AARHUS UNIVERSITY

Coversheet

This is the accepted manuscript (post-print version) of the article.

Contentwise, the accepted manuscript version is identical to the final published version, but there may be differences in typography and layout.

How to cite this publication

Please cite the final published version:

Jian-Li Mi, Peter Nørby, Martin Bremholm, and Bo B. Iversen (2017). Insight into Nucleation and Growth of Bi₂-xSbxTe₃ (x = 0-2) Nanoplatelets in Hydrothermal Synthesis. In *Chemistry of Materials*, 29 (12), pp 5070-5079

DOI: <https://doi.org/10.1021/acs.chemmater.6b05211>

Publication metadata

Title:	Insight into Nucleation and Growth of Bi ₂ -xSbxTe ₃ (x = 0-2) Nanoplatelets in Hydrothermal Synthesis
Author(s):	Jian-Li Mi, Peter Nørby, Martin Bremholm, and Bo B. Iversen
Journal:	<i>Chemistry of Materials</i>
DOI/Link:	https://doi.org/10.1021/acs.chemmater.6b05211
Document version:	Accepted manuscript (post-print)

This document is the Accepted Manuscript version of a Published Work that appeared in final form In *Chemistry of Materials*, 29 (12), pp 5070-5079. DOI: <https://doi.org/10.1021/acs.chemmater.6b05211>
- copyright © American Chemical Society after peer review and technical editing by the publisher.

General Rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognize and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

If the document is published under a Creative Commons license, this applies instead of the general rights.

Insight into Nucleation and Growth of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ ($x = 0-2$) Nanoplatelets in Hydrothermal Synthesis

Jian-Li Mi,^{*,†} Peter Nørby,[‡] Martin Bremholm[‡] and Bo B. Iversen^{*,‡}

[†]Institute for Advanced Materials, School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, China.

[‡]Center for Materials Crystallography, Department of Chemistry and iNANO, Aarhus University, DK-8000 Aarhus C, Denmark.

ABSTRACT: Controlled wet chemical synthesis of nanomaterials with tailored structures and properties, especially by hydrothermal/solvothermal methods, is difficult due to the complicated nucleation and growth processes. Therefore, it is important to gain a deeper understanding of the formation mechanisms involved in hydrothermal/solvothermal processes. In the present study, the formation mechanisms of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ ($x = 0-2$) nanoplatelets under hydrothermal conditions are studied by *in situ* synchrotron radiation powder X-ray diffraction (SR-PXRD). Synthesis using glucose as the reducing agent results in direct nucleation of Bi_2Te_3 from Bi and Te precursors without the presence of any intermediate products, and the nucleation stage is completed in only about 1 min at 250 °C. When Sb is added the nucleation process for $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ becomes slower with increasing Sb content. Depending on the Sb content and reaction temperature, an intermediate product of elemental Te nanostructures forms, and it is found to direct the morphology of the final products. Within the duration of the measurements, Sb_2Te_3 only forms at relatively high reaction temperatures due to the slower kinetics of the reaction. A two-stage nucleation mechanism is found for the formation of the ternary BiSbTe_3 with an initial nucleation stage of predominately Bi_2Te_3 followed by a second stage of slower

nucleation and alloying process to BiSbTe_3 . Both the composition and reaction temperatures affect the crystallization kinetics and crystallite growth mechanisms during synthesis of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ nanoplatelets.

1. INTRODUCTION

Bi_2Te_3 -based materials have attracted tremendous interest owing to their attractive properties, which are useful in fields such as thermoelectrics¹ and topological isolators.² Nanostructuring of materials is known to be an effective approach for the improvement of thermoelectric properties due to both an enhanced density of states and an increased phonon scattering.³ Among the many routes for synthesis of nanomaterials, the hydrothermal/solvothermal method has proven to be an efficient approach for producing nanostructured materials and it has a great potential to realize mass production for practical applications. The hydrothermal/solvothermal method has been widely used for the preparation of nanostructured Bi_2Te_3 -based materials.⁴⁻⁹ However, the processes occurring in the hydrothermal/solvothermal synthesis in sealed autoclaves are highly complex and generally not well understood. At present, the prediction of the formation of inorganic compounds from the solution precursors is very limited and the nanocrystal synthesis has been conducted by empirical optimization rather than by design.¹⁰

