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Wet-chemical Synthesis of different Bismuth Telluride Nanoparticles using Metal Organic Precursors - *Single Source* vs. *Dual Source* Approach

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Abstract. Thermolysis of the *single source precursor* $(Et_2Bi)_2$ Te **1** in DIPB at 80 °C yielded phasepure Bi₄Te₃ nanoparticles, while mixtures of Bi₄Te₃ and elemental Bi were formed at higher temperatures. In contrast, cubic Bi₂Te particles were obtained by thermal decomposition of Et₂BiTeEt **2** in DIPB. Moreover, a *dual source approach* (hot injection method) using the reaction of Te(SiEt₃)₂ and Bi(NMe₂)₃ was applied for the synthesis of different pure Bi-Te phases including Bi₂Te, Bi₄Te₃ and Bi₂Te₃, which were characterized by PXRD, REM, TEM and EDX. The influence of reaction temperature, precursor molar ratio and thermolysis conditions on the resulting material phase was verified. Moreover, reactions of alternate bismuth precursors such as Bi(NEt₂)₃, Bi(NMeEt)₃ and BiCl₃ with Te(SiEt₃)₂ were investigated.

Introduction

In the modern society, we are surrounded by waste heat emitters such as combustion engines, electronic components and even the human body. Since the amount of emitted heat is often only small, utilization of this energy is laborious but possible by thermoelectric generators TEG, which allow the conversion of thermal energy into electric energy and therefore provide a wear- and noiseless power source.^[1] The efficiency of a thermoelectric material is given by the dimensionless figure of merit (ZT= $(\alpha^2 \sigma / \lambda)$ T), where α is the Seebeck coefficient, σ is the specific electrical conductivity, λ is the thermal conductivity as sum of the electronic λ_{el} and the lattice λ_{la} contribution and T the absolute temperature in Kelvin. Unfortunately, the transport coefficients are linked together and typically can't be optimized independently from each other. For instance, metals show high electrical and thermal conductivities, whereas both values are small for insulators such as ceramics. The best choices for technical applications are semiconducting materials with heavy elements due to their high effective masses. For technical applications near room temperature, Sb₂Te₃ and Bi₂Te₃ as well as the solid ternary solutions $(Sb_xBi_{1-x})_2Te_3$ are the most effective materials due to their high electrical conductivities and high Seebeck coefficients combined with glass-like low thermal conductivities.^[2] The thermal conductivity of a given material can be further lowered by nanostructuring approaches, which result in an increased phonon scattering at grain boundaries smaller than the phonons mean free path.^[3] As a consequence,

intense research has been done on this field, leading to several preparation and optimization strategies.

Scheele et al. showed that nanosized Bi₂Te₃ particles can be synthesized in a two-step process by reducing bismuth acetate with olevlamine to elemental bismuth particles in dodecanthiole and further treatment with trioctyltellurophosphorane TOPTe, which is a widely used soluble Te-source, at 110 °C. The resulting rhombohedral bismuth-rich Bi2Te3-particles showed reduced thermal conductivity after SPS-treatment and a high power factor (5 µW·K⁻²·cm⁻¹).^[4] Modifying this general synthetic protocol also allowed the synthesis of $(Sb_xBi_{1-x})_2Te_3$ nanoparticles. Stavila et al. investigated the thermolysis of TOPTe and bismuth oleate and investigated the role of the reaction temperature on the resulting particle shape. Asobtained particles reached ZT values of 0.38 at room temperature.^[5] Moreover, bismuth nitrate and TOPTe were thermolyzed in octadecene and oleic acid by Ruan et al., resulting in the formation of hexagonal und rod-shaped particles,^[6] while Borca-Tasciuc et al. obtained hexagonal Bi₂Te₃ plates from the reaction of BiCl₃ and TOPTe in thioglycolic acid in a microwave assisted synthesis.^[7] The resulting material, which was sub-atomically doped with sulphur, showed a remarkably high ZT value (1.1).

Even though TOPTe is a suitable Te-precursor for the solutionbased synthesis of bismuth tellurides, alternative Te-precursors have been investigated. A promising candidate is bis(triethylsilyl)tellurane (Et₃Si)₂Te, whose general capability to serve as rather low-temperature Te-precursor for the deposition of Sb₂Te₃ and Bi₂Te₃ thin films by atomic layer Published on 15 July 2015. Downloaded by University of New England on 18/07/2015 13:16:28.

deposition $(ALD)^{[8]}$ as well as for the wet-chemical synthesis of GeTe-nanoparticles^[9] was recently demonstrated. In addition, bis(trimethylsilyl)tellurane $(Me_3Si)_2Te$ in combination with bismuth trisamides $Bi(NR_2)_3$ was also successfully applied as low-temperature MOCVD precursor for the deposition of Bi_2Te_3 thin films.^[10] Surprisingly, to the best of our knowledge, an analogous solution-based synthesis of Bi_2Te_3 nanoparticles using these specific precursors has not yet been reported.

Bi₂Te₃ crystallizes in the tetradymite-type structure with five membered stacks of alternating tellurium and bismuth layers along the *c*-axis with the sequence Te¹-Bi-Te²-Bi-Te¹, in which the indices correspond to tellurium atoms in different environments. Each stack has the composition Bi₂Te₃ and the hexagonal unit cell (R-3m:H) contains 3 formula units.^[2] A general problem in the wet-chemical synthesis of Bi₂Te₃ nanoparticles is their strong tendency to form so-called antisite defects, the occupation of either Te sites by Bi atoms or Bi sites by Te atoms in the tetradymite lattice, resulting in the formation of either p- or n-doped materials. This well-known process strongly influences the carrier concentration and therefore the thermoelectric properties of the resulting material.^[11] Moreover, the facile incorporation of excess bismuth into the tetradymite lattice leads to a series of sandwich-like structures of the general form $(Bi_2)_n(Bi_2Te_3)_m$, in which the quintuple layers are separated by Bi-bilayers^[12] as can be observed in tsumoite BiTe, pilsenite Bi₄Te₃ and hedleyite Bi₇Te₃, respectively.

