethodes en materialen voor bulk nanogestructureerde composieten. Bijgevolg was het onze doelstelling om bulk materialen te synthetiseren die bestaan uit een netwerk van nanodraden. Op deze manier probeerden we de betere TE eigenschappen die bekomen werden in nanostructuren, te verkrijgen in een bulk materiaal. Uit literatuuronderzoek bleken strontium titanaat en bismut uitzonderlijke eigenschappen te bezitten in de vorm van dunne lagen en nanodraden. Daarom was het doel van dit onderzoek om de thermo-elektrische efficiëntie van bismut antimoon legeringen ( $Bi_{1-x}Sb_x$ ) en strontium titanaat ( $SrTiO_3$ ) te verbeteren door middel van nieuwe nanostructureringstechnieken. Hiervoor werd gebruik gemaakt van de poriën van mesoporeuze silica templaten om nanodraden te synthetiseren. Door deze structuren te sinteren kan een bulk nanogestructureerd materiaal bekomen worden, zoals schematisch afgebeeld in Figuur 1.



Figuur 1. Schematische voorstelling van de synthese van bismut nanostructuren in een geordend mesoporeus silica templaat. Door het sinteren van het nanocomposiet poeder wordt een bulk nanogestructureerd materiaal bekomen.

De gebruikte mesoporeuze silica templaten worden gekenmerkt door een poriediameter van 2 tot 50 nm en kunnen gesynthetiseerd worden met verschillende poriestructuren. Voor onze toepassingen verkozen we een 3D-netwerk van vertakte poriën en een groot porievolume. Door het controleren van de syntheseparameters, zoals reactietemperatuur, reactietijd en het toevoegen van poriezwellers en co-solventen konden silica templaten met zowel lineaire cilindrische poriën met diameters van 6 tot 8 nm, als 3D vertakte poriën met diameters van ongeveer 7 tot 30 nm gesynthetiseerd worden. Typisch werden templaten gebruikt met een porievolume van ongeveer 1 mL/g, wat overeen komt met een porositeit van 70 v%.

Strontium titanaat (SrTiO<sub>3</sub>) is een interessant keramisch thermo-elektrisch materiaal voor energierecuperatietoepassingen bij hoge temperatuur. Uit literatuuronderzoek bleek dat de Seebeck coëficiënt aanzienlijk verhoogde wanneer nanometer dunne lagen van het materiaal werden geanalyseerd. Verschillende methodes werden getest voor de synthese van nanogestructureerd SrTiO<sub>3</sub>. In eerste instantie werd een precursor oplossing van het metaalzout strontium nitraat (Sr(NO<sub>3</sub>)<sub>2</sub>) en de titania precursor titanium isopropoxide Ti(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub> gecomplexeerd met chelaten, en vervolgens geïmpregneerd in het silica templaat. De invloed van het type chelaat, de pH en de impregnatieduur werden hierbij nagegaan. Hoewel de impregnatiekinetiek van het strontium- en het titanaatcomplex gecontroleerd kon worden, bleek de belading van SrTiO<sub>3</sub> in de poriën te laag om elektrisch geleidende nanodraden te bekomen. Vervolgens werd een alternatieve methode ontwikkeld om een hogere belading van SrTiO<sub>3</sub> in het templaat te kunnen bekomen. Hiervoor werd het dubbelzout strontium titanyl oxalaat of SrTiO(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>.2H<sub>2</sub>O in de poriën gevormd. Op deze manier kon strontium titanaat bereid worden zonder onzuiverheden en werd een correcte stoichiometrie bekomen na een thermische behandeling. De impregnatie gebeurde in drie fasen. Eerst werd strontiumchloride (SrCl<sub>2</sub>) geïmpregneerd, gevolgd door een behandeling met oxaalzuur, met de vorming van strontiumoxalaat SrC<sub>2</sub>O<sub>4</sub>. Uiteindelijk reageerde een oplossing van titaan oxalaat Ti(OXA)<sub>4</sub> met het geïmpregneerde materiaal met de vorming van strontium titanyl oxalaat Sr(OXA)<sub>2</sub>Ti.2H<sub>2</sub>O. Gedurende deze laatste fase werd echter een groot deel van het geïmpregneerde materiaal uitgeloogd, waardoor enkel bulk strontium titanaat bekomen werd. Hierdoor was het niet mogelijk om een nanogestructureerd composiet materiaal bestaande uit strontium titanaat nanodraden te maken.

Het tweede materiaal die we bestudeerden was bismut. Het bezit de unieke eigenschap dat het overgaat van een halfmetaal naar een halfgeleider wanneer nanodraden gemaakt worden met een diameter minder dan 40 nm. Hierdoor vergroot de verboden zone en verhoogt de Seebeck coëfficiënt van het materiaal. Tevens verbeteren de thermo-elektrische eigenschappen wanneer bismut gelegeerd wordt met antimoon. Heremans et al. publiceerde de eerste metingen op bismut nanodraden [7, 8], maar voor het eerst werden  $Bi_{1-x}Sb_x$ nanodraden opgemeten in dit onderzoek. Voor de synthese van bismut antimoon nanodraden werd een nieuwe impregnatie methode ontwikkeld voor het vullen van de poriën. Het mesoporeuze silica templaat werd gedispergeerd in een waterafstotend solvent zoals noctaan in een teflon kolf. De bismut antimoon precursor oplossing werd bereid door bismutoxide (Bi<sub>2</sub>O<sub>3</sub>) en antimoonoxide (Sb<sub>2</sub>O<sub>3</sub>) op te lossen in verdund chloorzuur en methanol. Vervolgens werd de oplossing toegedruppeld aan het systeem gedurende refluxen. Daarna impregneerde de waterige bismut precursor oplossing in de poriën van het templaat terwijl het water verdampte. Door middel van een Dean Stark opstelling werd het water verwijderd uit het systeem. Uiteindelijk werd bismut precursor afgezet in de poriën. Na impregnatie werd het poeder gefilterd en vervolgens gereduceerd tot bismutmetaal bij een temperatuur tussen 220 °C en 250 °C, gebruik makend van hydrazinedamp of mierenzuurdamp.





