Wet-Chemical Synthesis of Enhanced-Thermopower Bi_{1-x}Sb_{x} Nanowire Composites for Solid-State Active Cooling of Electronics

K. Vandaele, Bin He, P. Van Der Voort, K. De Buysser, and J. P. Heremans

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13
14 **Abstract**

15
16 In 1993, Hicks and Dresselhaus suggested that Bi nanowires could result in values of the

17 thermoelectric figure of merit $zT > 1$. The Dresselhaus group also calculated a ternary phase

18 diagram for $Bi_{1-x}Sb_x$ nanowires as a function of x and wire diameter. This manuscript reports a

19 new, wet-chemical method to synthesize $Bi_{1-x}Sb_x$/silica nanowire composites. Resistivity, Hall

20 electron concentration, electron mobility, Seebeck and Nernst coefficients, and thermal

21 conductivity of composites were measured and compared to bulk polycrystalline $Bi_{1-x}Sb_x$

22 samples prepared either by ingot casting or by the same wet chemistry, but without

23 nanostructuring. A clear increase of the thermopower in 20 nm $Bi_{94}Sb_6$/silica is reported when

24 compared to bulk samples, and the values are the highest found in the literature from 300 to 380

25 K, even though the electron concentration is higher than in the bulk. This suggests that,

26 consistent with theory, size quantization is responsible for the thermopower increase.

27

1. Introduction

Peltier-effect based solid-state cooling possesses many advantages over conventional cooling provided by thermodynamic cycles namely vibration-free operation from the absence of moving parts, a long lifetime, reliability, and compactness. Further, if we consider an ideal heat exchanger, thermoelectric (TE) devices have an extremely high specific cooling capacity. TE devices also have a short thermal response time. Their efficiency (today equivalent to 25% of that of vapor-compression coolers) is determined by the TE figure of merit of the materials, zT, which depends on thermal conductivity κ, electrical conductivity σ, and Seebeck coefficient α. Note that zT refers to the materials' figure of merit, whereas ZT is the device's figure merit (contribution of n-type and p-type legs). Together with the absolute temperatures of the hot side and the cold side of a thermoelectric energy converter (which determine its Carnot efficiency), the figure of merit zT of the thermoelectric materials governs its thermal efficiency. Here $zT \equiv \alpha^2 \sigma T / \kappa$, where α is the thermopower of the material, κ and σ are its thermal and electrical conductivities respectively, and T is the average temperature. By separating the electronic (κ_E) and lattice (κ_L) thermal conductivities, and applying the Wiedemann-Franz-Lorenz law ($\kappa_E = LT\sigma$, where $L \approx$ 1.6 to 2.5x10^{-8}V^2/K^2 is the Lorenz ratio), the figure of merit becomes $zT = \alpha^2 / L \left(1 + \kappa_L / \kappa_E \right)^{-1}$. This illustrates how important it is to maximize α, and how only κ_L should be minimized, whereas a high κ_E is actually beneficial to zT.

The vast majority of applications for TE technology are in cooling applications such as automotive climate control via cooled seats, medical and scientific instrumentation, and camping gear. A large expansion of these applications into active TE cooling for thermal management of electronic circuits and batteries might be possible if the zT were enhanced enough and the

1   materials cost sufficiently controlled. Choosing between active TE cooling and passive cooling

2   of such devices depends on the ratio between the required device temperature T_d and the

3   temperature T_a at which the heat can be rejected. Active TE cooling implies that the heat

4   exchanger system not only must handle the heat load from the device, but also that generated by

5   the TE device itself, which is related to the TE figure of merit of the device (*ZT*). In the

6   supplement[1], we show how this consideration imposes the condition

7
$$T_d < T_a \frac{1+\sqrt{1+ZT}}{2} \tag{1}.$$

8   Only if condition (1) is met will an active TE cooler be more compact than a passive cooler.

9   Given the importance of heat management to developing batteries and electronic circuits, *zT*

10   improvements for cooling materials could have great technological impact. Cryogenic coolers

11   are another potential field of applications. Today's six-stage Peltier coolers can reach

12   temperatures as low as 170 K for a hot side of 300 K. Enhancements in the material's *zT* below

13   room temperature could impact the cooling of IR detectors and other sensors in which thermal

14   noise must be minimized by keeping them at temperatures below ambient.

15   Unfortunately, the interdependence of the material properties determining *zT* and their

16   counter-indicated nature makes it difficult to increase *zT*. By far, the best cooling materials near

17   room temperature are tetradymites, generally $(Bi_{1-x}Sb_x)_2(Te_{1-y}Se_y)_3$ compound semiconductors

18   that crystallize with the $\overline{3}m$ space group. This is because the strong spin-orbit coupling in those

19   compounds results in a very high electron mobility, while the high degeneracy of the pockets that

20   form the Fermi surface result in a favorable thermopower.[2] The same arguments hold for $Bi_{1-x}Sb_x$

21   alloys. These are particularly suitable below room temperature. Until now, they have not

22   been considered seriously for applications because, in bulk, they must be used as mechanically

23   fragile single crystals. Preparing bulk $Bi_{1-x}Sb_x$ TEs is also difficult because the large temperature

1 difference between the liquidus and solidus impedes the reasonably accurate control of x.[3] The

2 wet-chemistry route described here circumvents this problem.

3   Hicks and Dresselhaus predicted that zT would be enhanced greatly in quantum well[4] and

4 wire[5] structures because size-quantization effects result in a sharpening of the features of the

5 density of states (DOS), in turn, increasing the thermopower. Due to its charge carriers' small

6 effective mass, particularly electrons,[6,7,8] elemental Bi was the chosen paradigm for this effect.

7   Bulk Bi is a semimetal[9] with valence bands (VB) centered around the Brillouin zone (BZ)

8 T-points; the Fermi level cuts these VBs about 11 meV below their extremum. Conduction bands

9 are centered at the BZ L-points with L_s symmetry, which cut the Fermi energy ~ 27 meV above

10 their minimum, leading to an energy overlap of E_{gTLs}= -38 meV (a positive value indicates a

11 band gap; an energy overlap is treated as a negative band gap).[9] Also at the L-point, there is a

12 VB of L_a symmetry, separated from the L_s band by a direct energy gap E_{gLsa} = 13.6 meV.[6] In

13 semimetals, the electron and hole partial thermopowers counter each other; thus, the overall

14 thermopower is smaller than that of each separate carrier type, greatly reducing zT. Indeed, it was

15 predicted that if we could lift the band overlap in bulk Bi and reduce the electron density at room

16 temperature from the semimetal's 3×10^{18}cm^{-3} to 1×10^{18}cm^{-3} in this hypothetical semiconductor,

17 its zT could reach 1.3.[10] Then, simply opening a gap by size quantization in the Bi electron band

18 structure should result in a great zT improvement. A theoretical calculation[11] predicted that zT

19 values >5 could be reached in 5 nm-diameter Bi nanowires via three effects: sharp features in the

20 DOS energy dependence, opening a gap, and reducing lattice thermal conductivity. This

21 promising result stimulated renewed TE research efforts.[12]