Single source precursors (SSPs), which contain the elements of the desired material already pre-formed in a single molecule, are promising alternative precursors for the synthesis of nanoparticles and thin films.^[13] They are typically easier to handle, their thermal properties can be modified by the precursor design and they typically exhibit lower decomposition temperatures, which render them very attractive as low-temperature precursors. While the use of SSPs for the synthesis of several main group and transition metal chalcogenides^[14] including M_2E_3 nanoparticles (M = Sb, Bi; E = S, Se) is well established,^[15] suitable SSPs for Sb₂Te₃ have only been recently developed. Sb₂Te₃ nanoplates were obtained from aerosol assisted chemical vapor deposition (AACVD) using [Sb{(TePⁱPr₂)₂N}₃].^[16] In addition, Ph₂SbTeEt^[17] and $MeSb(TeBu)_2^{[18]}$ were recently shown to be promising SSPs for the wet-chemical synthesis of Sb₂Te₃ nanoparticles and the CVD deposition of Sb₂Te₃ thin films. While early AACVD studies with Et₂SbTeEt and Te(SbEt₂)₂ failed to give Sb₂Te₃ films,^[19] we successfully demonstrated the promising potential of Te(SbEt₂)₂ to serve as SSP for the solution based^[20] and gas phase based^[21] synthesis of highly stoichiometric Sb₂Te₃ nanoparticles and thin films with high Seebeck coefficients. These studies clearly demonstrated that the formation of antisite defects in Sb₂Te₃ nanoplates can be significantly reduced by use of this specific SSP. Moreover, the studies showed that the ligand design of the precursors is of high interest in order to control the specific decomposition mechanism and therefore the level of impurities incorporated into the resulting material. In remarkable contrast, single source precursors for the solutionbased synthesis of high-quality Bi₂Te₃ nanoparticles have not been reported to the best of our knowledge, while Read et al. recently demonstrated that the bismuth chloride telluroether complex [BiCl₃(TeBu₂)₃] is a suitable single source precursor for the MOCVD deposition of high-quality Bi2Te3 thin films.^[22] Herein we report on our attempts to prepare suitable single source and dual source precursors for the wet-chemical synthesis of crystalline Bi₂Te₃ nanoparticles at rather mild reaction condition below 100 °C.

Results and discussion

Thermolysis of (Et₂Bi)₂Te 1

Since $(Et_2Sb)_2Te$ was previously shown to exhibit superior properties as SSP for the solution-based synthesis of highquality hexagonal Sb₂Te₃ nanoplates,^[20] the heavier homologue $(Et_2Bi)_2Te$ **1**, which is readily accessible by insertion reaction of elemental Te into the weak Bi-Bi bond of tetraethyldibismuthine Et_4Bi_2 in *n*-pentane at low temperature,^[23] was investigated.

((Scheme 1 here))

Scheme 1. Synthesis of 1.

1 is a red solid, whose thermal properties were studied by differential scanning calorimetry (DSC). The endothermic peak at 51.3 °C indicates the melting point of 1, followed by a broad exothermic peak between 60 and 100 °C, corresponding to its thermal decomposition (SI, Fig. S3). From the resulting product mixture, Et₃Bi and Et₂Te were clearly identified. Et₃Bi (170 °C) and Et₂Te (225 °C) decompose at higher temperatures, which was confirmed by comparison with the DSC curves of the pure compounds (SI Fig. S1, Fig. S2). These findings were confirmed by thermolysis studies of 1 in a sealed melting point capillary, showing melting of 1 at 53 °C followed by a colour change from red to black upon further temperature increase. In addition, Et₃Bi and Et₂Te were clearly identified as decomposition products of 1 in a thermolysis experiment in a sealed NMR-tube. According to these studies, the decomposition of 1 occurs by a different and more complex reaction mechanism, which most likely includes the formation of radicals, compared to that of (Et₂Sb)₂Te, which proceeded in a stoichiometric reaction with subsequent formation of Sb₂Te₃ and four equivalents of SbEt₃.^[20]

((Figure 1 here))

Figure 1. X-ray diffractogram of Bi_4Te_3 nanoparticles as obtained by thermal decomposition of **1** at 80 °C in DIPB and reference (green: Bi_4Te_3 , JCPDS 33-216).

The thermolysis reaction of 1 was performed with 200 mg (Et₂Bi)₂Te 1, which was dissolved in 10 mL DIPB, slowly heated to 170 °C and stirred for 1 h. The red solution turned into a black suspension around 80 °C. After cooling to ambient temperature, macroscopic, shiny metallic-like particles were isolated from the colourless liquid by centrifugation and were shown by EDX studies to consist of pure bismuth metal. The thermolysis temperature was therefore lowered to 80 °C, yielding a black powder after work up. The chemical composition of the material as-determined by EDX analysis revealed a bismuth to tellurium ratio of 56:44 at%, which is close to the theoretical value for Bi_4Te_3 (57:43). All observed peaks in the PXRD pattern (Fig. 1) can be indexed on the basis of rhombohedral Bi₄Te₃ (JCPDS 33-216). The lattice parameters were refined to (a = 4.43(1) Å, c = 41.84(1) Å and $V = 415.5(4) \text{ Å}^3$ (SI Fig. S10. The broad full width half maximum (FWHM) of the peaks indicate a small particle size of roughly 20 nm.