Gaining insight in the synthesis processes is an essential step for the further development of controlled synthesis of nanomaterials. The control of composition, morphology, dimensions, and architecture of nanomaterials is difficult by hydrothermal/solvothermal methods owing to the complicated nucleation and growth processes, but it is critical for tailoring the physical and chemical properties of nanomaterials. For example, bimetallic nanoparticles show significant difference in catalytic activity when configured into different architectures such as alloy, core-shell, or monometallic

mixture.¹¹ Likewise, the architectures of ternary $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ ($x = 0-2$) can be alloy, core-shell, or mixture. For example, recently, core-shell heterostructure¹² and heterojunction of $\text{Sb}_2\text{Te}_3/\text{Bi}_2\text{Te}_3$ ¹³ were prepared by solvothermal methods. Establishing control over the composition, morphology, dimensions, and architecture requires a comprehensive understanding of the nucleation and growth mechanisms involved in the synthesis process. One of the main challenges in studying the formation and growth mechanisms is the lack of powerful techniques to investigate the hydrothermal/solvothermal reactions taking place inside the heated and pressurized autoclaves. The recent development of different *in situ* techniques has resulted in tremendous progress in studies of the synthesis of nanoparticles taking place in solutions.¹⁴⁻²² In particular, by using synchrotron radiation powder X-ray diffraction (SR-PXRD), it has become possible to follow the formation processes as they occur during hydrothermal/solvothermal synthesis. The advantage of using *in situ* SR-PXRD is that it provides valuable information on the structural and microstructural changes of nanoparticles with reaction time. Indeed, detailed information about the formation and growth have been obtained for synthesis of a wide range of nanoparticles.²³⁻²⁹ Instead of using bulky steel autoclaves, sapphire capillary reactors have been developed for *in situ* SR-PXRD experiments. These overcome the significant challenges of X-ray absorption and diffraction from the steel autoclaves.³⁰ Moreover, conventional autoclaves require a long time heating period, which additionally increases the difficulty in controlling the synthesis. The effect of the heating period can be eliminated by the rapid heating used in the sapphire capillary reactors.

In a previous study, we performed an *in situ* SR-PXRD investigation of the formation of Bi_2Te_3 using alginate acid as reducing agent, and found that Te forms as an intermediate product in the synthesis of Bi_2Te_3 nanoparticles.³¹ Ternary compounds such as $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ ($x = 0-2$) nanostructured materials may further improve the thermoelectric properties by altering the electronic band structure and enhancing

the phonon scattering, whereas the formation processes are more complex. There are very few systematic studies of the formation and growth of Bi_2Te_3 -based ternary compounds where temperature and composition are varied. Recently, Song *et al.* suggested an oriented attachment mechanism for the solvothermal growth of $\text{Bi}_2\text{Se}_x\text{Te}_{3-x}$ ($x = 0-3$) nanoplatelets by an *in situ* PXRD study.³² Here, we report an *in situ* SR-PXRD investigation of the nucleation and growth mechanisms of $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ ($x = 0-2$) nanoparticles under hydrothermal condition using glucose as reductant at varied temperatures. Abundant information about phase transformation, microstrain, crystallization kinetics and crystal growth is achieved for the hydrothermal synthesis of $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$. Both the composition and reaction temperature affect the crystallization and growth kinetics. A two-stage nucleation mechanism is found for the formation of the ternary BiSbTe_3 . To complement the *in situ* study, separate *ex situ* experiments for the synthesis of $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ ($x = 0, 1, 2$) were performed in a custom-designed coil autoclave with the same reaction conditions as the *in situ* SR-PXRD experiments.

2. EXPERIMENTAL SECTION

Five different *in situ* experiments for the hydrothermal synthesis of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ with $x = 0, 0.5, 1, 1.5$ and 2 , were performed in the present study. BiCl_3 , SbCl_3 and $\text{K}_2\text{TeO}_3 \cdot 3\text{H}_2\text{O}$ were used as reactants. Ethylenediaminetetraacetic acid disodium dihydrate (EDTA-Na_2) and glucose were used as complexing agent and reductant, respectively. The precursor solutions were prepared as follows: Typically, 0.8 g of EDTA-Na_2 was first dissolved in 10 ml of distilled water under vigorous stirring. Then, a total amount of 1.2 mmol of BiCl_3 and/or SbCl_3 was added and the mixture was stirred for several minutes. After that, 1.8 mmol of $\text{K}_2\text{TeO}_3 \cdot 3\text{H}_2\text{O}$ and 0.8 g of glucose were added. Finally, 0.2 g of NaOH was added and followed by stirring for 10 min.