22   Early experiments on Bi nanowires and nanowire composites proved the theory

23 essentially correct. Two methods were developed to synthesize Bi nanowires inside porous

media, typically silica or alumina: high-pressure injection[13] and in-situ vapor growth.[14] It was shown experimentally[15] that confining Bi into nanowires resulted in the opening of a band gap, as predicted[11] for wire diameters of 49 nm and below, although the mobility was reduced.[16] The thermopower enhancement was observed experimentally in nanocomposites containing Bi nanowires with diameters decreasing from 50 to 9 nm.[17,18]

Still, zT enhancement proved elusive. Thermal conduction through the porous matrix constitutes a thermal short,[19] limiting the composite's effective zT. Because Bi oxidizes readily, sintered felts of nanowires extracted from their porous matrix cannot be measured; thus, this short cannot be avoided with today's technology. Mean free path limitations[20] increase the resistivity and affect zT negatively. Further, wires with diameters significantly below 10 nm display localization effects.[18] This is understood readily from the Anderson-Ioffe-Regel criterion for band conduction: the product of the Fermi wavevector k_F and the mean free path ℓ must obey $k_F\ell > 1$. For electrons in Bi, k_F is highly anisotropic, as shown by de Haas–van Alphen and Shubnikov–de Haas measurements,[9] and show a lower bound of $k_F \approx 1\mathrm{x}10^8$ m^{-1}. Assuming that the wire diameter limits ℓ, localization is expected to appear for diameters around $k_F^{-1} \approx 10$ nm, as observed. In hindsight, this limits the applicability range of the early theoretical predictions.

Dresselhaus and co-workers suggested studying quantum wells,[21] nanowires, and nanocomposites of Bi$_{1-x}$Sb$_x$ alloys. Sb is isoelectronic with Bi, and the alloys are solid solutions throughout the concentration range with no change in space group ($\overline{3}m$). Alloying Sb into Bi has three principal effects on its *bulk* band structure: with increasing Sb content, *(i)* the direct energy gap E_{gLsa} closes and ultimately inverts, *(ii)* the T-point hole band decreases in energy vis-à-vis the L-point bands, and *(iii)* the H-point VB increases in energy vis-à-vis the L-point bands.[22]

1   Bulk single-crystal semiconducting $Bi_{1-x}Sb_x$ alloys yield the highest zT of all n-type

2   materials at cryogenic temperatures when the fluxes are oriented along the trigonal axis.[23,24]

3   Potassium is a resonant dopant in Bi and its alloys; a record $zT = 0.7$ was reported[25] at 100 K on

4   K-doped $Bi_{95.5}Sb_{4.5}$, a composition near where the L-point bands have the Dirac dispersion. That

5   sample yields $zT > 0.5$ from 40 to 300 K. P-type $Bi_{1-x}Sb_x$ alloys generally have lower zT values

6   than n-type alloys, despite that Ga is a resonant acceptor in the material.[26] While the best

7   materials still are single crystals, the best p-type materials zT values are obtained when the fluxes

8   are oriented in the trigonal plane.[27] $Bi_{97}Sb_3$ is also one of the alloys best suited for Ettingshausen

9   coolers[28]. Most bulk alloys give slightly better TE performance in Peltier and Ettingshausen

10   geometries when the electron concentration is lowered by light p-type counter doping.[29]

11   The Dresselhaus group calculated size-quantization effects in $Bi_{1-x}Sb_x$ alloys for quantum

12   wells[30] and wires:[31] size quantization and alloying effects cooperate to increase energy gaps. As

13   a result, the semimetal-semiconductor transition occurring in 49 nm-diameter wires of elemental

14   Bi or 9 at.% Sb in bulk $Bi_{1-x}Sb_x$ alloys occurs at lower Sb concentrations in nanostructures, or at

15   larger diameters in $Bi_{1-x}Sb_x$ than in Bi. The calculated (diameter, composition) phase diagrams

16   are reported in Refs. [30,31]. By adding Sb to Bi, one can reasonably hope to increase the

17   thermopower by size quantization in quantum wires of diameters substantially larger than the

18   limit where localization effects occur. The present manuscript aims to show this experimentally.

19   The Dresselhaus group pioneered the first experiments on 65 nm- and 40 nm-diameter

20   $Bi_{1-x}Sb_x$ (x=0.05–0.10) nanowires by using high-pressure injection synthesis,[32] but they observed

21   a more modest Seebeck coefficient enhancement than predicted, and the total thermopower

22   remained significantly lower than single-crystal bulk alloys along the trigonal direction,[29]

23   reaching only -60 µV/K (100–300 K) for 45 nm $Bi_{0.95}Sb_{0.04}$ wires. The in-situ vapor-deposition

1   method was applied successfully to other elements, such as Sb[33] and Zn[34], but was unsuccessful

2   preparing $Bi_{1-x}Sb_x$ alloy nanowires due to the large vapor pressure difference between Bi and Sb.

3   **2. Experimental**

4   Here, we report on a new, wet-chemical synthesis route to prepare $Bi_{1-x}Sb_x$ nanowires

5   that show enhanced thermopower compared to polycrystalline equivalent alloys. The synthesis

6   and characterization of elemental Bi nanowires using the same route as is used here for Bi-Sb

7   alloys is described in detail in Ref. [35], and the same reference contains TEM analysis of Bi

8   nanowires and transport measurements on elemental Bi nanowire composites, which are

9   extended here to Bi-Sb/silica composites. In particular, temperature-dependent Hall

10   measurements on a Bi nanowire/silica composite indicates a carrier concentration that increases

11   as in an intrinsic semiconductor, with an energy gap of 45 meV, which corresponds quite well

12   with the prediction of the Dresselhaus group[11] for 20 nm nanowires.

13   The wet-chemistry synthesis route given here applies to $Bi_{1-x}Sb_x$ alloy nanocomposites.

14   Since these materials undergo a last heat treatment far below their melting point, they have a

15   lower mobility than ingot-cast samples. Therefore, a comparison is made first between the

16   galvanomagnetic (resistivity, Hall effect), thermomagnetic (Seebeck and Nernst coefficients),

17   and thermal (thermal conductivity) properties of bulk $Bi_{1-x}Sb_x$ alloys synthesized via the

18   conventional melt-casting process and those made by the wet-chemistry method used in the

19   synthesis of the nanocomposites. The results of the latter are then compared in the next section to

20   similar measurements on chemically synthesized nanocomposites. We report a clear

21   enhancement of the thermopower in nanowire composites of $Bi_{94}Sb_6$, at high temperature (250 –

22   400 K). This is particularly interesting because, in the existing literature, neither Sb content nor

23   even extrinsic doping of Bi with acceptor or donor impurities is reported to affect the room

1 temperature thermopower of either Bi or Bi-rich Bi-Sb alloys significantly. These data indicate

2 that size confinements alter that in a particularly meaningful way, implying that size-quantization

3 effects influence that band structure.

2.1. Materials

5 Hydrochloric acid trace metal grade (36 wt%), 98% methanol, and 99% n-butanol were

6 purchased from Sigma Aldrich. 99.999% bismuth(III) oxide, 99.999% antimony(III) oxide, 99%

7 hydrazine monohydrate, and 99% n-octane were purchased from Alfa Aesar. 65 wt% trace metal

8 grade nitric acid was obtained from Fisher Scientific. Elemental bismuth and antimony with

9 99.999% purity were obtained from 5N Plus. All reagents were used as received.