TEM studies of the nanoparticles (Fig. 2) show the formation of agglomerated particles of roughly 200 nm in size, consisting of smaller particles with diameter ranging from 10 to 40 nm. The particles are crystalline and lattice fringes of the randomly orientated crystals are easily resolved in HRTEM. A d-spacing

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of roughly 310 pm is often observed, which refers to the 100% peak (107) in the PXRD. The corresponding ring diffraction pattern (SI Fig. 14) from an area with several crystals is in good agreement with the PXRD result and proves the formation of crystalline Bi_4Te_3 nanoparticles by simulation^[24] using 30526-ICSD.^[25]

((Figure 2 here))

Figure 2. TEM images of Bi_4Te_3 nanoparticles as obtained by thermal decomposition of **1** at 80 °C in DIPB.

In an attempt to suppress the agglomeration of the particles, the thermolysis reaction of **1** according to scheme 1 was performed at 80 °C in DIPB in the presence of 3 wt % of poly(1-vinylpyrolidone)-graft-(1-triacontene) PVP* as capping agent. After workup, a black powder was obtained. TEM analysis of the powder showed less agglomeration and the size of the crystalline particles (Fig. 3) increased as can be seen by the diffraction contrast of the grains, which however showed no distinct morphology. The SAED (SI Fig. S15) pattern again corresponds well to the calculated pattern of Bi_4Te_3 .

((Figure 3 here))

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Figure 3. TEM images of Bi_4Te_3 nanoparticles as obtained by thermal decomposition of 1 at 80 °C in DIPB in the presence of 3 wt % of PVP*.

Thermolysis reactions at higher temperatures between 100 and 130 °C yielded mixtures of Bi_4Te_3 and elemental Bi as a second crystalline phase as was proven by PXRD (SI, Fig. S18). Analogous findings were observed for thermolysis reactions in this temperature range in DIPB in the absence of any capping agent. These findings show, that the decomposition mechanism of **1** and its lighter homologue (Et₂Sb)₂Te strongly differ at enhanced temperatures, which most likely has its origin in the low Bi-Te bond energy, rendering homolytic bond cleavage with subsequent formation of radical species more likely.

Thermolysis of Et₂BiTeEt 2

Since the decomposition of 1, in which the Bi:Te ratio is 2:1, only yielded the Bi-rich binary bismuth-tellurium phase Bi_4Te_3 (pilsenite), we became interested in the thermal decomposition of a precursor with lesser amount of Bi. Et₂BiTeEt 2, which was prepared by reaction of Et₄Bi₂ and Et₂Te₂,^[26] was therefore chosen as promising *single source precursor*.

((Scheme 2 here))

Scheme 2. Synthesis of 2.

The reaction of Et_4Bi_2 and Et_2Te_2 in toluene-d₈ was monitored by temperature dependent ¹H-NMR spectroscopy (SI, Fig. S5). Below 75 °C, no reaction was observed, while new signals with growing intensity appeared at temperatures above 75 °C, proving the formation of $Et_2BiTeEt 2$, which decomposes at 85 °C with formation of Et_3Bi and Et_2Te as well as insoluble solid material (SI; Fig. S6). According to our DSC study (SI, Fig. S4), decomposition of 2 yields Et_3Bi and Et_2Te , which decompose at 270 °C and 225 °C, respectively.

Thermolysis reactions of **2** were performed in DIPB and in oleylamine (OA) for 3 and 14 h, respectively, in order to investigate the role of solvent and reaction time on the composition and morphology of the resulting material. For these studies, **2** was freshly prepared *in situ* by stirring a solution of Et_4Bi_2 and Et_2Te in the respective solvent at ambient temperature for 30 minutes, followed by heating to 100 °C for

14 h. The resulting black suspension was centrifuged and the black solid repeatedly washed (3x) with chloroform.

((Figure 4 here))

Figure 4. X-ray diffractogram of black powders as obtained by thermal decomposition of **2** at 100 °C in DIPB and reference (red: Bi₂Te, JCPDS 42-540).

The chemical composition of resulting materials was analysed by EDX (Bi:Te ratio 65:35 at% (DIPB) and 62:38 at% (OA)). These results again show the formation of Bi-rich materials. Xray diffraction studies confirmed the EDX results, proving the formation of phase-pure Bi₂Te in DIPB (Fig. 4), while the material formed in OA contained elemental Bi as second phase (SI, Fig S19). Any attempts to increases the Te-content in the material by adding TOPTe as soluble Te-source failed. In all cases, Bi₂Te was formed as was proven by EDX and XRD, respectively.

SEM pictures of the resultant black particles proved the formation of pseudo-cubic particles with edge lengths of several 100 nm (Fig. 5). With increasing reaction time, the particle size increases to 500 nm, proving an Ostwald ripening of the initially formed nanoparticles.

((Figure 5 here))

Figure 5. SEM images of Bi_2Te nanoparticles as obtained by thermal decomposition of 2 at 100 °C in DIPB (a) and OA (b).