Figuur 2. (Links) Transmissie elektron microscoop afbeelding van geïmpregneerd silica templaat. Merk op dat bismut deeltjes aanwezig zijn rond het templaat. Er wordt vermoed dat de stroom door het "bulk" bismut rond het templaat gaat in plaats van door de nanodraden. Hier is het bulkmateriaal afgebeeld in het groen. Doordat het bulkmateriaal de nanodraden kortsluit, worden de verbeterde thermo-elektrische eigenschappen teniet gedaan. (Rechts) Schematische weergave van nanogestructureerd composiet materiaal waarbij de matrix (dikke zwarte lijnen) een hogere resistiviteit bezitten dan de nanodraden (dunne zwarte lijnen). Het elektrisch pad door de nanodraden is weergegeven in het groen terwijl het elektrisch pad met een hogere resistiviteit door de matrix is weergegeven met rode lijnen.

Na de impregnatie en reductie van de bismut precursor werd het bekomen nanocomposiet poeder gesinterd, gebruik makend van spark plasma sinteren of SPS. Via deze sinter techniek werd het materiaal opgewarmd tussen 180 °C en 250 °C door een alternerende stroom te sturen door het monster, terwijl een druk van 50 Mpa werd aangebracht. De verkregen schijfjes werden vervolgens verzaagd tot balkjes van 2 x 2 x 7 mm waarop

thermo-elektrische metingen werden uitgevoerd. Afhankelijk van de compositie van het composiet materiaal werd al dan niet een verhoging van de Seebeck coeffiicient waargenomen.

In het geval van een homogene composite, zoals in Figuur 2, werd geen verhoging van de Seebeck coëfficiënt bekomen. De hypothese dat de stroom preferentieel door bulk materiaal rond het templaat gaat in plaats van door de nanodraden, werd nagegaan door een composiet materiaal te maken met verschillende Bi<sub>1-x</sub>Sb<sub>x</sub> composities. Hiervoor werden de poriën van het silica templaat geïmpregneerd met Bi<sub>0.94</sub>Sb<sub>0.06</sub>, wat een lage resistiviteit heeft, terwijl Bi<sub>0.88</sub>Sb<sub>0.12</sub> met een hogere resistiviteit werd gebruikt als matrix. Doordat Bi<sub>0.94</sub>Sb<sub>0.06</sub> een lagere resistiviteit heeft dan Bi<sub>0.88</sub>Sb<sub>0.12</sub> kan ervan uitgegaan worden dat de stroom prefererentieel getransporteerd wordt door het materiaal met de laagste resistiviteit, wat in dit geval de nanodraden zijn. Op deze manier wordt het nefaste effect van eventueel extern materiaal buiten de poriën gelimiteerd.

Aan de hand van resistiviteitsmetingen was het waarneembaar dat kwantisatie-effecten optraden in het monster. Dit betekent dat het uitgevoerde nano structurerings prinicipe het transport van de ladingdragers beïnvloedde. Uit de transportmetingen van nanocomposiet bismut monsters bleek verder dat de Seebeck coëfficiënt verhoogd was, wat eveneens het concept bewijst. In het temperatuursgebied vanaf 250 K was de opgemeten Seebeck coëfficiënt hoger dan eender welke compositie van Bi<sub>1-x</sub>Sb<sub>x</sub> legeringen. Verdere optimalisatie van de carrier concentratie is echter vereist om ook een hogere Seebeck coëfficiënt te bekomen bij lagere temperaturen.

Naast de synthese en karakterisatie van thermo-elektrische materialen werd de ontwikkelde "nanocasting" synthese ook toegepast voor het maken van poreuze materialen voor elektrokatalyse en batterijtoepassingen, zoals mesoporeus Ni met Pt nanodeeltjes op het oppervlak en TiS<sub>2</sub>.

Dit onderzoek heeft mogelijk gemaakt dat mesoporeuze metalen, metaaloxides en metalloïden op een efficiënte manier kunnen bereiden worden. Dit kan leiden tot de synthese van nieuwe materialen op het gebied van katalyse en in het bijzonder voor de verbetering van de efficiëntie van thermo-elektrische materialen.

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# С

# Scientific disseminations

### Patent

• **Pending patent application (filing date: 14-01-2017)** EP16151288.4. European Patent Office.

### **Book chapter**

Low temperature thermoelectric materials, Bi-Sb
 <u>Vandaele, K</u>., Heremans, J. (Bookchapter, Chapter 2.1). Advanced Thermoelectrics:
 Materials, Contacts, Devices, and Systems to be published by CRC Press / Taylor &
 Francis.

## A1 publications related to the PhD thesis

- Observation of Spin Seebeck contribution to the transverse thermopower in Ni-Pt and MnBi-Au bulk nanocomposites
   S. R. Boona, <u>K. Vandaele</u>, I. N. Boona, D. W. McComb, and J. P. Heremans, 2016, Nature Communications, (Published). DOI:10.1038/ncomms13714
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- Continuous-feed nanocasting process for the synthesis of Bi nanowire composites

<u>Vandaele, K.</u>, Heremans, J.P., Van Driessche, I., Van Der Voort, P., and De Buysser, K. (Resubmitted to Chemical Communications, 2017)

- Thermoelectric properties of bulk and nanostructured Bi<sub>1-x</sub>Sb<sub>x</sub> <u>Vandaele, K</u>., He, B., Van Der Voort, P., De Buysser, K., and Heremans, J. (Phys. Rev. Applied, in preparation)
- Electrocatalysis of mesoporous Ni-Pt <u>Vandaele, K.</u>, Co, A. Van Der Voort, P., and De Buysser, K. (In progress)

## A1 publications not related to the PhD thesis

## Thermal spin transport and energy conversion

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# C3 Conference

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Novel synthesis of bismuth and bismuth antimony nanowire composites for thermoelectric energy conversion

K. Vandaele, M. J. Adams, B.He, J. Heremans, P. Van Der Voort and K. De Buysser

International & European Conference on Thermoelectrics - Dresden, Germany – 2015

Synthesis and incorporation of  $ZrO_2$  nanoparticles in  $Bi_2Te_3$ Verdonck, T., <u>Vandaele, K.</u>, Van der Voort, P., De Buysser K.

- DZA meeting Ghent, Belgium 2014
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• ChemCYS – Blankenberghe, Ghent, Belgium – 2012 Template materials for functional mesoporous ceramics <u>K. Vandaele</u>, I. Van Driessche and K. De Buysser

# **Journal Name**

# COMMUNICATION



# Continuous-feed nanocasting process for the synthesis of bismuth nanowire composites

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We present a novel, continuous-feed nanocasting procedure for the synthesis of bismuth nanowire structures embedded in the pores of a mesoporous silica template. The immobilization of a bismuth salt inside the silica template from a diluted metal salt solution yields a sufficiently high loading to obtain electrically conducting bulk nanowire composite samples after reduction and sintering the nanocomposite powders. Electrical resistivity measurements of sintered bismuth nanowires embedded in the silica template reveal size-quantization effects.