2.2. Synthesis

2.2.1. Bulk polycrystalline $Bi_{1-x}Sb_x$ compounds by ingot casting/quenching

12 A series of $Bi_{1-x}Sb_x$ bulk polycrystalline samples with $x = 0.03$, 0.04, 0.05, and 0.06 were

13 prepared with a melting-quenching procedure. Bulk 99.999% Bi and 99.999% Sb were weighed

14 to stoichiometry and approximately 10 g of material was loaded into a quartz ampoule. The

15 ampoule was then sealed under vacuum and heated in a furnace at 800 °C for 8 hours, with

16 frequent shaking. Subsequently, the melts were cooled to 350 °C, followed by quenching in

17 water to minimize phase segregation. For transport measurement, the as-quenched ingots were

18 cut into parallelepipeds with dimensions of about $7 \times 2 \times 1.5$ mm^3 using a diamond saw.

2.2.2. Bulk polycrystalline $Bi_{1-x}Sb_x$ compounds by wet-chemistry route

20 Bulk $Bi_{1-x}Sb_x$ samples with $x = 0.02$, 0.04, and 0.10 were prepared by dissolving

21 appropriate amounts of Bi_2O_3 and Sb_2O_3 in 36 v% hydrochloric acid and subsequently

22 hydrolyzing the obtained precursor solution in distilled water. The precipitate was collected

23 through filtration and dried at room temperature. Next, the Bi-Sb precursor was reduced to

1 remove all oxygen and chloride from the precursor at 230 °C for 12 h in a flow of hydrazine

2 vapor carried by N_2 - 5% H_2 gas. During the low temperature reduction treatment of the

3 precursor a mixture of elemental Bi, Sb and Bi-Sb phase were obtained. $Bi_{1-x}Sb_x$ samples were

4 obtained by sintering the Bi-Sb powders at 245 °C for 90 min at 30 MPa under vacuum using a

5 spark plasma sintering (SPS) device. The compacted discs were cut into parallelepipeds with

6 dimensions of approximately $7 \times 2 \times 1.5$ mm^3 using a diamond saw for transport measurements.

7 *2.2.3. $Bi_{1-x}Sb_x$ nanocomposites by wet-chemistry route*

8      $Bi_{1-x}Sb_x$ nanowire composite samples with $x = 0.03$ and 0.06 were prepared according to

9 the process depicted in Fig. 1. First, the pores of a mesoporous silica template were impregnated

10 with a mixture of bismuth and antimony salts, followed by the reduction of the salts to remove

11 all Cl and O, yielding a mixture of elemental Bi, Sb and $Bi_{1-x}Sb_x$. Next, the nanocomposite

12 powder was mixed with bulk $Bi_{88}Sb_{12}$, which promotes sintering while simultaneously acting as

13 a resistive matrix by filling the voids between adjacent silica grains and presenting an energy gap

14 much larger than that of the $x = 0.03$ or 0.06 material. Finally, bulk-sized samples composed of

15 $Bi_{1-x}Sb_x$ nanowires were obtained by sintering the nanocomposite powder using an SPS device.

16   The mesoporous silica template, pore-expanded FDU-12 (Fudan University-type

17 mesoporous materials), was synthesized according to Ref. [36], while SBA-16 (Santa Barbara

18 Amorphous-type material) was prepared as reported in Ref. [37]. The amounts of precursor

19 impregnated into the template's pores were based on the quantities of precursor required to fill

20 the pores completely with $BiCl_3$ and $SbCl_3$. Typically, an excess of precursors were added since

21 the $BiCl_3$ precursor salt decomposes to denser BiOCl during the impregnation, allowing a higher

22 pore filling with BiOCl compared to $BiCl_3$. As a reference, when the pores are filled completely

23 with $BiCl_3$, the reduced samples can yield up to 32 v% Bi nanowires within the template's pores,

1 whereas that value can be as high as 60 v% when the pores are completely filled with BiOCl.

2 After filling the pores with $Bi_{94}Sb_6$ or $Bi_{97}Sb_3$ precursor, the nanocomposite powders were mixed

3 with 10 to 25 v% bulk polycrystalline $Bi_{88}Sb_{12}$. The continuous-feed nanocasting process used to

4 impregnate the template's pores with an aqueous precursor solution is detailed in Ref. [35]. A

5 schematic of the setup is shown in Fig. 2.

6   In a typical synthesis of $Bi_{94}Sb_6$ nanocomposites, 1 g FDU-12 mesoporous silica powder

7 with a BJH pore volume of 0.9 cm^3/g and a pore diameter of approximately 15-25 nm was

8 dispersed in 100 mL octane and brought into a 250 mL perfluoroalkoxy alkane polymer (PFA)

9 round-bottom flask equipped with a Dean Stark separator and condenser. The recipient was

10 heated to 165 °C to enable the solvent to reflux gently. The $Bi_{94}Sb_6$ precursor solution was

11 prepared by dissolving 5.8646 g Bi_2O_3 (12.6 mmol) and 0.2342 g Sb_2O_3 (0.8 mmol) in 21 mL 36

12 w% hydrochloric acid and diluting with 5 mL water, 13 mL formic acid, and 120 mL methanol.

13 The solution was injected into the PFA flask at a rate of 4 mL/h using a syringe pump. The

14 template's pores were considered completely filled upon the addition of an excess of 200%

15 $Bi_{94}Sb_6$ precursor solution, based on the supposition that the addition of any further precursor

16 solution would lead only to deposition of precursor salt on the template's exterior surface. The

17 voids between the $Bi_{94}Sb_6$/silica grains were filled deliberately with a resistive matrix of $Bi_{88}Sb_{12}$

18 by adding an excess of $Bi_{88}Sb_{12}$ precursor solution. As the template's pores already were filled

19 with the $Bi_{94}Sb_6$ precursor, it was assumed that the $Bi_{88}Sb_{12}$ precursor was deposited on the

20 $Bi_{94}Sb_6$/silica grains' exterior surface. The amount of $Bi_{88}Sb_{12}$ accounted for 10 v% of the total

21 volume.

22       $Bi_{97}Sb_3$ nanocomposites were synthesized using SB-16 mesoporous silica template with a

23 pore diameter between 25 and 35 nm and a pore volume of 1.3 cm^3/g. An excess of 160%

1 precursor salt was impregnated into the template, consisting of 6.8101 g Bi_2O_3, 0.2720 g Sb_2O_3,

2 25 mL 36w% HCl, 25 mL H_2O, and 25 mL formic acid, while 25 v% $Bi_{88}Sb_{12}$ matrix was added

3 (4.7848 g Bi_2O_3 and 0.4082 g Sb_2O_3).