The *in situ* SR-PXRD experiments were carried out at beamline I711 at MAX-lab, Sweden, using a home-built sample stage and an Oxford Diffraction Titan CCD detector. The experimental setup used for *in situ* studies consists of a custom-designed high-pressure flow cell using a sapphire capillary heated by a flow of hot air as described in detail by Becker *et al.*³⁰ The precursor was injected into the sapphire capillary, which was pressurized to 250 bar hydrostatic pressure. The reaction was initiated by applying rapid heating to the desired reaction temperatures. At the same time, sequential exposure of X-ray frames with a time resolution of 5 s (of which 1 s was detector dead time for readout) was started. Experiments with different temperatures from 200 to 300 °C were performed. The X-ray wavelength of $\lambda = 0.98803 \text{ \AA}$ ($E = 12.5 \text{ keV}$) was calibrated using a LaB₆ standard.

The data sets were integrated using Fit2D.³³ The SR-PXRD data were refined using the Rietveld method implemented in the FullProf program³⁴ and corrected for instrumental broadening using data measured on a LaB₆ standard. A Thompson-Cox-Hastings pseudo-Voigt axial divergence asymmetry profile function and a background modeled with linear interpolation were used in the refinement.

Separate *ex situ* experiments for the synthesis of Bi_{2-x}Sb_xTe₃ ($x = 0, 1, \text{ and } 2$) were performed in a custom-designed coil autoclave at a temperature of 250 °C, a pressure of 250 bar, and a reaction time of 30 min. The detailed description of the coil autoclave is provided in the supporting information (Figure S1). The products were centrifuged and washed several times in distilled water and ethanol and finally dried at room temperature. The dry products were analyzed by powder X-ray diffraction (PXRD) on a Rigaku SmartLab diffractometer using Cu K $_{\alpha}$ radiation. The morphology of the products was characterized with a FEI Talos scanning transmission electron microscope (STEM) with an accelerating voltage of 200 keV. Elemental mapping was performed with four energy-dispersive X-ray spectroscopy (EDX) detectors equipped on the FEI Talos.

3. RESULTS AND DISCUSSION

3.1. Phase Transformation

The SR-PXRD patterns for the synthesis at 200 °C, 250 °C, and 300 °C are included in the supporting information as Figure S2, S3, and S4, respectively. To highlight the rapid changes in the early stage the SR-PXRD data for $t < 8$ min are displayed in the SI. Figure 1 shows the selected SR-PXRD patterns in 2θ range of 22-27° at different reaction times for Bi_2Te_3 , $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_3$, BiSbTe_3 , $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$, and Sb_2Te_3 , respectively, at the reaction temperature of 200 °C. The heating was initiated at $t = 0$ min and data were recorded up to $t = 25$ min. Depending on the composition, different formation processes are displayed for the synthesis of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$. Before the heat is turned on ($t = 0$ min), the broad diffuse diffraction intensity of the SR-PXRD patterns indicates amorphous features of the precursors for all the *in situ* experiments. It shows that the precursors are homogenous with all constituents either soluble or forming amorphous complexes. During the reaction, Te forms as an intermediate depending on the composition, indicating different formation mechanisms through the series of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$. For example, Bi_2Te_3 formed very fast and directly from the Bi and Te precursors without the presence of any intermediate products at the reaction temperature of 200 °C. However, when the Sb content increases (e.g., BiSbTe_3 and $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$), the formation of the $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ product is slower and an obvious phase transformation is detected during the synthesis. Within the duration of the measurements, Sb_2Te_3 is not observed while only Te is present at 200 °C as shown in Figure 1e. The data clearly show that the synthesis processes of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ depend strongly on the composition. Reaction temperature also significantly affects the formation process of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$. As seen in the SI (Figure S2, S3 and S4), the time-resolved SR-PXRD patterns clearly show faster formation kinetics at 300 °C compared with that at 200 °C and 250 °C. The detailed formation mechanisms of different $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ will be further

discussed below.

Figure 1. Selected SR-PXRD patterns in 2θ range of $22\text{--}27^\circ$ at different reaction times at 200°C for (a) Bi_2Te_3 , (b) $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_3$, (c) BiSbTe_3 , (d) $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$, and (e) Sb_2Te_3 .