Thermoelectrics could play an important role in waste heat recovery and solid-state cooling as they possess the ability to convert heat directly to electricity and vice versa.<sup>1,2</sup> The advantages of thermoelectrics include quiet operation, no mechanical moving parts, and a long lifetime. However, the limiting factor preventing the large-scale production of thermoelectrics for both power production and solid-state cooling is their low efficiency. A material's efficiency is described by the figure of merit, denoted *zT*, and is defined as:  $zT = S^2 T / \rho \kappa$ , with *S* the Seebeck coefficient,  $\rho$  the electrical resistivity, and  $\kappa$  the thermal conductivity.

Pioneering work by Hicks and Dresselhaus<sup>3</sup> theoretically predicted that nanostructured thermoelectrics, could have an enhanced zT value compared to their bulk counterparts<sup>3,4</sup>. Such increase of zT was predicted in cylindrical Bi nanowires by Lin et al.<sup>5</sup> The synthesis of Bi nanowires by pressure injection<sup>6</sup> of a melt in porous, anodized alumina was reported Zhang et al., while Heremans et al. reported the synthesis of Bi nanowires by the impregnation of Bi vapour in an alumina template<sup>7</sup>. Attempts at making Bi nanowire thermoelectrics<sup>7</sup> have resulted in large thermopowers, but comparatively small zTs. One issue has been that no Bi<sub>1-x</sub>Sb<sub>x</sub> nanowires could be prepared by conventional methods due the large difference in melting point and vapour pressure between Bi and Sb, whereas theory<sup>8</sup> predicted superior performance in these alloy wires. In addition, the high thermal

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conductivity of an alumina matrix causes parasitic thermal losses, deteriorating the zT.

A suitable chemical route to synthesize non-siliceous nanostructured and mesoporous materials is by means of a hard template replication method, known as nanocasting.<sup>9,10</sup> Typically, the pores of mesoporous silica are used as a nano-mold or template. Since mesoporous silica materials possess pores with dimensions ranging from approximately 2 to 50 nm, they are perfect as a template material to synthesize Bi nanowire composites with diameters well below the threshold of 50 nm to observe a semimetal-to-semiconductor transition.<sup>5</sup>

A crucial step in the nanocasting replication process is the impregnation of the precursor material inside the template's pores and the conversion of that precursor to the target material. Typically, a metal salt dissolved in ethanol or water is loaded inside the mesoporous template through conventional solvent



Figure 1. Schematic of the continuous-feed impregnation procedure in refluxing noctane (bp. 125°C). (1) The aqueous precursor solution is added to the silica/n-octane dispersion using an addition funnel or syringe pump. (2) The polar precursor solution and n-octane from a two-phase system. Meanwhile, the precursor infiltrates the silica template through capillary impregnation. (3) As the impregnation is performed in refluxing n-octane, the water boils off and the diluted precursor solution inside the pores becomes more concentrated until all water is removed and only the precursor salt remains. Partial decomposition of the precursor salt may occur. (4) The aqueous solution is collected by means of a Dean-Stark separator.

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impregnation,<sup>11</sup> dry impregnation or incipient wetness,<sup>12</sup> double solvent,<sup>13,14</sup> or evaporation-induced impregnation method, and subsequently subjected to a thermal treatment.<sup>9,10,15,16,17</sup> The replicated mesoporous material is obtained after template removal through chemical etching with NaOH or HF. However, problems associated with the current impregnation methods of mesoporous templates include the low filling degree, inhomogeneous filling of the pores, or the deposition of precursor material on the external surface of the porous template. In many cases, multiple loading steps are required to obtain an acceptable degree of loading.<sup>11,18,19</sup> Ordered, mesoporous silica templates were used by Xu et al. for the synthesis of Bi nanowires by the decomposition of triphenylbismuth in supercritical toluene.<sup>20</sup> However, only small quantities of material were obtained.

In the present work, a scalable, continuous-feed impregnation process based on the two-solvent impregnation method<sup>21</sup> was used. This process was developed to fill the pores of a mesoporous silica template with bismuth metal salt by impregnating the template with a diluted acidic precursor solution. A low-temperature reduction treatment (220 to 230 °C) allowed the conversion of the impregnated bismuth salt to metallic bismuth nanowires confined in the template's pores. Powder processing techniques allowed the synthesis of bulk-sized samples composed of Bi nanowires, referred to as bulk nanowire composites. Electrical resistivity measurements were performed to identify size quantization effects in the bulk nanowire composite.

The two-solvent impregnation method<sup>21</sup> (Figure ESI 3) consists of the addition of precursor solution in an amount equal to the pore volume of the template in a dispersion of the template in hexane. In the process described here, the precursor solution is added continuously to a dispersion of the mesoporous silica template in refluxing toluene or n-octane. By means of a Dean-Stark separator, the aqueous phase is eliminated from the system, leading to the immobilization of the metal precursor salt inside the template's pores. All chemicals are listed in the electronic supplementary information (ESI section 1).

In a typical synthesis, 1 g SBA-15 or KIT-6 mesoporous silica (ESI section 3) with a pore volume of  $1 \text{ cm}^3/\text{g}$  was dispersed in 100 mL noctane in a 250 mL fluoropolymer (PFA) round bottom flask (ESI section 4). The amount of metal salt required to fill the template's pores was derived based on the template's pore volume and the density of the precursor salt. For the impregnation of BiCl<sub>3</sub>, the precursor solution was prepared by dissolving 3.5 g Bi<sub>2</sub>O<sub>3</sub> in 12 mL 36 w% HCl and 24 mL H<sub>2</sub>O. The precursor solution was added to the dispersion of silica in n-octane at a rate of 4 mL/h using a syringe pump, while the non-polar solvent was refluxing (Figure ESI 4). All studied samples are listed in Table ESI 1. The impregnated silica powder was collected through filtration and subsequently reduced in a sealable flow furnace at 230 °C for 12 h in a N<sub>2</sub> - 5% H<sub>2</sub> gas flow mixed with hydrazine vapour. The hydrazine vapour was carried through the furnace by bubbling the  $N_2$  - 5%  $H_2$  gas through a hydrazine monohydrate solution (Figure ESI 7). The Bi - SiO<sub>2</sub> nanowire composite powder was removed from the flow furnace inside an argon glovebox, and approximately 2 g sample was transferred to a 10 mm  $\emptyset$  graphite die, which was sealed with rubber glue to avoid oxidation when transferred to the spark plasma sintering (SPS) device. The nanowire composite powder was sintered at 230 °C for 20 min in a vacuum under a uniaxial pressure of 50 MPa. The sample preparations for four-probe electrical transport measurements and mounting inside the cryostat were performed in an argon glovebox. Typical sample dimensions for electrical transport measurements were 1.5 x 1 x 7 mm. For N<sub>2</sub> sorption analysis, the silica template of the reduced  $Bi - SiO_2$  powder was dissolved in a 1 mol/L NaOH solution for 3 h. The mesoporous Bi powder was isolated by centrifugation and washed four times with water.