4   The as-synthesized nanocomposite powders were collected through filtration, washed

5 with hexane, and subjected to the reduction treatment discussed earlier for bulk wet-chemistry

6 synthesized $Bi_{1-x}Sb_x$. Bulk nanocomposite samples were formed by SPS sintering the powders as

7 mentioned above. Note that all processes, including cutting the sample, sample mounting and

8 transport measurements, were conducted under air-free conditions to prevent any oxidation of

9 the nanowires.[35]

10

11 **_2.4_**   **_Characterization_**

12   X-ray powder diffraction (XRD) (Fig. 3) patterns were recorded on a Rigaku Miniflex

13 Diffractometer with the Bragg–Brentano theta-2 theta configuration and using Cu Kα radiation.

14 Nitrogen sorption experiments were performed at 77 K with a Micromeritics TriStar 3000

15 device. Samples were vacuum dried at 180 °C for 12 h prior to analysis. The pore-size

16 distribution, and consequently the pore diameter, was determined by analysis of the adsorption

17 branch of the isotherms using the Barrett, Joyner, and Halenda method (BJH, procedure for

18 calculating pore size distributions from experimental isotherms using the Kelvin model of pore

19 filling). X-ray fluorescence (XRF) measurements were performed on a Rigaku NEXCG device.

20 The sample compositions were analyzed by dissolving small pieces of samples into 3:1

21 hydrochloric acid–nitric acid. The recorded intensities were related to their composition using a

22 calibration curve.

1   Galvanomagnetic and thermomagnetic properties (including thermopower, resistivity,

2   Hall coefficient, and Nernst coefficient) were measured in a self-built cryostat from 80 K to 400

3   K using the method described in Ref. [38]. Thermal conductivity was measured using a steady-

4   state heat-sink method. Mobility is calculated from the measured resistivity and Hall coefficient.

5   The error in the thermopower mainly results from electrical noise in voltage and thermocouples

6   because the mounting ensures that the temperature and voltage differences are measured at the

7   same point. Two copper-constantan thermocouples were attached to the sample with silver

8   epoxy; the attachment spot was made intentionally small to minimize error in the thermopower

9   measurement, estimated to be ~3%. The errors in the resistivity, Hall coefficient and Nernst

10   coefficient mainly come from geometric uncertainties. The error in the Hall coefficient and

11   Nernst coefficient is estimated to be 5% and the error in resistivity 10%. The error in thermal

12   conductivity comes from 2 sources: geometric uncertainty and radiation heat loss, which is

13   measured in a cryostat without the sample as a function of temperature. The samples have a

14   relatively high thermal conductivity, and the measurements are cut off at the temperature at

15   which it is estimated that the radiation loss is ~10% of the sample conductance. To this, one adds

16   the geometric uncertainty of also ~10%. Note that the geometric uncertainty in thermal

17   conductivity and in electrical resistivity will compensate each other when calculating zT.

18   **3. Galvanomagnetic and thermomagnetic data**

19   In this section, the galvanomagnetic and thermomagnetic properties of cast ingots and of

20   wet-chemistry-prepared $Bi_{1-x}Sb_x$ alloys are compared. Fig. 4 (a) shows the temperature-

21   dependence of the resistivity of bulk polycrystalline cast ingots of $Bi_{1-x}Sb_x$ with x=3, 4, 5, and 6

22   at.%, which are quite similar to the average of results obtained in the literature[23,24] along the

23   binary and trigonal axes. The chemically prepared polycrystals in Fig. 4 (b) for x = 2, 4, and 10

1   at.% are more resistive by a factor of ~2 at room temperature, and more at 100 K. The results on

2   the nanowire composites of diameter around 15-25 and 25-35 nm for x = 3 and 6 at.% are

3   another factor of ~5 more resistive. However, we note that the resistivity is measured using the

4   physical dimensions of the composite, and is not corrected for the volume fraction of the Bi-Sb

5   material in it. Given that Bi-Sb fills in only about 35v% of the template's pore volume, while the

6   rest (SiO_2 and voids) does not conduct, roughly a factor of 2 from the total increase in resistivity

7   is simply due to the geometric effect.

8   To analyze further the origin of these temperature dependences, low-field (i.e. at field

9   where the product of mobility and magnetic induction is below unity, $\mu.B$<1) Hall effect data are

10 taken. For the nanocomposites, the Hall resistivity is corrected for the volume fractions of Bi-Sb

11 by using the effective medium theory[39] for the Hall effect; for a 35% Bi-Sb filling by volume,

12 that correction is a factor of 2. It is known that the Hall and magnetoresistance data of elemental

13 Bi are the result of the contributions of both electrons and holes, necessitating a complicated fit

14 to obtain electron and hole concentrations and mobilities separately.[40] However, the

15 semiconducting Bi-Sb alloys can, in principle, be treated as a single, n-type carrier system, and

16 the carrier concentration then becomes the inverse of the Hall constant R_H times the electron

17 charge e. This quantity is represented in Fig. 5 for samples of a composition such that they are

18 semiconducting. The carrier concentration increases monotonically with temperature, the

19 classical behavior of narrow-gap semiconductors, and the model should hold at least up to 150-

20 200 K, given the projected values for the band gaps. From this and the resistivity in Fig. 4, one

21 can derive the electron mobilities in the different samples, which are reported in Fig. 6. The

22 mobility of the bulk ingots at liquid N_2 temperature is roughly 50% higher than that of the bulk

23 samples prepared by wet chemistry and become comparable around room-temperature; that of

13

1　the nanowire composites are approximately one order of magnitude lower than bulk samples

2　prepared by wet chemistry. For the resistivity, a factor of 2 of that ratio is due to geometry alone

3　(a calculation of the purely geometric effects based on the effective medium theory is presented

4　in the supplement[1]).

5　　　　In the high-temperature regime where $d\rho/dT > 0$, the temperature dependence of the

6　resistivity is due to the decrease in mobility with increasing temperature, an indication of the

7　presence of electron-acoustic phonon scattering over the increase in electron concentration. In

8　the temperature range where $d\rho/dT < 0$, the temperature dependence of the resistivity is

9　dominated by the increase in carrier concentration, presumably by thermal excitations of the

10　carriers across the energy gap.

11　　　　The total thermal conductivity is shown in Fig. 7. For the bulk ingots, the order of

12　magnitude of the electronic contribution can be estimated from the Wiedemann-Franz-Lorenz

13　law, using the free-electron Lorenz number, to be of the order of 2 W/mK at 100 K and > 4

14　W/mK at 300 K. For the bulk samples prepared with wet-chemical methods, values > 3 W/mK

15　are estimated at 300 K, but much less for the 4 and 10% Sb samples at 100 K. It is known that

16　ambipolar conduction dominates the thermal conduction in semimetallic Bi at 200 K.[10] The

17　samples studied here are narrow-gap semiconductors, so that the ambipolar conduction should be

18　much lower, but it cannot be dismissed at the temperatures where the samples essentially become

19　intrinsic semiconductors. Separating the ambipolar term requires knowledge of the partial

20　conductivities and thermopowers of both electrons and holes, for which we have too few data in

21　polycrystals (Ref. [10] used single crystals of two separate orientations, together with

22　assumptions about the band structure.) It is clear from the numbers above that the thermal

23　conductivity of the bulk ingots at all temperatures, and that of the 4 and 10% Sb ingots prepared

14

1   by wet chemistry at 300 K, has a very substantial electronic contribution. The thermal

2   conductivity of the nanowire composites remains nearly temperature independent at 2 W/mK.