In order to obtain detailed information about the nucleation and growth of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ nanostructured materials during the hydrothermal synthesis, the *in situ* SR-PXRD data were analyzed using the

Rietveld method. Besides the scale factor, background parameters, unit cell parameters, and the atomic positions, the Lorentzian peak-shape parameters were refined to calculate the volume-weighted crystallite sizes along a,b -plane ($D_{a,b\text{-plane}}$) and along the c -axis ($D_{c\text{-axis}}$).^{23,35} Figure 2 shows the representative Rietveld refinements of SR-PXRD data with good agreement between the observed and calculated patterns for the synthesis of Bi_2Te_3 , BiSbTe_3 and Sb_2Te_3 at 250 °C at the reaction time of 0.17 min and 25 min, respectively. The Rietveld refinements of selected PXRD patterns of $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_3$ and $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ are shown in Figure S5. A temperature calibration shows that heating of the reactor is very fast and the reaction temperature reaches 250 °C in about 0.08 min. This dramatically eliminates the effect of long heating period on the nucleation and growth processes. The refinements further confirm the phases that formed at different reaction periods. Bi_2Te_3 is formed directly after heating of 0.17 min. With the increase of Sb content, Te and $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ coexist in the initial products at 0.17 min for the synthesis of $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_3$ and BiSbTe_3 . $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ phase together with crystalline Te and trace of Sb_2O_3 are detected at 0.17 min for the synthesis of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ and Sb_2Te_3 . Particularly, the weight percentages of Te, Sb_2O_3 and Sb_2Te_3 are 64.3(9)%, 18.4(4)% and 17.3(8)%, respectively, for the synthesis of Sb_2Te_3 at $t = 0.17$ min and $T = 250$ °C (Figure S6), indicating that there are other possible species of Sb such as solubilized Sb complexes in the system besides crystalline Sb_2O_3 . A phase pure product of rhombohedral $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ phase can be obtained for all the synthesis at $t = 25$ min and $T = 250$ °C. Table 1 displays the Rietveld refinement parameters of the SR-PXRD data for the *in situ* synthesis of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ ($x = 0, 0.5, 1, 1.5, \text{ and } 2$) at the reaction temperature of 250 °C and the reaction time of 25 min.

Figure 2. Representative Rietveld refinements with observed, calculated, and difference patterns at 250 °C. (a) Bi_2Te_3 at 0.17 min, (b) BiSbTe_3 at 0.17 min, (c) Sb_2Te_3 at 0.17 min, (d) Bi_2Te_3 at 25 min, (e) BiSbTe_3 at 25 min, and (f) Sb_2Te_3 at 25 min.

Table 1. Selected data from the Rietveld refinement in the form of refined unit cell parameters (a and c), fractional coordinates (z (Bi/Sb), and z (Te2)) and crystallite sizes ($D_{a,b\text{-plane}}$ and $D_{c\text{-axis}}$) for $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ ($x = 0, 0.5, 1, 1.5$, and 2) at a reaction temperature of 250 °C and a reaction time of 25 min. Agreement factors: profile factor (R_p); weighted profile factor (R_{wp}); Bragg factor (R_i); crystallographic R_F factor (R_F).

$\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$	$x = 0$	$x = 0.5$	$x = 1$	$x = 1.5$	$x = 2$
Data points	1788	1791	1798	1788	1793
Refined parameters	43	46	43	41	45
Reflections	41	41	41	40	39
R_p (%)	13.5	14.5	13.1	13.9	12.6

R_{WP} (%)	9.85	10.3	10.3	9.99	8.18
R_I (%)	1.36	1.79	1.74	1.38	1.11
R_F (%)	1.69	2.53	1.86	1.62	1.36
a (Å)	4.4388(2)	4.4545(2)	4.4303(3)	4.3483(3)	4.3294(2)
c (Å)	30.776(2)	31.018(2)	31.258(3)	30.960(2)	30.965(2)
z (Bi/Sb)	0.4003(3)	0.4108(2)	0.4126(3)	0.3995(3)	0.3998(3)
z (Te ₂)	0.7881(2)	0.7931(3)	0.7910(3)	0.7853(2)	0.7858(1)
$D_{a,b\text{-plane}}$ (nm)	14.4(3)	12.1(3)	6.4(1)	9.9(2)	17.1(3)
$D_{c\text{-axis}}$ (nm)	5.4(1)	5.4(1)	3.9(1)	4.9(1)	9.5(2)