In summary, all thermolysis reactions using 1 and 2 resulted in the formation of tellurium-poor phases, while Bi₂Te₃ was not formed. These findings point to different decomposition mechanisms of 1 and 2 compared to analogous antimony compounds as well as bismuth selenolates (R₂Bi)₂Se and R₂BiSeR', which have been reported to decompose with formation of trialkylbismuthanes R₃Bi and Bi₂Se₃ or RBi(SeR')₂, respectively,^[27] and may be attributed to the decreasing Bi-E bond energy with increasing atomic number of the chalcogen atom. Breunig et al. investigated the decomposition mechanism of 1 and 2 by mass spectroscopy and detected multiple species in the gas phase, indicating a complex decomposition mechanism.^[28] According to Pauling's postulate, that heteronuclear bonding is always stronger than homonuclear bonding,^[29] it seems reasonable to assume that the Bi-Te bond is the weakest bond within 1 and 2, since the electronegativity difference between Bi and Te is less compared to that between Bi and C as well as Te and C. 1 and 2 are therefore expected to undergo homolytic Bi-Te bond breakage reactions, even though the corresponding metal-centered radicals have not been identified directly by ESR experiments to the best of our knowledge, to date. However, the same is true for tetraalkyldistibines and -dibismuthines, for which homolytic Sb-Sb and Bi-Bi bond cleavage reactions with subsequent formation of metal centered radicals are widely accepted, despite the lack of broad experimental proof. To the best of our knowledge, only one persistend Bi-centered radical, which was formed by a homolytic bond cleavage reaction of a dibismuthine containing sterically demanding organic substituents, was clearly identified.^[30] In contrast, ESR experiments with Me₄Bi₂ as well as Ph₄Bi₂ failed to give signals due to the formation of Ph₂Bi radicals, even though reactivity studies agreed with their formation.^[31]

Compounds of the type R_2BiTeR' have been previously described to decompose in solution at elevated temperature with formation of BiR₃ and RBi(TeR')₂, but mechanistic studies

were not presented.^[27,32] In contrast, our DSC and NMR studies using 1 and 2 only proved the formation of Et₃Bi and Et₂Te, while no indication for the formation of EtBi(TeEt)₂ was found. Any attempts to detect radical intermediates by addition of TEMPO to the reaction solution remained without success. We assume, that the formation of temperature stable Et₂Te, which was experimentally proven by DSC and NMR studies, is an efficient process for the transport of Te out of the reaction mixture, always resulting in the formation of Te-poor (Bi-rich) materials. However, the exact decomposition mechanism for the formation of Bi_4Te_3 or Bi_2Te using either 1 or 2 as SSPs remain still unclear and are expected to depend on the specific organic substituents as was previously reported by Bochmann et al. for several tris-selenolato-bismuthines Bi(SeR)₃.^[33] Thermal decomposition reactions of Bi(SeR)₃ in solution preferentially proceeded with formation of elemental Bi due to the favorable breakage of the Bi-Se bond compared to the Se-C bond. However, the decomposition mechanism was found to strongly depend on the organic substituents. (2,4,6-t-Bu₃C₆H₂Se)₃Bi was found to decompose with elimination of the selenane R₂Se and formation of a mixture of elemental bismuth and Bi₂Se₃, while (2,4,6-Me₃C₆H₂Se)₃Bi yielded elemental Bi and the diselenane R₂Se₂.

Reaction of Bi(NMe₂)₃ with Te(SiEt₃)₂

Since the thermal decomposition reactions of both single source precursors 1 and 2 failed to give the desired Bi_2Te_3 phase, we became interested in the development of a suitable dual source approach. ALD studies have revealed that Bi(NMe₂)₃ and $Te(SiEt_3)_2$ are suitable precursors for the formation of Bi_2Te_3 thin films,^[10] so we expanded our studies on the reactions of $Bi(NR_2)_3$ and $Te(SiEt_3)_2$. Addition of $Bi(NMe_2)_3$ to a solution of Te(SiEt₃)₂ in DIPB at ambient temperature resulted in an immediate darkening, indicating a fast reaction. Monitoring the reaction in THF-d₈ by ¹H-NMR spectroscopy proved that the reaction proceeded with elimination of N.Ndimethylaminotriethylsilane Me₂NSiEt₃, which is the only detectable product after 15 minutes (SI, Fig. S7). According to these studies, the reaction occurs by the following mechanism:

((Scheme 3 here))

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Scheme 3. Reaction of Bi(NMe₂)₃ and Te(SiEt₃)₂

Influence of reaction temperature. Since the reaction temperature is known to play an important role for the formation of nanoparticles and has major impacts on size, shape and crystallinity of the resulting nanoparticles, we systematically varied the reaction temperature from 30 °C to 120 °C. PXRD studies of the resulting materials obtained at low temperatures showed broad peaks, which did not allow the detailed assignment of any specific phases, and SEM studies showed the formation of small particles with undefined morphology (Fig. 6).

((Figure 6 here))

Figure 6. SEM images of Bi_2Te_3 nanoparticles as obtained by reaction of $Bi(NMe_2)_3$ and $Te(SiEt_3)_2$ at 120 °C in DIPB.

((Figure 7 here))

Figure 7. X-ray diffractogram of black powders as obtained by reaction of $Bi(NMe_2)_3$ and $Te(SiEt_3)_2$ at different temperatures. Bi_2Te_3 ((black: JCPDS 015-0863) and Bi_4Te_3 (red, JCPDS 33-216).

With increasing reaction temperature, the peaks in the PXRDs became sharper, pointing to the formation of larger crystallites, and revealed Bi_2Te_3 to be present as dominate phase as well as small contributions of Bi_4Te_3 (Fig. 7). The SEM studies showed increasing particle size and a star-like morphology of the nanoparticles. EDX analysis revealed the formation of Bi-rich material (Bi:Te ratio 44:56 at%), which clearly deviates from the expected 40:60 ratio for phase-pure Bi_2Te_3 .

((Figure 8 here))

Figure 8. X-ray diffractograms of black powders as obtained by reaction of Bi(NMe₂)₃ and Te(SiEt₃)₂ in DIPB in 2:3 (a), 4:3 (b) and 1:1 (c) molar ratios at 100 °C and references (red: Bi₂Te₃, JCPDS 015-0863; green: Bi₄Te₃, JCPDS 33-216; blue: BiTe, JCPDS 44-0667).