3   Since that of the SiO_2 is of the order of 0.2 W/mK, and the Bi-Sb fills about 35 v% of the

4   sample, it appears that the thermal conductivity of the Bi-Sb in the pores dominates the measured

5   values. The thermal short through the porous host material, which had affected the zT of

6   nanowire array samples in the past[19], is apparently less of a problem in this material. This is

7   probably because the fraction of the pores filled by Bi-Sb nanowires that are electrically in

8   contact with each other is much improved by the present wet-chemical method and by the

9   multiple connectivity of the host material's channels.

10   Most interesting are the thermopower results, given in Fig. 8. It is known that the

11   thermoelectric power of elemental Bi[10] and of the semimetallic $Bi_{1-x}Sb_x$ alloys[23] is anisotropic,

12   with the thermopower along the c-axis $\alpha_{//}$ as much as twice the in-plane thermopower $\alpha_{\perp}$. In

13   contrast, the thermopower of the semiconducting alloys (x = 12, 15 and 18 at.%)[23] is more

14   isotropic. Since this manuscript concerns polycrystals, it is assumed that the thermopower α

15   shown in Fig. 8 is an average given by $\alpha = \frac{2}{3}\alpha_{\perp} + \frac{1}{3}\alpha_{//}$. The thermopower reported for the cast

16   ingots and the bulk samples prepared by wet chemistry all follow the values reported in the

17   literature[23] for their respective values of x. The low-temperature value reported for x = 0.1 (Fig.

18   8b) is the highest reported here, but also quite usual at that concentration.[23] Generally, as the

19   temperature increases to and above room temperature, the thermopower of all samples converge

20   to a value between -50 and -80 µV/K, probably because k_BT approaches the energies of the

21   details of $E_{gLsa}(T)$, $E_{gTLs}(T)$, and $E_{gTLa}(T)$.

22   In contrast, the thermopower of the 20 nm-diameter nanocomposite sample of $Bi_{96}Sb_6$

23   maintains a thermopower with an absolute value in excess of 100 µV/K from 300 to 380 K (see

1 Fig. 8b). A comparison of the thermopower of this polycrystalline sample with literature values,

2 given in Fig. 8c, shows that, to the best of our knowledge, this value has not been equaled

3 previously by Sb-alloying of Bi alone. This change in thermopower also cannot result from an

4 effective medium effect, which is calculated in the supplement.[1] The sample has a quite high

5 carrier concentration (2 to 3 x 10^{19}cm^{-3}) and mobility (200 to 100 cm^2/Vs) in that temperature

6 range, indicating band conduction. The thermopower is also much larger than what can be

7 achieved with $Bi_{88}Sb_{12}$, indicating that the effect cannot be due to the material in the channels

8 between the nanowires. Therefore, we suggest that size quantization increases the gap of this

9 material above what is possible with Sb alloying.

10   The Nernst effect is typically larger than the Seebeck effect at moderate magnetic fields

11 (i.e. μB ~1) in semimetals[41] in general and in Bi in particular,[42] because the contributions of

12 electrons and holes are additive. The low-field adiabatic Nernst coefficients N (i.e. the slope of

13 the transverse thermopower with field) of the alloys measured here are given in Fig. 9 and

14 generally confirm the conclusions. N decreases as x is increased, but is generally quite large with

15 $N \times 1$ T > $|\alpha|$ at 100 K (specifically $N \times 1$ T ~ 350 to 100 µV/K whereas α ~ -50 to -120 µV/K)

16 in semimetallic samples for $x < 0.08$, while the reverse is true at $x = 0.1$. The exceptions are the

17 nanowire composites, which behave like the semiconducting samples.

18   The thermoelectric power factor $PF \equiv \alpha^2/\rho$ and figure of merit $zT \equiv \alpha^2 T/\rho\kappa$ are

19 calculated from the above data and reported in Figures 10 and 11, respectively. It is known[23,24]

20 that power factors of the bulk single-crystal $Bi_{1-x}Sb_x$ alloys along the trigonal direction reach 100

21 µW/cm K^2, far exceeding those of the tetradymites.[2] The present results extend that to

22 polycrystals. The relatively lower zT of $Bi_{1-x}Sb_x$ alloys compared to tetradymites are due to their

23 high lattice thermal conductivity and modest Seebeck coefficient. The fact that the present

1   samples are polycrystals is a second major disadvantage inherent in nanocomposites, since, as

2   outlined in the introduction, the best zT (≤ 0.7) values are achieved in trigonal crystals doped

3   with the resonant impurity potassium. However, from a practical standpoint, polycrystalline

4   samples are preferred over single crystals since they are mechanically stronger and easier to

5   synthesize. In addition, the values obtained for the nanowire composites in Fig. 10 are orders of

6   magnitude better than those measured on previous Bi nanocomposites.[19] According to

7   calculations by Rabin et al.,[43] n-type $Bi_{85}Sb_{15}$ nanowires with a diameter of 20 nm have the

8   potential to reach zT values as high as 2.5, which would drastically enhance the efficiency of

9   thermoelectric solid-state cooling devices and make them competitive with vapor-compression

10   based cooling systems. However, Cornett et al.[44] reported that the extent of the zT enhancement

11   in nanowire thermoelectrics also depends on single-band versus multi-subband transport, which

12   previously was not considered and makes the expected zT arguable.

13   **Conclusions**

14   The wet-chemical method presented here enables the preparation of nanowire composites

15   of semiconducting $Bi_{1-x}Sb_x$ alloys that previous nanowire impregnation methods (vapor

16   deposition and high-pressure liquid injection) could not. Both a reduction of the nanowire

17   diameter and the increase of Sb concentration x (up to 18%) are ways to potentially transform the

18   semimetal Bi into a thermoelectrically relevant Te-free semiconductor. In the present work, both

19   effects are used together. The work shows experimentally that 300 K thermopower values can be

20   obtained in 20 nm $Bi_{94}Sb_6$ nanowire composites that exceed the thermopower of bulk

21   polycrystals of any Sb concentration. Although smaller than the zT of single-crystals of Bi-Sb,

22   and particularly ones resonantly doped with K, the zT values reported here are much improved

23   over those obtained on nanocomposites in the past. This is because the wet-chemical method fills

1   the pores better than the vapor-deposition or high-pressure liquid injection methods. The

2   improvement comes from the fact that a much larger fraction of the Bi-Sb nanowires are in

3   electrical contact with one another in these composites than in those prepared in the past.[19]

4   Further research involves the optimization of the alloy composition and the carrier concentration

5   of the nanowires to maximize their zT.

6

12

1 **Figure captions**
2
3 **Fig. 1** Schematic representation of the synthesis procedure of bulk $Bi_{1-x}Sb_x$ nanowire composite

4 samples, starting from the porous silica in (a). The different steps towards the end product

5 consists of: (1) impregnation of the aqueous Bi-Sb precursor solution into the template's pores;

6 (2) reduction of the Bi-Sb precursor to metallic Bi-Sb; (3) mixing of the nanocomposite powder

7 with a resistive $Bi_{88}Sb_{12}$ matrix; and (4) SPS sintering of the nanocomposite powder into a bulk

8 sized sample. The different intermediate products are: (a) mesoporous silica grain with tuneable

9 pore diameters from 2 to 50 nm, a typical density of 30%, and an interconnected pore structure

10 that allows better percolation between the nanowires; (b) mesoporous silica with a mixture of

11 $BiCl_3$ and $SbCl_3$ deposited in the pores; (c) mesoporous silica with metallic Bi-Sb inside it's

12 pores; (d) Bi-Sb nanowire composite mixed with $Bi_{88}Sb_{12}$ matrix; and (e) bulk sized sample

13 containing nanowires embedded in the silica pores. Note that Bi-Sb leaches partially outside the

14 pores during the reduction treatment, which is shown in (c). To help with sintering while

15 minimizing the effects of electrical short circuits through the leached material, a resistive matrix

16 of $Bi_{88}Sb_{12}$ was added.