Figure 2. (a) TEM image of SBA-15 filled with 12 v% Bi, prepared by the impregnation of Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O dissolved in 5 mol/L HNO<sub>3</sub>, with toluene as non-polar solvent and reduced at 220 °C in a hydrazine loaded Ar-5% H<sub>2</sub> gas flow for 12 h. (b) Bi nanowires after chemical etching of the silica template of the sample in 1 mol/L NaOH solution for 3 h. (c) TEM image of SBA-15 filled with 30 v% Bi, prepared by the impregnation of BiCl<sub>3</sub> dissolved in a 4 mol/L HCl – 80 v% MeOH solution, with n-octane as non-polar solvent and reduced at 220 °C in a hydrazine loaded Ar-5% H<sub>2</sub> gas flow for 12 h. (d) Bi nanowires after chemical etching of sample c. Note that Bi nanowires oxidize spontaneous in air, therefore the analysed samples referred to as Bi are oxidized.

The X-ray powder diffraction (XRPD) patterns in Figure ESI 10 show that the bismuth precursor salt reduced to bismuth at 230 °C for 12 h in the presence of hydrazine vapour. When measured under argon atmosphere, no secondary phases were observed. However, upon removing the tape, which sealed the sample from air, the XRPD pattern indicates the presence of  $Bi_2O_{2.5}$ , which formed within seconds. KIT-6 mesoporous silica, with a 3D interconnected mesopore system, was used as template for the preparation of mesoporous bismuth powder for N<sub>2</sub> physisorption measurements and for electric transport measurements. Mesoporous bismuth, was obtained after chemical etching of the KIT-6 silica template. A BET surface area of 20 m<sup>2</sup>/g and 13 m<sup>2</sup>/g was obtained when Bi(NO<sub>3</sub>)<sub>3</sub> and BiCl<sub>3</sub>, respectively, were used as precursor salts (Figure ESI 11). The pore volumes were 0.14 and 0.06 cm<sup>3</sup>/g, respectively.

SBA-15 mesoporous silica, which possesses hexagonally packed, cylindrical mesopores, was used as template for the TEM analysis shown in Figure 2. The TEM images depict oxidized bismuth nanowires (due to sample preparation for TEM) with a diameter between 5 and 10 nm confined in the template's pores (a and c) and the replicated nanowires after etching the template (b and d). The appearance of the nanowires depends on the precursor salt used. Namely, for  $Bi(NO_3)_3$ , rough nanowires were obtained, whereas smooth wires were obtained for  $BiCl_3$ . The latter also forms a melt at approximately 228 °C according to DTA shown in

Figure ESI 6. The theoretical volume fractions of Bi confined in the pores are 12 v% and 30 v% for Bi(NO<sub>3</sub>)<sub>3</sub> and BiCl<sub>3</sub>, respectively.

Figure 3 depicts the carrier concentration of a sintered  $Bi - SiO_2$  (KIT-6) nanowire composite sample as function of 1/2kT. By fitting the carrier concentration for an intrinsic semiconductor through the data points, a band gap of 45 meV was calculated. Figure 4 compares the electrical resistivity of bulk Bi with that of Bi nanowire composites normalized by their value at 300 K. The data shows the occurrence of size-quantization effects in the nanowire composite samples, since the electrical resistivity behaviour follows a semiconducting behaviour instead of a metallic one, as in bulk Bi.

The loading of the pores changes significantly depending on the precursor salt used, given the difference in density and molecular weight of Bi(NO<sub>3</sub>)<sub>3</sub> and BiCl<sub>3</sub>. If we consider complete filling of the pores with the precursor salts, 12 v% and 30 v%, Bi can be deposited in the pores after reduction of Bi(NO<sub>3</sub>)<sub>3</sub> and BiCl<sub>3</sub>, respectively. How the loading could be further enhanced is shown in Table ESI 2. KIT-6, a mesoporous silica template with an interconnected pore system, was used for the synthesis of mesoporous Bi. No high-BET surface area was obtained for either sample, which primarily is due to the high density of Bi (9.78 g/cm<sup>3</sup>) and its low melting point (271.5 °C). Bismuth also can leach out of a template's pores during reduction of the bismuth salt. This was mostly observed for BiCl<sub>3</sub>, as it also forms a melt at approximately 228 °C (Figure ESI 6). We believe that the smooth nanowires in Figure 2 were obtained specifically because of the formation that melt. The use of BiCl<sub>3</sub> as precursor was preferred since it can lead to a higher loading of Bi inside the template. This is particularly important for the synthesis of nanocomposites, as a sufficiently high loading of Bi in the template is required to form an electrical percolation path when the Bi - SiO<sub>2</sub> nanowire composite powder were sintered. For the same reason, the use of a silica template with 3D interconnected pore system (KIT-6) is preferred over a template with linear pores (SBA-15). Electric transport measurements were performed on a bulk nanowire composite



Figure 3. Carrier concentration of bulk bismuth and 29 v% Bi – SiO<sub>2</sub> (KIT-6) nanowire composite sample as function of 1/2kT. The lower carrier concentration of the nanocomposite sample compared to bulk Bi can be attributed to size-quantization effects in the nanowires. The carrier concentration for the intrinsic semiconductor was derived by  $n_i=n_0 e^{-ig/2kT}$ . The band gap obtained by the fit through the data points yields:  $E_g = 45$  meV, which corresponds to Bi nanowires with diameter 20 nm according to Lin et al.<sup>5</sup> Note that all sample preparations and measurements were performed under inert atmosphere.