Influence of thermolysis procedure and precursor ratio. Since only biphasic bismuth tellurides were formed as described before, the thermolysis conditions were slightly modified. The Te precursor was dissolved in DIPB and heated to 100 °C. $Bi(NMe_2)_3$ was then rapidly injected (hot injection) to this solution, immediately resulting in the formation of a black powder, which was isolated by centrifugation after 3 h. PXRD studies proved the formation of phase-pure Bi₂Te₃ (Fig. 8a) The refined lattice parameters for the nanosized Bi₂Te₃ particles as determined by Rietveld analysis (Fig. S11) for Bi_2Te_3 (a = 4.399(1) Å, c = 20.297(3) Å and V = 507.7(1) Å³) are in good agreement with values reported for Bi₂Te₃ (JCPDS 015-0863). Since a multiplicity of bismuth telluride phases with different bismuth concentration exists, we carefully investigated thermolysis reaction of Bi(NMe₂)₃ and Te(SiEt₃)₂ also with two different precursor molar ratios (1:1; 4:3). The solution of Te(SiEt₃)₂ in DIPB was heated to 100 °C, followed by addition of different amounts of a solution of Bi(NMe₂)₃ in DIPB, also yielding black suspensions, from which black powders were isolated by centrifugation after 3 h. Depending on the precursor ratio, two different phases with Bi:Te molar ratios of 1:1 (BiTe) and 4:3 (Bi₄Te₃) were obtained (Fig. 8b,c). In each case, the chemical composition is close to the theoretical value with respect to the experimental error. The refined lattice parameters for the nanosized particles as determined by Rietveld analysis for BiTe (a = 4.420(5) Å, c = 24.09(2) Å and V = 407.5(9) Å³; Fig. S12) and Bi_4Te_3 (a = 4.462(1) Å, c = 41.84(1) Å and V = 721.1(4) Å³, Fig. S13) are in good agreement with values reported in the literature for these binary bismuth-tellurium phases (JCPDS No. 015-0863 (Bi₂Te₃), No. 015-0863 (Bi₄Te₃) and No. 44-0667 (BiTe).

Since the formation of the desired Bi_2Te_3 phase was of particular interest, the particles were further analysed by TEM, showing small pseudo-cubic particles with edge lengths of roughly 40 nm (Fig. 9). The SAED pattern (Fig. S16) of these particles is in good agreement with the literature data and clearly shows the formation of phase pure Bi_2Te_3 as proven by comparison with calculated ED-pattern using data from ICSD-42546.^[34]

((Figure 9 here))

Figure 9. TEM images of Bi_2Te_3 nanoparticles as obtained by reaction of $Bi(NMe_2)_3$ and $Te(SiEt_3)_2$ (2:3 molar ratio) in DIPB at 100 °C.

Figure 10 displays a HRTEM image of a Bi_2Te_3 nanoparticle from $Bi(NMe_2)_3$ and $Te(SiEt_3)_2$ (2:3 molar ratio) in DIBP at 100 °C in [110] zone axis orientation, thus perpendicular to the Published on 15 July 2015. Downloaded by University of New England on 18/07/2015 13:16:28.

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stacking of the five membered Bi_2Te_3 building units. The contrasts in the image change strongly with increasing thickness as common in HRTEM, but the Fourier transform of the whole image shown in figure 10b) indicates that the periodicity is perfect. The Fourier transform matches perfect with the simulation of the electron diffraction for Bi_2Te_3 (Fig. 10c), and as no additional peaks or streaking is observed, an intergrowth of different phases of the Bi-Te system can be excluded. A closer inspection of the thin areas of the sample shows periodic 1 nm stacks perpendicular to the *c*-axis of Bi_2Te_3 . Each of the stacks has five rows of well resolved contrast maxima, which match the positions of the atoms of Bi_2Te_3 in this projection. This is illustrated by an overlay of a ball and stick plot of Bi_2Te_3 (Fig. 10a).

((Figure 10 here))

Figure 10. HRTEM image of a Bi_2Te_3 nanoparticle from $Bi(NMe_2)_3$ and $Te(SiEt_3)_2$ (2:3 molar ratio) in DIBP at 100 °C. a) Zoom of the boxed area with structure model as overlay; b) Fourier transform of the whole HRTEM image; c) FT with simulation of the diffraction pattern in [110] as overlay.

Variation of the Bi-precursor. Since the reaction of Bi(NMe₂)₃ **4** and Te(SiEt₃)₂ yielded phase-pure Bi₂Te₃, we expanded our studies on analogous reactions of alternate bismuth triamides. Bi(NEt₂)₃ **5** as well as the asymmetric Bi(NMeEt₂)₃ **6** were chosen, which are oily liquids at ambient temperature, while **4** is a solid. The reaction of **5** and **6** with Te(SiEt₃)₂ at ambient temperature in THF-d₈ were monitored by ¹H-NMR spectroscopy. Compared to the reaction of **4**, which is finished after 15 min, the reaction of **5**, which proceeds with formation of the expected elimination product *N*,*N*-diethylaminotriethylsilane, is decelerated and incomplete even after 20 h (SI, Fig X). Surprisingly, **6** didn't show any reaction at ambient temperature even after 20 h (Fig. S9). One the basis of the NMR results, **5** and **6** are less suitable bismuth precursors for the synthesis of bismuth telluride nanoparticles than **4**.