17

18 **Fig. 2** Continuous-feed nanocasting setup used to impregnate the mesoporous silica's pores. The

19 setup consists of a heating plate, a round-bottom flask, a Dean Stark separator, an addition

20 system, such as a syringe pump, and a condenser. The silica template and n-octane are brought

21 into the PFA flask and connected with the Dean Stark separator and the addition system. First,

22 the temperature is increased to 165 °C, allowing the non-polar solvent to boil. Second, the

23 precursor solution is added at a rate of 4 mL/h and infiltrates the pores through capillary

24 impregnation. Next, the immiscible aqueous phase is separated from the n-octane based on

1   difference in density. Consequently, the process allows the deposition of $BiCl_3$ and $SbCl_3$ metal

2   salts inside the template's pores, starting from a diluted precursor solution.

3

4   **Fig. 3** Normalized X-ray powder diffraction (XRD) patterns of (a) the Bi-Sb precursor embedded

5   in the silica template, (b) the reduced samples, and (c) SPS sintered samples. (a) Upon

6   impregnating the mesoporous silica template with a mixture of $BiCl_3$ and $SbCl_3$, the precursor

7   salts hydrolyzed with the formation of BiOCl. Neither $SbCl_3$ nor SbOCl were detected, which

8   may be due to low content or their presence as an amorphous phase or phases. (b) The reduced

9   samples were obtained by treating the powders at 230 °C in a flow of N_2, 5% H_2 saturated with

10 hydrazine hydrate vapor for 12 h. The diffraction peaks of elemental Bi and Sb can be observed

11 as indicated on the figure. (c) $Bi_{1-x}Sb_x$ alloys were formed during the SPS sintering process at

12 245 °C for 90 min as can be seen from the shift in 2Theta values and absence of elemental Sb. 10

13 w% Si was added as internal standard to confirm the peak shift was due to alloying.

14

15 **Fig. 4** Temperature dependence of the resistivity of (a) polycrystalline cast ingots of $B_{1-x}Sb_x$

16 alloys of the compositions indicated. Frame (b) shows the same quantity measured on

17 polycrystals sintered from powders prepared using the same wet-chemistry as for the nanowire

18 composites. The latter are labelled as 20 nm-diameter nanowire (NW) composites of $Bi_{94}Sb_6$ and

19 30 nm-diameter NW composites of $Bi_{97}Sb_3$.

20

21 **Fig. 5** Temperature dependence of the inverse of the low-field Hall coefficient of (a)

22 polycrystalline cast ingots of semiconducting $B_{1-x}Sb_x$ alloys ($x > 0.04$) of the compositions

23 indicated. Frame (b) shows the same quantity measured on polycrystals sintered from powders

1 prepared using the same wet-chemistry as for the nanowire composites. The latter are labelled as

2 20 nm-diameter NW composites of $Bi_{94}Sb_6$ and 30 nm-diameter NW composites of $Bi_{97}Sb_3$.

3

4 **Fig. 6** Temperature dependence of the electron mobility of (a) polycrystalline cast ingots of

5 semiconducting $B_{1-x}Sb_x$ alloys ($x > 0.04$) of the compositions indicated. Frame (b) shows the

6 same quantity measured on polycrystals sintered from powders prepared using the same wet-

7 chemistry as for the nanowire composites. The latter are labelled as 20 nm-diameter NW

8 composites of $Bi_{94}Sb_6$ and 30 nm-diameter NW composites of $Bi_{97}Sb_3$.

9

10 **Fig. 7** Temperature dependence of the thermal conductivity of (a) polycrystalline cast ingots of

11 $B_{1-x}Sb_x$ alloys of the compositions indicated. Frame (b) shows the same quantity measured on

12 polycrystals sintered from powders prepared using the same wet-chemistry as for the nanowire

13 composites. The latter are labelled as 20 nm-diameter NW composites of $Bi_{94}Sb_6$ and 30 nm-

14 diameter NW composites of $Bi_{97}Sb_3$.

15

16 **Fig. 8** Temperature dependence of the Seebeck coefficient of (a) polycrystalline cast ingots of

17 $B_{1-x}Sb_x$ alloys of the compositions indicated. Frame (b) shows the same quantity measured on

18 polycrystals sintered from powders prepared using the same wet-chemistry as for the nanowire

19 composites. The latter are labelled as 20 nm-diameter NW composites of $Bi_{94}Sb_6$ and 30 nm-

20 diameter NW composites of $Bi_{97}Sb_3$. Frame (c) compares the Seebeck coefficient of the 20 nm-

21 diameter NW composites of $Bi_{94}Sb_6$ with values collected from the literature for the various Bi-

22 Sb alloys labelled. The references are: YIM, 1972: Ref. [23]; Tanuma 1961: Ref. [45]; Lucas

23 2012: Ref. [46]

1

2 **Fig. 9** Temperature dependence of the low-field Nernst coefficient of (a) polycrystalline cast

3 ingots of $B_{1-x}Sb_x$ alloys of the compositions indicated. Frame (b) shows the same quantity

4 measured on polycrystals sintered from powders prepared using the same wet-chemistry as for

5 the nanowire composites. The latter are labelled as 20 nm-diameter NW composites of $Bi_{94}Sb_6$

6 and 30 nm-diameter NW composites of $Bi_{97}Sb_3$.

7

8 **Fig. 10** Temperature dependence of the thermoelectric power factor of (a) polycrystalline cast

9 ingots of $B_{1-x}Sb_x$ alloys of the compositions indicated. Frame (b) shows the same quantity

10 measured on polycrystals sintered from powders prepared using the same wet-chemistry as for

11 the nanowire composites. The latter are labelled as 20 nm-diameter NW composites of $Bi_{94}Sb_6$

12 and 30 nm-diameter NW composites of $Bi_{97}Sb_3$.

13

14 **Fig. 11** Temperature dependence of the thermoelectric figure of merit *zT* of (a) polycrystalline

15 cast ingots of $B_{1-x}Sb_x$ alloys of the compositions indicated. Frame (b) shows the same quantity

16 measured on polycrystals sintered from powders prepared using the same wet-chemistry as for

17 the nanowire composites. The latter are labelled as 20 nm-diameter NW composites of $Bi_{94}Sb_6$

18 and 30 nm-diameter NW composites of $Bi_{97}Sb_3$.

19

1 References

[1] See Supplemental Material at [URL will be inserted by publisher]. The supplement has two sections. In the first, we derive the condition under which active cooling (e.g. with a Peltier cooler) results in a mre compact heat exchange system than passive cooling, i.e. we derive Eq. (1). The second part gives effective medium calculations of the thermoelectric power. Resistivity and thermal conductivity of te Bi-Sb / alumina composites.