Figure 4. Electrical resistivity of 29 v% Bi –  $SiO_2$  nanowire composite sample and bulk bismuth normalized by their value at 300 K. Where the normalized resistivity of bulk Bi drops, and thus exhibits a metallic character when cooled down to 77 K, the relative resistivity of 29 v% Bi –  $SiO_2$  increases, providing evidence for sizequantization effects in sintered bismuth nanowire composites. The carrier mobility is depicted on the right axis. Note that all sample preparations and measurements were performed under inert atmosphere.

sample using KIT-6 with a pore diameter of approximately 7 nm as silica template. Based on the amount of  $BiCl_3$  precursor salt impregnated in the template, the estimated composition of the composite sample was 33 v% silica, 29 v% Bi nanowires and 38 v% voids.

Evidence of size quantization in the bismuth nanowire composites was obtained from measurements of the Hall effect (Figure 3) and resistivity (Figure 4) of the sintered samples. The inverse of the low-field (< 1 Tesla) Hall slope  $R_H$  was interpreted to give the charge-carrier concentration via  $n = (e R_H)^{-1}$  with e the electron charge.  $R_H$  was positive, so the dominant carriers are holes. Figure 3 shows the temperature dependence of *n* measured on the sample (29 v% Bi - SiO<sub>2</sub>), in an Arrhenius plot. A very clean, activated behavior is observed, following a law  $n(T) = n_0 e^{-Eg/2kBT}$ valid for intrinsic semiconductors, where  $E_g$  is the band gap of the semiconductor. A mixture of very narrow nanowires with bulk-like Bi (which displays a metal-like conductivity) will not generate such a simple temperature-dependence. Furthermore, the charge-carrier concentration measured on the nanowire sample is an order of magnitude smaller than that (also shown in Figure 3) of bulk Bi.<sup>22</sup> Finally, the value of  $E_g$  = 45 meV obtained from the Arrhenius plot in Figure 3 corresponds very well to the theoretical value of the band gap opened by size-quantization effects in Bi nanowires of about 20 nm diameter, providing evidence of size quantization effects in the nanowire composites.

At first sight, the 20 nm diameter measured by electrical measurements appears to contradict the observation that the template's pores were 7 nm, which should correspond to a bandgap exceeding 100 meV. However, it has been observed experimentally<sup>7</sup> that conduction in nanowires of diameter smaller than 9 nm becomes localized. In contrast, no localization is observed in the sample measured here, as is illustrated by the resistivity data in Figure 4. These data show a temperature dependence consistent with the decrease in carrier concentration, very different from bulk Bi (also shown) and conducive to mobilities

(shown using the right-hand ordinate axes) of the order of 500 to 50 cm<sup>2</sup>/V sec. Because there is always a statistical distribution of nanowire diameter, these observations lead to the conclusion that the conduction is dominated by nanowires with diameters near 20 nm with conduction in all the narrower wires simply localized. Indeed, there is a lower limit to the range of validity of the theoretical calculations by Lin et al.<sup>5</sup> set by the condition for Anerson localization<sup>23</sup>: the product  $k_{F} l > 1$ , where  $k_{F}$  is the Fermi wavevector and *l* is the electronic mean-free path, here limited by the wire diameter. For bulk Bi,  $k_F$  is given in Ref. 24 to be very anisotropic with the smallest value 1 x  $10^8$  m<sup>-1</sup>, meaning that nanowires with diameters below 10 nm should not conduct. Because of quantization, the carrier concentration in the present sample is smaller still, leading to a smaller k<sub>F</sub>; therefore, the minimum wire diameter must be larger, e.g. on the order of the observed 20 nm.

In conclusion, a facile nanocasting technique was developed for the synthesis of bismuth nanowire composites. By means of the continuous-feed nanocasting process and a low-temperature reduction treatment of the impregnated bismuth salt, we were able to synthesize bismuth nanowires embedded in the pores of a mesoporous silica powder. The nanocasting method enabled a sufficiently high loading of bismuth inside the pores of a 3D interconnected silica template to form electrically conducting nanowire composite samples. This provides the opportunity to fabricate a bulk material composed of nanowires with potentially enhanced thermoelectric properties. Evidence of size-quantization effects was obtained from electrical resistivity and carrier concentration data, which show the clear signature of semiconducting band conduction with an energy gap of 45 meV and no signs of localization. The results suggest several directions for further research, e.g. aliovalent doping and alloying Bi with Sb, as well as measurements of the thermoelectric properties of the material, in order to enhance the material's zT.

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#### **Electronic Supplementary Information**

Continuous-feed nanocasting process for the synthesis of bismuth nanowire composites

#### 1 Materials

Pluronics P123 (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>, Mw = 5800), 98% reagent grade tetraethylorthosilicate (TEOS), 65w% nitric acid, 36w% hydrochloric acid, 98.5 % xylenes and 99% n-butanol were purchased from Sigma Aldrich. 99.999% bismuth(III) oxide and 98% hydrazine monohydrate were supplied by Alfa Aesar. 99% toluene and 98% methanol were supplied by Fiers, while 97% n-octane was purchased from TCI Europe N.V. All reagents were used as received.

#### 2 Characterization

X-Ray powder Diffraction (XRD) patterns were recorded on a Thermo Scientific ARL X'TRA X-Ray Diffractometer with the Bragg–Brentano theta-2 theta configuration and using Cu Ka radiation. Topas Academic V4.1 software was used for Rietveld refinement<sup>1</sup>. Nitrogen sorption experiments were performed at 77 K with a Micromeritics TriStar 3000 device. Samples were vacuum dried at 120 °C for 12 h prior to analysis. The surface area was calculated using the BET method while the pore-size distribution was determined by analysis of the adsorption branch of the isotherms using the BJH method. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 449-F3 Jupiter device and TEM images were taken with a JEOL JSM-207 7600F device. X-ray fluorescence (XRF) measurements were performed on a Rigaku NEXCG device under helium atmosphere and RX5 target.