Finally, we investigated the reaction of BiCl₃ with Te(SiEt₃)₂, which was expected to proceed with elimination of Et₃SiCl (dehalosilylation reaction). Since BiCl₃ is not soluble in noncoordinating solvents such as DIPB, we used oleylamine (OA) as solvent. The thermolysis reaction was performed at 160 °C for 14 h. The SEM of the resulting product showed very small particles without defined structure (Fig S17). The Bi:Te ratio (42 at% : 58 at%) is close to the expected value for Bi₂Te₃. These results were confirmed by PXRD, which proved the formation of Bi₂Te₃ as the only crystalline product (Fig. 11). The lattice parameters for the Bi₂Te₃ particles (a = 4.405(1) Å and c = 20.284(4) Å) are in good agreement with values reported in the literature for Bi₂Te₃ (JCPDS No. 015-0863).

((Figure 11 here))

Figure 11. X-ray diffractogram of the material as obtained by reaction of BiCl₃ and Te(SiEt₃)₂ in OA at 160 °C and reference (red: Bi_2Te_3 , JCPDS 015-0863).

Experimental

Synthetic procedures, Materials and methods

PVP* (Sigma-Aldrich) was used as received while 1,3diisopropylbenzene (DIPB, Sigma-Aldrich) was carefully dried over Na/K alloy and oleylamine (OA, Acros) was degassed prior to use. $(Et_2Bi)_2Te$,^[35] $Te(SiEt_3)_2$,^[36] Et_4Bi_2 ,^[37] Et_2Te_2 ,^[38]

Thermolysis of (Et₂Bi)₂Te 1

200 mg (0.3 mmol) $(Et_2Bi)_2$ Te were dissolved in 10 mL of DIPB. The solution was heated to 80 °C for 14 h. 10 mL of MeOH were added after cooling the solution to ambient temperature and the precipitate was isolated by centrifugation and purified by repeated washing with chloroform (2-3 times). Yield: 53 mg (28% based on Bi content in 1) Bi₄Te₃.

Thermolysis of Et₂BiTeEt 2

106.8 mg (0.2 mmol) Et_4Bi_2 and 62.7 mg (0,3 mmol) Et_2Te_2 were dissolved in either 15 mL of DIPB or OA at ambient temperature. Attempts to increase the Te content were performed with 15.4 mg (0.03 mmol) of TOPTe (Te excess of 15%). The red solution was heated to 100 °C and stirred at this temperature for either 3 or 14 h. The black solid was isolated as described before. Yield: 55 mg (55.4% based on Bi content in **2**) Bi_2Te .

Thermolysis of Bi(NMe₂)₃ and Te(SiEt₃)₂

Influence of reaction temperature. 53.6 mg (0.15 mmol) Te(SiEt₃)₂ were added to a yellow solution of 31.5 mg (0.1 mmol) Bi(NMe₂)₃ in 15 mL of DIPB, immediately yielding a greenish suspension. This suspension was heated to the desired temperature and stirred for 3 h at this temperature. After cooling to ambient temperature, 10 mL of MeOH were added and the black solid was separated from the liquid by centrifugation and repeatedly washed with chloroform (2-3 times). Biphasic mixtures of Bi₂Te₃ (major phase, > 95 % according to PXRD) and Bi₄Te₃ in different molar ratios depending on the reaction temperature were obtained.

Influence of precursor ratio. A solution of 107.4 mg (0.3 mmol) Te(SiEt₃)₂ in 15 mL of DIPB was heated to 100 °C and a solution of either 68.2 mg (0.2 mmol), 102.4 mg (0.3 mmol) or 136.5 mg (0.4 mmol) Bi(NMe₂)₃ in 2 mL of DIPB was added to the hot solution (hot injection method). The resulting black suspension was stirred at 100 °C for 3 h. After cooling to ambient temperature, 10 mL of MeOH were added and the solid was isolated from the solution by centrifugation and washed with chloroform (2-3 times). **Bi₂Te₃**: Yield: 79.9 mg (0.094 mmol, 94%); **BiTe**: Yield: 96.9 mg (0.29 mmol, 96%); **Bi₄Te₃**: Yield: 114 mg (0.093 mmol, 93%).

Influence of Bi-precursor. 107.4 mg (0.3 mmol) Te(SiEt₃)₂ and either 87.1 mg (0.2 mmol) Bi(NEt₂)₃ or 76.7 mg (0.2 mmol) (Bi(NEtMe)₃, respectively, were dissolved in 15 mL of DIPB and heated to 120 °C. The solution was stirred for 3 h at this temperature. Due to the insolubility of BiCl₃ in DIPB, the thermolysis reaction of 63.1 mg (0.2 mmol) BiCl₃ and 107.4 mg (0.3 mmol) was performed in 15 mL of OA. The solution was heated to 160 °C for 3 h and the isolation and purification of the resulting black solid was performed as described before.

Characterization

X-ray Powder Diffraction (PXRD). PXRD patterns were obtained at ambient temperature ($25\pm2^{\circ}$ C) using a Bruker D8 Advance powder diffractometer in Bragg–Brentano mode with Cu K_a radiation (λ = 1.5418 Å, 40 kV, and 40 mA). The powder samples were investigated in the range of 5 to 90° 20 with a step size of 0.01° 20 and a counting time of 0.3 s. Rietveld

refinement was performed with the program package TOPAS 4.2 from Bruker.

SEM Analysis. Scanning electron microscopy (SEM) studies were carried out on a Jeol JSM 6510 equipped with an energy-dispersive X-ray spectroscopy (EDX) device (Bruker Quantax 400).

TEM Analysis. TEM studies were conducted on transmission electron microscopes (i) FEI Philips CM30 T/LaB₆ operated at 300 kV and (ii) FEI-Philips CM300 UT/FEG operated at 300 kV. Both microscopes are equipped Gatan CCD's for image recording and with Thermo NSS systems for EDS analysis using a Si(Li) Nanotrace and a HP-Ge EDS detector, respectively. The samples were prepared on perforated carbon foils without further grinding.