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a   pores

1

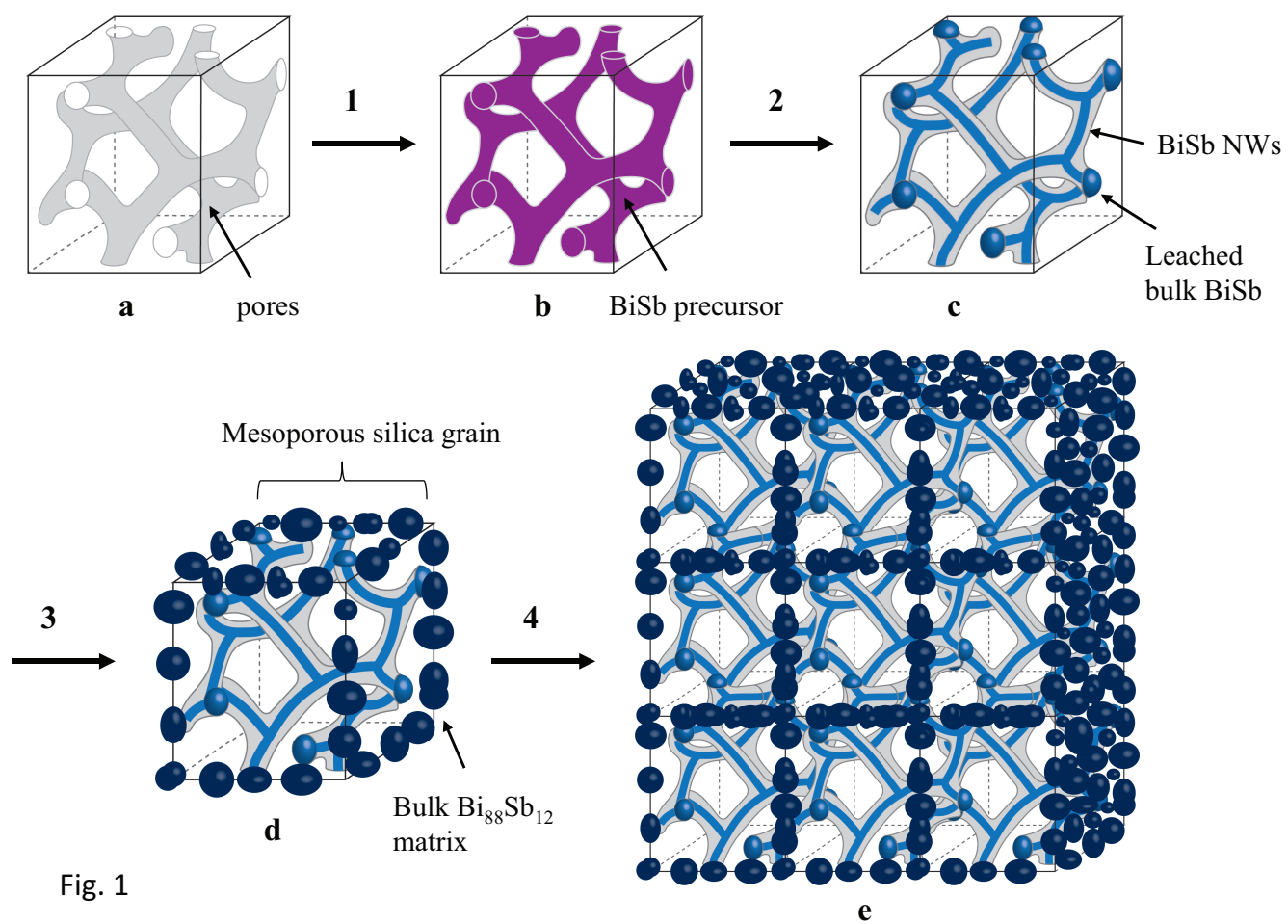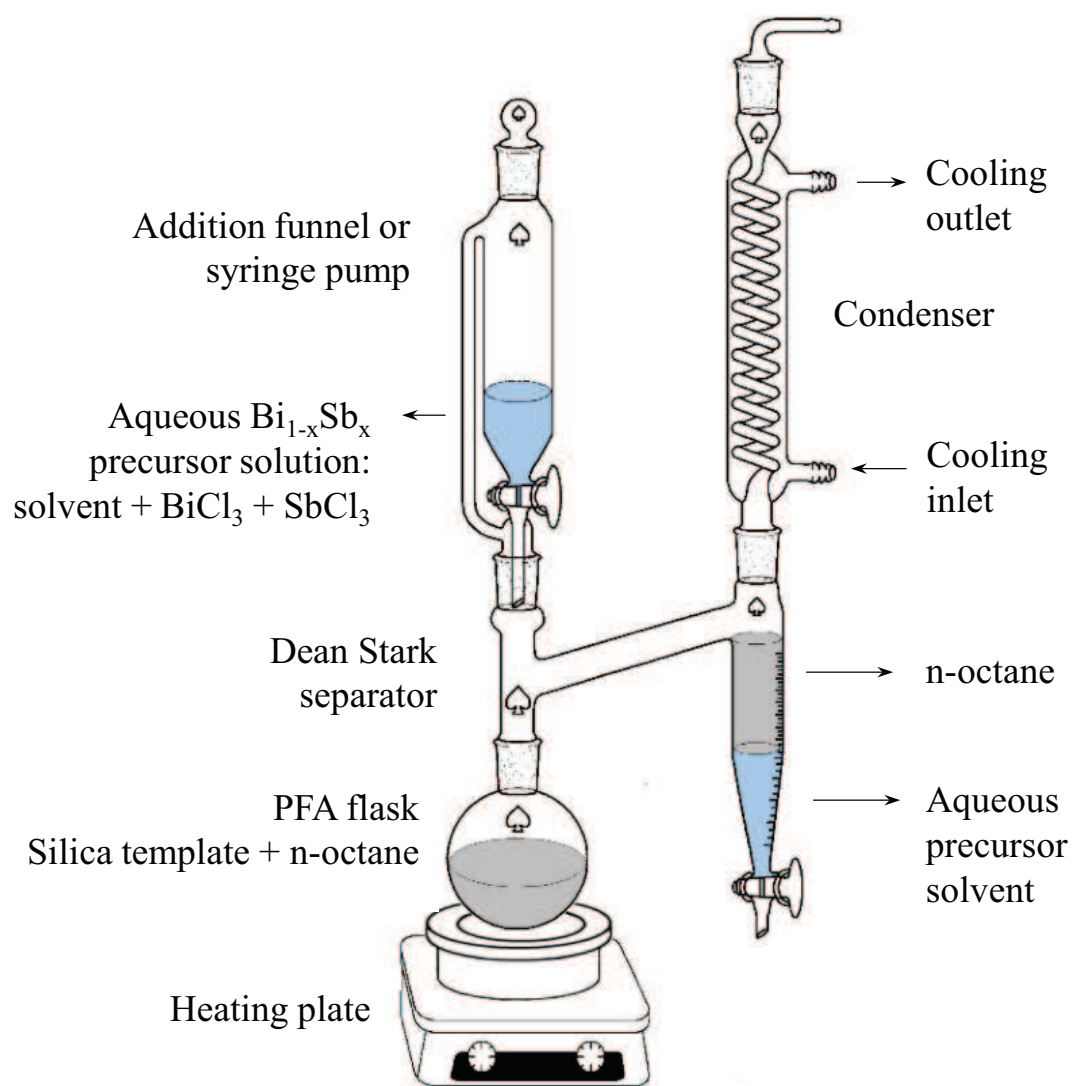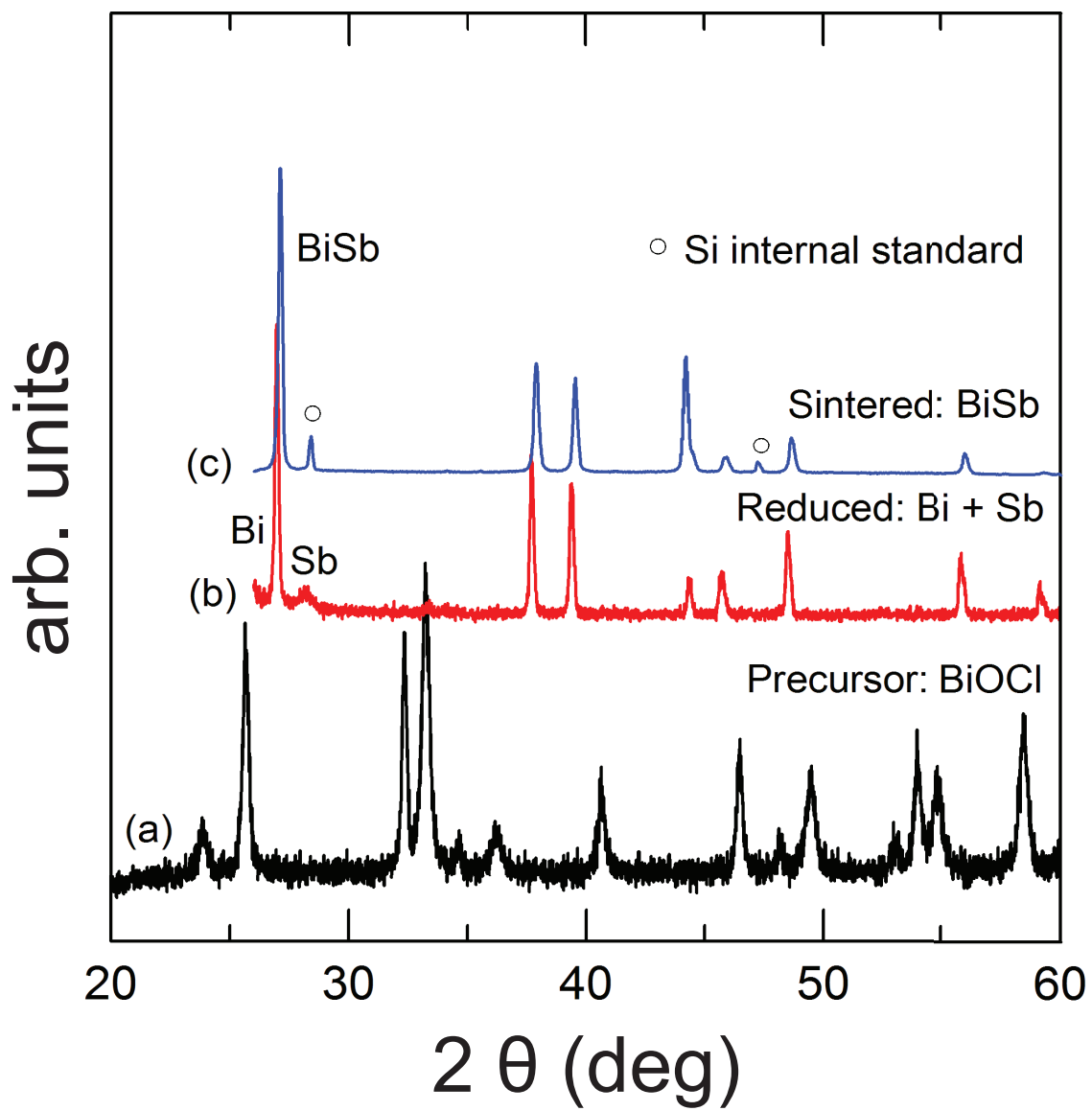b   BiSb precursor