#### 3 SBA-15 and KIT-6 mesoporous silica templates

SBA-15 was synthesized by dissolving 4 g P123 in 120 mL 2 mol/L HCl solution and 30 mL distilled water at RT. Next, the solution was heated to 45 °C and 9.1 mL TEOS was added while vigorously stirring for 5 h. Subsequently, the mixture was aged at 90 °C for 18 h under static conditions. Finally, the precipitate was collected via filtration, dried overnight at RT, and calcinated at 550 °C for 6 h in air with a heating rate of 2 °C/min.<sup>2</sup>

KIT-6 was synthesized by dissolving 4 g P123 in 150 mL 0.5 mol/L HCl solution and 4.9 mL butanol at RT. Next the solution was heated to 35 °C and 9.2 mL TEOS was added while vigorous stirring. The mixture was stirred at that temperature for 24 h and subsequently aged at 90 °C for 24 h under static conditions. Finally, the precipitate was collected via filtration, dried overnight at RT and calcinated at 550 °C for 6 h in air with a heating rate of 2 °C/min.<sup>3</sup> Low angle X-ray powder diffraction data (XRPD) of SBA-15 and KIT-6 are shown in Figure ESI 1a, indicating that the synthesized KIT-6 mesoporous silica possesses a cubic, interconnected pore system with the  $Ia\overline{3d}$ -space group symmetry, while SBA-15 shows a *P6mm* hexagonal ordered pore system. Figure ESI 1b and c show respectively the N<sub>2</sub> sorption

isotherms and the BJH pore size distribution plot of both silica templates. The pore diameter according to the BJH model was calculated on the desorption branch of the isotherm. Typically, SBA-15 had pores with a diameter of approximately 7.5 nm. The BET surface area and pore volume were typically between 600 and 1000 m<sup>2</sup>/g and 0.7 to 1 mL/g, respectively. The pore diameter of KIT-6 was generally approximately 7 nm, while the BET surface area ranged from 700 to 900 m<sup>2</sup>/g and the pore volume from 0.8 to 1.2 mL/g. SBA-15 was used as template material for the synthesis of Bi nanowires for TEM analysis, while KIT-6 mesoporous silica was used as template for the preparation of mesoporous Bi for N<sub>2</sub> sorption analysis and for the electric measurements of a Bi – SiO<sub>2</sub> (KIT-6) nanowire composite.



Figure ESI 1. (a) Low angle XRD diffractogram, (b)  $N_2$  sorption isotherms and (c) BJH pore size distribution plot of SBA-15 and KIT-6 mesoporous silica.

#### 4 Continuous-feed nanocasting process

Upon replicating the pore structures of SBA-15 and KIT-6 mesoporous silica, nanowire-like structures and 3D interconnected "nanowire" networks, respectively, were obtained. A schematic representation of the nanocasting process is shown in Figure ESI 2.

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Figure ESI 2. Schematic representation of nanocasting process for (top) SBA-15 and (bottom) KIT-6 mesoporous silica. First, a bismuth precursor solution is impregnated, resulting in the deposition of  $BiCl_3$  salt inside the pores. Second, the  $BiCl_3$ -SiO<sub>2</sub> nanocomposite powder is reduced to  $Bi - SiO_2$ . Finally, the nanocomposite powder is either sintered, forming a bulk nanowire composite sample, or the silica is chemically etched, allowing TEM imaging or analysis of the mesoporosity.

The impregnation procedure developed in this research is based on the double solvent method<sup>4</sup> and incipient wetness technique<sup>5</sup>. The example in Figure ESI 3 explains both methods. In Figure ESI 3a-c, a 0.5 mL titania peroxo solution was added to 50 mL toluene. Due to the immiscibility of both solvents, a two-phase system forms. Upon the addition of 1 g SBA-15 with a pore volume of 1 cm<sup>3</sup>/g, the coloured solution infiltrates the silica template. Since the volume of precursor solution is lower than the total pore volume of the mesoporous silica, all precursor was impregnated inside the template through capillary impregnation. The term "incipient wetness" indicates that the amount of precursor outside the template is prevented. It can be understood from the example that the template's pores are filled with a diluted precursor solution. Consequently, the amount of metal salt deposited inside the pores depends on the metal concentration of the precursor solution.



Figure ESI 3. Visual representation of "double solvents" impregnation method: (a-c) a titanium peroxo complex in diluted hydrochloric acid (dark orange aqueous precursor solution) in toluene while vigorously stirring. (d-g) Titania precursor solution in a dispersion of mesoporous silica in toluene after 0, 2, 5, and 10 min stirring, respectively.

In contrast to the double solvent method, the process presented here makes use of refluxing non-polar solvent with a boiling point higher than water, such as toluene, xylene, or n-octane. The polar precursor solution is added continuously and the total volume added is many times larger than the template's pore volume. By means of a Dean-Stark separator, all water from the metal precursor solution is removed from the system while the metal solution immobilizes inside the template's pores, which enables the complete filling of the template with the metal salt by impregnation of a diluted precursor solution. A PFA round bottom flask was used since its hydrophobic properties prevent the wetting of the internal surface or the reaction vessel. The low addition rate of the aqueous precursor solution to the dispersed silica was chosen to ensure that the amount of precursor solution added was always lower than the total pore volume of the template.

Both mesoporous silica templates, SBA-15 and KIT-6, were impregnated using the same procedure described below. Prior to the impregnation of either of the silica templates, the pore volume was measured by means of N<sub>2</sub> sorption analysis to derive the mount of metal salt the pores can contain. The polar precursor solution is defined as an aqueous solution of the precursor salts BiCl<sub>3</sub> or Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O dissolved in a mixture of precursor solvents, HCl, H<sub>2</sub>O, methanol (MeOH) and/or formic acid. The non-polar solvents toluene, xylene, or n-octane are used in such combination that they are immiscible with the polar precursor solution. The different impregnations performed in this study are listed in Table ESI 1.

Precursor salt	Precursor solvent	Non-polar solvent			Precursor addition speed (mL/h)	Temperature heater (°C)
Bi(NO₃)₃·5H₂O	Water, HNO <sub>3</sub>	toluene, xy octane	/lene, i	n-	4	140-145
BiCl₃	Water, HCl, formic acid (FA), methanol	n-octane			4	160-165

Table ESI 1. List of impregnation conditions.

The impregnation setup depicted in Figure ESI 4 was used for the synthesis of bismuth nanowires and nanocomposite structures. An aluminium heat exchanger was used for efficient heating of the PFA round bottom flask. A syringe pump was used to inject the precursor solution in a controlled manner, whereas the temperature of the heater controlled the evaporation rate of the aqueous solution. Note that the simplicity of the system did not allow us to monitor the rate of water removal by means of the Dean-Stark separator.