Conclusions

We investigated the suitability of two possible single source precursors, (Et₂Bi)₂Te 1 and Et₂BiTeEt 2, for the solutionbased synthesis of Bi2Te3 nanoparticles. The thermal decomposition pathways of both precursors were elucidated by ¹H-NMR spectroscopy and differential scanning calorimetry (DSC). Thermolysis of 1 in DIPB led to the formation of Bi_4Te_3 at 80 °C and mixtures of Bi₄Te₃ and elemental Bi at higher temperatures, while thermolysis of in situ generated 2 in DIPB or OA gave pseudo-cubic Bi2Te particles, whose size increase with increasing reaction time. To the best of our knowledge, this is the first report of the solution based formation of Bi₂Te. For all thermolysis reactions, the formation of tellurium poor phases were observed. 1 and 2 are therefore unsuitable for the synthesis of Bi₂Te₃, which may be attributed to the comparable low Te-Bi binding energy and complex decomposition mechanism. We assume that the formation of temperature stable Et₂Te is an efficient process for the transport of Te out of the reaction mixture, leading to Te-poor (Bi-rich) materials.

In contrast to the *single source precursors*, the *dual source approach* using the reaction of $Te(SiEt_3)_2$ and $Bi(NMe_2)_3$ was successfully applied for the synth esis of multiple Bi-Te phases including Bi_2Te_3 depending on the precursor ratio. In contrast, analogous reactions of $Bi(NEt_2)_3$ and $Bi(NMeEt)_3$ occurred with formation of a mixture of elemental tellurium and bismuth and a mixture of Bi_4Te_3 and tellurium, respectively, while the reaction of $BiCl_3$ and $Te(SiEt_3)_2$ gave Bi_2Te_3 nanoparticles. The reaction conditions leading to phase pure material are summarized in figure 11.

((Figure 12 here))

Figure 12. Summary of the ideal reaction conditions for the formation of phase-pure binary bismuth-tellurium materials.

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Notes and references

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- M. H. Elsheikh, D. A. Shnawah, M. F. M. Sabri, S. B. M. Said, M. H. Hassan, M. B. A Bashir and M. Mohamad, *Renewable Sustainable Energy Rev.*, 2014, 30, 337.
- 2 a) D. M. Rowe, CRC Handbook of Thermoelectrics, CRC Press, Boca Raton, FL, 1995; b) J. R. Drabble and C. H. L. Goodman, J. Phys. Chem. Solids, 1958, 5, 142
- 3 Z. Wang, J. E. Alaniz, W. Jang, J. E. Garay and C. Dames, *Nano Lett.*, 2011, **11**, 2206.
- 4 M. Scheele, N. Oeschler, I. Veremchuk, K.-G. Reinsberg, A.-M. Kreuziger, A. Kornowski, J. Broekaert, C. Klinke and H. Weller, *ACS Nano*, 2010, 4, 4283.
- 5 V. Stavila, D. B. Robinson, M. A. Hekmaty, R. Nishimoto, D. L. Medlin, S. Zhu, T. M. Tritt and P. A. Sharma, ACS Appl. Mater. Interfaces, 2013, 5, 6678.
- 6 L. Chen, Q. Zhao and X. Ruan, Mater. Lett., 2012, 82, 112.
- 7 R. J. Mehta, Y. Zhang, C. Karthik, B. Singh, R. W. Siegel, T. Borca-Tasciuc and G. Ramanath, *Nat. Mater.*, 2012, 11, 233.
- a) K. Knapas, T. Hatanpää, M. Ritala and M. Leskelä, *Chem. Mater.*, 2010, 22, 1386; b) S. Zastrow, J. Gooth, T. Boehnert, S. Heiderich, W. Toellner, S. Heimann, S. Schulz and K. Nielsch, *Semicond. Sci. Technol.*, 2013, 28, 035010; c) C. Bae, T. Bohnert, J. Gooth, S. Lim, S. Lee, H. Kim, S. Heimann, S. Schulz, H. Shin and K. Nielsch, *Semicond. Sci. Technol.*, 2014, 29, 064003.
- 9 S. Schulz, S. Heimann, K. Kaiser, O. Prymak, W. Assenmacher, J. T. Brüggemann, B. Mallik and A.-V. Mudring, *Inorg. Chem.*, 2013, 52, 14326.
- 10 a) T. J. Groshens, R. W. J. Gedridge and C. K. Lowe-Ma, Chem. Mater. 1994, 6, 727; b) T. Groshens, R. Gedridge, R. Scheri and T. Cole, in Fifteenth International Conference on Thermoelectrics Proceedings ICT '96, IEEE, 1996, p 430.
- 11 Z. Stary, J. Horak, M. Stordeur and M. Stölzer, J. Phys. Chem. Solids, 1988, 49, 29.
- 12 J. W. G. Bos, H. W. Zandbergen, M.-H. Lee, N. P. Ong and R. J. Cava, *Phys. Rew. B*, 2007, **75**, 195203.
- 13 a) M. A. Malik, M. Afzaal and P. O'Brien, *Chem. Rev.*, 2010, 110, 4417; b) H. J. Gysling, A. A. Wernberg and T. N. Blanton, *Chem. Mater.*, 1992, 4, 900.
- a) J. S. Ritch, T. Chivers, M. Afzaal and P. O'Brien, *Chem. Soc. Rev.*, 2007, 36, 1622; b) P. L. Musetha, N. Revaprasadu, G. A. Kolawole, R. V. S. R. Pullabhotla, K. Ramasamy and P. O'Brien, *Thin Solid Films*, 2010, 519, 197; c) N. O. Boadi, M. Azad Malik, Paul O'Brien and J. A. M. Awudza, *Dalton Trans.*, 2012, 41, 10497; d) K. Yu, X. Liu, Q. Zeng, M. Yang, J. Ouyang, X. Wang and Y. Tao, *Angew. Chem. Int. Ed.*, 2013, 52, 11034.
- a) N. Maiti, S. H. Im, C.-S. Lim and S. I. Seok, *Dalton Trans.*, 2012,
 41, 11569; b) F. T. F. O'Mahony, U. B. Cappel, N. Tokmoldin, T. Lutz, R. Lindblad, H. Rensmo and S. A. Haque, *Angew. Chem. Int. Ed.*, 2013, 52, 12047; c) J. R. Castro, K. C. Molloy, Y. Liu, C. S. Lai, Z. Dong, T. J. White and E. R. T. Tiekink, *J. Mater. Chem.*, 2008, 18, 5399; d) M. Bochmann, X. Song, M. B. Hursthouse and A. Karaulov, *J. Chem. Soc., Dalton Trans.*, 1995, 1649; e) H.-W. Chang, B. Sarkar and C. W. Liu, *Cryst. Growth Des.*, 2007, 7, 2691; f) W. Lou, M.