2

BiSb NWs

Leached bulk BiSb

c

Mesoporous silica grain

3

4

Bulk $Bi_{88}Sb_{12}$ matrix

d

e

Fig. 1

Figure 1   NG10094   28DEC2017

Addition funnel or
syringe pump

Aqueous $Bi_{1-x}Sb_x$
precursor solution:
solvent + $BiCl_3$ + $SbCl_3$

Cooling
outlet

Condenser

Cooling
inlet

Dean Stark
separator

n-octane

PFA flask
Silica template + n-octane

Aqueous
precursor
solvent

Heating plate

Fig. 2

Figure 2   NG10094   28DEC2017

Fig. 3

Figure 3   NG10094   28DEC2017

Fig. 4

Figure 4   NG10094   28DEC2017

(a)

(b)

Fig. 5

Figure 5   NG10094   28DEC2017

(a)

(b)

Bi$_{96}$Sb$_4$

Bi$_{90}$Sb$_{10}$

Bi$_{96}$Sb$_4$
Bi$_{95}$Sb$_5$
Bi$_{94}$Sb$_6$

20nm ⌀ Bi$_{94}$Sb$_6$ NWs
30nm ⌀ Bi$_{97}$Sb$_3$ NWs

μ (cm^2/Vs)

T (K)

Fig. 6

Figure 6   NG10094   28DEC2017

(a)

(b)

Fig. 7

Figure 7   NG10094   28DEC2017

(a)

(b)

Fig. 8 (a,b)

Figure 8ab   NG10094   28DEC2017

(c)

α (μV/K) vs T (K)

Legend:
- 20nm Ø Bi$_{94}$Sb$_6$ NWs
- Bi [Yim, 1972]
- Bi$_{95}$Sb$_5$ [Yim, 1972]
- Bi$_{88}$Sb$_{12}$ [Yim, 1972]
- Bi [Tanuma, 1961]
- Bi$_{96}$Sb$_4$ [Tanuma, 1961]
- Bi$_{91}$Sb$_9$ [Tanuma, 1961]
- Bi$_{84}$Sb$_{16}$ [Tanuma, 1961]
- Ho - doped Bi$_{88}$Sb$_{12}$ [Lucas, 2012]

Fig. 8c

Figure 8c   NG10094   28DEC2017

(a)

(b)

Fig. 9

Figure 9   NG10094   28DEC2017

Fig. 10

Figure 10   NG10094   28DEC2017

(a)

(b)

Bi₉₀Sb₁₀

Bi₉₈Sb₂

Bi₉₆Sb₄

Bi₉₇Sb₃

Bi₉₆Sb₄

Bi₉₅Sb₅

Bi₉₄Sb₆

20nm Ø Bi₉₄Sb₆ NWs

30nm Ø Bi₉₇Sb₃ NWs

Fig. 11

Figure 11   NG10094   28DEC2017