Figure ESI 4. Schematic representation of the continuous-feed nanocasting setup for the impregnation of a polar precursor solution into a mesoporous silica template dispersed in a high-boiling, non-polar solvent. The polar precursor solution is added to the PFA reaction flask at a constant rate and migrates into the pores. Meanwhile, the polar precursor solvent is removed selectively from the system by means of the Dean-Stark separator. The precursor salt or its decomposition product is deposited inside the template's pores. The refluxing solvents boil off and condense in the Graham condenser. Due to the higher density and the immiscibility of both solvents, the aqueous phase is selectively collected in the right arm of the Dean Stark, while the non-polar solvent returns to the system.

Since the bismuth precursor salt BiCl<sub>3</sub> hydrolyses in water, an acidified aqueous precursor was prepared. However, we observed from Figure ESI 5 that the metal salt decomposed to BiOCl during the impregnation of a 30 w% HCl and 60 mL methanol, both with and without the addition of 15 mL formic acid in n-octane (bp. 125 °C) as non-polar solvent.



Figure ESI 5. X-ray powder diffraction pattern of SBA-15 mesoporous silica powder impregnated with  $BiCl_3$  dissolved in 15 mL 30 w% HCl and 60 mL methanol, with or without 15 mL formic acid (FA), while octane was used as non-polar solvent. It can be seen that the metal salt decomposed to BiOCl as the solvent was removed during the impregnation process.

Since the molecular weight of the precursor salt is typically higher and the density lower than the desired product, volume constriction of the impregnated precursor during the conversion of, e.g., a metal salt to its oxide or metallic form is inevitable. However, the loading efficiency of a certain material can be enhanced if the difference in molecular weight between the decomposed precursor and the target product is reduced. The decomposition of BiCl<sub>3</sub> to BiOCl during the impregnation is an example how the pore loading can be enhanced. Table ESI 2 shows the theoretical maximum pore loading efficiencies of Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O and BiCl<sub>3</sub> depending on their decomposed precursor when they are converted to their metallic form.

Table ESI 2. Theoretical maximum pore loading efficiencies with metallic bismuth depending on the precursor salt used and its decomposition product during the impregnation.

Precursor salt	Decomposed precursor	Target product	Pore loading efficiency (%)
Bi(NO₃)₃·5H₂O	None (Bi(NO <sub>3</sub> ) <sub>3</sub> .5H <sub>2</sub> O)	Bi	12.5
Bi(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	BiONO <sub>3</sub>	Bi	36.7
BiCl <sub>3</sub>	None (BiCl <sub>3</sub> )	Bi	32.2
BiCl₃	BiOCI	Ві	60.5

To obtain a better understanding of the decomposition process of the precursor salt during the impregnation, TGA measurements were performed. The thermal decomposition of  $Bi(NO_3)_3.5H_2O$  and  $BiCl_3$  in air is shown in Figure ESI 6. It can be calculated from the analysed mass loss that the nitrate salt lost 4.4 hydrate water molecules when heated to 108 °C, the boiling temperature of toluene, while a mass loss equivalent to 6 water molecules was obtained at 125 °C, the boiling temperature of n-octane. The latter suggests that on top of the removal of all water molecules of  $Bi(NO_3)_3.5H_2O$ , the nitrates also

started to decompose. Dry BiCl<sub>3</sub>, on the other hand, started to decompose only above 250 °C, while a melt was formed at approximately 228 °C (endothermic peak in DTA signal). We believe the drastic weight loss of BiCl<sub>3</sub> between approximately 200 and 330 °C was due to sublimation of the salt, which could be suppressed by using humidified air. The decomposition of the precursor salt during impregnation is possible due to the high temperature used during the impregnation, namely, refluxing toluene, n-octane, or xylene. Due to removal of the acidic precursor solvent during the impregnation, the BiCl<sub>3</sub> metal salt hydrolysed to BiOCl, while Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O decomposed through the loss of hydrate waters. The extent of these effects depends on the boiling temperature of the non-polar solvent.



Figure ESI 6. Thermogravimetric analysis of  $Bi(NO_3)_3.5H_2O$  and  $BiCl_3$  in humidified and dry air at 2 °C/min heating rate. The weight loss due to the loss of hydrate waters is clear from the TGA signal of  $Bi(NO_3)_3.5H_2O$ . The TGA signal of  $BiCl_3$  shows a drastic weight loss in dry air, whereas the weight loss was suppressed in humidified air. The endothermic peak on the DTA signal of  $BiCl_3$  shows the formation of a melt at 228 °C.

#### 5 Reduction of BiCl<sub>3</sub> – SiO<sub>2</sub> nano composite powder

A sealable tube flow furnace (Figure ESI 7) was used for the reduction of  $BiCl_3/Bi(NO_3)_3$  – silica composite powder. Approximately 0.5 g of sample was placed in a ceramic crucible and placed in the centre of the furnace. Different reducing agents were tested to reduce  $Bi(NO_3)_3.5H_2O$  and  $BiCl_3$  to metallic bismuth. However, the low melting point of metallic Bi, 271 °C, was a major limitation on the applicability of conventional reducing gas, such as Ar-5% H<sub>2</sub>. The reduction was performed by bubbling an Ar-5 % H<sub>2</sub> gas flow through a solution of 98 % hydrazine monohydrate, transferring hydrazine vapour in the furnace. The reduction was performed between 220 and 265 °C for 10 h.



Figure ESI 7. Sealable horizontal flow furnace for the reduction of  $Bi(NO_3)_3/BiCl_3 - SiO_2$  nanocomposite powder. The glass furnace tube can slide out of the furnace and transferred to the glovebox for further manipulation of the powder.

Bulk Bi<sub>2</sub>O<sub>3</sub> and BiCl<sub>3</sub> powder were used to investigate the influence of different atmospheres on their reduction to metallic Bi. ZnO was used as internal standard to perform Rietveld refinement and calculate the fraction of crystalline vs amorphous Bi, as well as the amount of secondary phases. The heat treatments were conducted in a tubular furnace in a flow of Ar – 5% H<sub>2</sub> gas, either pure or bubbled through a solution of hydrazine monohydrate (N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O). A flow rate of 20 mL/min was used and the samples were reduced for 10 h at 220 °C, 250 °C, and 265 °C. Hydrazine was used here as it is a powerful and clean reducing agent, since all decomposition products are gaseous.<sup>6,7</sup> However, a minimum concentration of 64 % hydrazine solution is required to obtain sufficient reducing power. Namely, the reducing capacity reduces quickly as the solution becomes more diluted. X-ray diffraction (XRD) patterns of BiCl<sub>3</sub> reduced at different temperatures in a flow of Ar - 5% H<sub>2</sub> and in the presence of N<sub>2</sub>H<sub>4</sub> vapour are depicted in Figure ESI 8.