Published on 15 July 2015. Downloaded by University of New England on 18/07/2015 13:16:28.

Chen, X. Wang and W. Liu, *Chem. Mater.*, 2007, **19**, 872; g) R. K. Sharma, G. Kedarnath, V. K. Jain, A. Wadawale, M. Nalliath, C. G. S. Pillai and B. Vishwanadh, *Dalton Trans.*, 2010, **39**, 8779.

- 16 S. S. Garje, D. J. Eisler, J. S. Ritch, M. Afzaal, P. O'Brien and T. Chivers, J. Am. Chem. Soc., 2006, 128, 3120.
- 17 G. Gupta and J. Kim, Dalton Trans., 2013, 42, 8209.
- 18 S. L. Benjamin, C. H. de Groot, A. L. Hector, R. Huang, E. Koukharenko, W. Levason and G. Reid, J. Mater. Chem. C, 2015, 3, 423.
- R. S. Dickson and K. D. Heazle, J. Organomet. Chem., 1995, 493, 189.
- 20 S. Schulz, S. Heimann, J. Friedrich, M. Engenhorst, G. Schierning and W. Assenmacher, *Chem. Mater.*, 2012, 24, 2228.
- 21 G. Bendt, S. Schulz, S. Zastrow and K. Nielsch, Chem. Vap. Deposition, 2013, 19, 235.
- 22 S. L. Benjamin, C. H. de Groot, C. Gurnani, A. L. Hector, R. Huang, E. Koukharenko, W. Levason and G. Reid, *J. Mater. Chem. A*, 2014, 2, 4865.
- 23 S. Heimann, D. Bläser, C. Wölper and S. Schulz, Organometallics 2014, 33, 2295.
- 24 P.A. Stadelmann, JEMS electron microscopy software java version 3.
- 25 K. Yamana, K. Kihara and T. Matsumoto, Acta Cryst., 1979, B35, 147.
- 26 S. Heimann, A. Kuczkowski, D. Bläser, C. Wölper, R. Haak, G. Jansen and S. Schulz, *Eur. J. Inorg. Chem.* 2014, 4858.
- 27 M. Wieber and I. Sauer, Z. Naturforsch. B, 1987, 42, 695.
- 28 H. J. Breunig and D. Müller, Z. Naturforsch., 1986, 41b, 1129.

- 29 L. Pauling and D. M. Yost, Proc. Nat. Acad. Sci., 1932, 18, 414; L. Pauling, J. Am. Chem. Soc., 1932, 54, 3570.
- 30 S. Ishida, F. Hirakawa, K. Furukawa, K. Yoza and T. Iwamoto, Angew. Chem. Int. Ed., 2014, 53, 11172.
- 31 a) A. J. Ashe, III, E. G. Ludwig and J. Oleksyszyn, *Organometallics*, 1983, 2, 1859; b) F. Calderazzo, R. Poli and G. Pellini, *Dalton Trans.*, 1984, 2365.
- 32 a) H. J. Breunig, *Phosph. Sulf. Rel. El.*, 1988, **38**, 97; b) H. J. Breunig and S. Gülec, *Z. Naturforsch. B*, 1986, **41**, 1387; c) S. Schulz, *Coord. Chem. Rev.*, 2015 297-298, 49.
- 33 M. Bochmann, X. Song, M. B. Hursthouse and A. Karaulov, *Dalton Trans.*, 1995 1649.
- 34 S. Nakajima, J. Phys. Chem. Solids, 1963, 24, 479.
- 35 H. J. Breunig, K. H. Ebert and R. E. Schulz, Z. Naturforsch., 1995, 50b, 735.
- 36 M. R. Detty and M. D. Seidler, J. Org. Chem., 1982, 47, 1354.
- 37 R. King and J. Eisch, Organometallic Syntheses, Vol. 3, Elsevier, Amsterdam, 1986.
- 38 K. Hamada and H. Morishita, Syn. React. Inorg. Met., 1981, 11, 597.
- 39 F. Ando, T. Hayashi, K. Ohashi and J. Koketsu, J. Inorg. Nucl. Chem., 1975, 37, 2011.
- 40 M. Vehkamäki, T. Hatanpää, M. Ritala and M. Leskelä, J. Mater. Chem., 2004, 14, 3191.

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Graphical and textual abstract

Thermolysis of metal organic *single source* and *dual source precursors* yielded phase-pure Bi_xTe_y nanoparticles at low temperatures.





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