Figure ESI 8. X-ray diffraction patterns of  $BiCl_3$  reduced at different temperatures in Ar - 5% H<sub>2</sub> and in the presence of N<sub>2</sub>H<sub>4</sub> vapour. The diffraction peaks of the internal standard ZnO, which was used to quantify the amount of crystalline Bi and secondary phase BiOCl.

The Rietveld refining data calculated from the recorded X-ray diffraction pattern is reported in Table ESI 3. It is shows that a minimum temperature of 250 °C and a reduction time of 10 h is required to

reduce  $BiCl_3$  in  $N_2H_4$  vapour to metallic Bi. In the absence of hydrazine vapour, very little Bi phase was formed when reduced at 265 °C in Ar-5% H<sub>2</sub>.

Table ESI 3. Rietveld refinement data of BiCl<sub>3</sub> powder reduced at different temperatures and atmospheres for 10 h. The data shows that the presence of  $N_2H_4$  vapour was crucial to reduce BiCl<sub>3</sub> to metallic Bi. A temperature of 250 °C and a reduction time of 10 h in  $N_2H_4$  loaded Ar - 5%  $H_2$  was required to reduce BiCl<sub>3</sub>.

Material	Red. Temp.	Atmosphere	Ві	Bi <sub>2</sub> O <sub>3</sub>	BiOCI	Amorphous
BiCl <sub>3</sub>	220 °C	5 % H <sub>2</sub> + N <sub>2</sub> H <sub>4</sub>	32 %	0 %	17 %	51 %
BiCl <sub>3</sub>	250 °C	5 % H <sub>2</sub> + N <sub>2</sub> H <sub>4</sub>	34 %	0 %	0 %	66 %
BiCl <sub>3</sub>	265 °C	5 % H <sub>2</sub> + N <sub>2</sub> H <sub>4</sub>	26 %	0 %	0 %	74 %
BiCl <sub>3</sub>	265 °C	5 % H <sub>2</sub>	1%	0 %	44 %	55 %

Although a minimum temperature of 250 °C was required to reduce bulk BiCl<sub>3</sub> powder with  $N_2H_4$ , the nanocomposite powders were typically reduced at 220 °C. We believe that the highly exposed surface area facilitated the reduction of BiCl<sub>3</sub> – silica nanocomposite powder. Also, we can see from TEM analysis that bismuth leached out of the pore channels upon increasing reduction temperature to 265 °C, as shown in Figure ESI 9. The occurrence of bismuth outside the template can be either by leaching of BiCl<sub>3</sub> precursor due to the formation of a melt at 228 °C, or due to the melting of Bi.



Figure ESI 9. (a) TEM image of 30 v% Bi loaded in SBA-15 and subsequent leaching of the template. BiCl<sub>3</sub> was impregnated dissolved in a 20 v% 7.5 mol/L HCl - MeOH solution, with n-octane as non-polar solvent and subsequently reduced at 220 °C in a hydrazine-loaded Ar-5% H<sub>2</sub> gas flow for 10 h. The template was chemically etched with a 1 mol/L NaOH – 0.5 mol/L hydrazine solution for 3 h. (b) TEM image of 30 v% Bi loaded in SBA-15. BiCl<sub>3</sub> was impregnated dissolved in a 10 % 7.5 mol/L HCl - MeOH solution, with n-octane as non-polar solvent and subsequently reduced at 265 °C in a hydrazine-loaded Ar - 5% H<sub>2</sub> gas flow for 10 h. The template, while the black spheres are bismuth spheres which were formed due to leaching of Bi out of the pores and sintering on the template's exterior surface. Note that the Bi nanowires were compromised during TEM sample preparation, depicting oxidized Bi nanowires.



Figure ESI 10. X-ray powder diffraction (XRPD) data of Bi nanowires embedded in KIT-6 mesoporous silica template. (top) Measurement performed under argon atmosphere by applying tape on sample prepared in glovebox. (bottom) XRPD pattern of same sample without tape shows presence of  $Bi_2O_{2.5}$  reflections. The sharp reflections indicate single-crystal nanowires. However, this has not yet been confirmed by HR TEM, as oxidation occurs during TEM sample preparation

After completing the nanocasting process, the replica was separated from the silica template by etching the silica using a 1 mol/L sodium hydroxide solution for 3 h. The nanostructures were recovered through centrifugal separation and washed 4 times with water and ethanol. The N<sub>2</sub> sorption isotherms of mesoporous Bi replicated from a KIT-6 mesoporous silica is shown in Figure ESI 11. The samples were prepared by impregnating a BiCl<sub>3</sub> precursor solution in refluxing n-octane or the impregnation of Bi(NO<sub>3</sub>)<sub>3</sub> in toluene. The composite powders were reduced at 230 °C for 12 h in hydrazine vapour and subsequently the silica template was removed by chemical etching. The powders were dried for 24 h at 140 °C prior to analysis. A BET surface area of 20 and 13 cm<sup>3</sup>/g were obtained for the samples prepared with respectively Bi(NO<sub>3</sub>)<sub>3</sub> and BiCl<sub>3</sub>. No long-range ordering of the pores was observed in low-angle XRD.



Figure ESI 11.  $N_2$  sorption isotherms of mesoporous Bi replicated from KIT-6 mesoporous silica, by the impregnation of  $Bi(NO_3)_3$  or  $BiCl_3$  precursor salt, reduction at 230 °C and template removal in 1 mol/L NaOH solution.

#### 6 Synthesis of Bi – SiO<sub>2</sub> nano composite powder

KIT-6 mesoporous silica was used as template for the synthesis of Bi nanowire composites. The replicated structure after chemically etching the silica template is shown in Figure ESI 12. The nanowire composite powder was sintered at 230 °C for 20 min in a vacuum under a uniaxial pressure of 50 MPa and subsequently cut for further analysis. Note that all steps of the sample preparation and the electrical measurements were performed under inert atmosphere.



Figure ESI 12. TEM images of Bi nanowire arrays replicated from KIT-6 mesoporous. The silica template was impregnated with a BiCl<sub>3</sub> precursor in 10 w% HCl – 80 v% MeOH solution, reduced at 220 °C in  $N_2H_4$  vapour for 12 h and subsequently subjected to 1 mol/L NaOH etching solution to remove the silica template. Note that the interconnected Bi nanowires were compromised during TEM sample preparation, depicting oxidized Bi nanowires.

#### 7 References

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