3.2. Crystallization Kinetics

The relative crystalline content of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ during the synthesis can be obtained from the refined scale factors (α) of the $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ phase. The scale factors for each formation curve were normalized to the α -value at 25 min. Figure 3a shows representative formation curves of Bi_2Te_3 , BiSbTe_3 and Sb_2Te_3 at 250 °C. It can be seen that the formation of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ phase becomes much slower with increasing Sb content, indicating different crystallization kinetics. For Bi_2Te_3 , the nucleation stage is completed in only 1 min. The nucleation processes of BiSbTe_3 and Sb_2Te_3 are much slower and reach the maximum values after about 4 and 15 min, respectively. Figure 3b shows the formation curves of BiSbTe_3 at 200 °C, 250°C, and 300 °C. It is obvious that the formation rate becomes faster at higher reaction temperatures. At a low reaction temperature of 200 °C, the formation curve of ternary BiSbTe_3 clearly shows a two-stage nucleation mechanism: an initial fast nucleation stage with a crystallization content reaching to 60% in 0.3 min, and a second slow nucleation stage up to 25 min. Actually, the

second nucleation stage appears to be even longer at 200 °C since the scale factor is still increasing with reaction time. This behavior was investigated in another *in situ* experiment for a reaction time up to 80 min with the synthesis of $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_3$ at the reaction temperature of 200 °C (Figure 3d), and the scale factors were normalized to the value at 25 min. It shows that after a fast formation process, there is a slow nucleation with a continuous increase of the scale factors and the crystallization content at 80 min is 5% higher than that at 25 min.

The crystallization kinetics of solid-state phase transformation can be described using the Avrami equation:^{36,37}

$$\alpha = 1 - \exp [-k^n(t - t_0)^n] \quad (1)$$

where k is a rate constant, α is the fraction of transformation, t is the reaction time, t_0 is the induction time, and n is the Avrami exponent related to the crystallization mechanisms. There are different nucleation mechanisms for solid-state phase transformation. n parameters are normally larger than 1 for bulk nucleation mechanisms, and n parameters are close to 1 for surface nucleation mechanisms.^{38,39} Even though the formation process under hydrothermal/solvothermal conditions is not the same as a solid-state phase transformation, the Avrami equation has been successfully applied to analyze the hydrothermal/solvothermal formation of several materials.⁴⁰⁻⁴³ Here, we attempt to use the Avrami equation to describe the formation of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ as well. The solid lines of Figure 3a and 3b are the fits of the formation curves using the Avrami equation. Despite of the different nucleation process of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ with varying Sb content, it shows that most of the formation curves at high reaction temperatures of 250 and 300 °C can be reasonably described by the Avrami equation. Here, the Avrami models describe the entire nucleation process. However, as discussed above, the formation process of ternary $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ at 200 °C normally splits into two distinct nucleation stages, and the single Avrami

equation can not get reasonable fit for the entire formation curve. As a result, the formation curves of ternary $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ at 200 °C are modeled by Avrami equation only in the first 5 min. Table 2 displays the parameters k , n , and t_0 obtained by fitting the formation curves of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ at different reaction temperatures. Basically, the rate constant k increases with the reaction temperature due to an increase of motion and energy of the atoms. It also shows a lower rate constant with increasing Sb content in $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ indicating a slower kinetic process. The values of n are less than 1 at the reaction temperatures of 200 and 250 °C. The solvent has a large impeding effect on the crystallization kinetics under hydrothermal synthesis conditions, which is different from the known bulk or surface nucleation mechanism for solid-state transformations. However, the value of n increases with reaction temperature and it can be larger than 1 at 300 °C. Thus, at 300 °C the kinetics is similar to a solid-state phase transformation and the impeding effect of solvent is low. The n values of $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_3$ and Sb_2Te_3 are relative small at 300 °C.

Figure 3. (a) Formation curves of Bi_2Te_3 , BiSbTe_3 and Sb_2Te_3 at 250 °C. (b) Formation curves of BiSbTe_3 at 200 °C, 250 °C, and 300 °C, respectively. The formation curves are obtained from the scale factors normalized to the values at 25 min. The solid lines are the fits to the Avrami equation. (c) Arrhenius plot for obtaining the activation energy for the formation of BiSbTe_3 . (d) Formation curve of $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_3$ at 200 °C.

From the rate constant values (k) at different reaction temperatures, and thereby the activation energy (E_a) of the formation of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ can be obtained by plotting $\ln(k)$ against $1000/T$ following the Arrhenius equation:⁴³

$$k = A \exp(-E_a/RT) \quad (2)$$

where A is the pre-exponential factor, E_a the activation energy, R the gas constant. For example, from the slope of the plot (Figure 3c), the activation energy E_a for BiSbTe_3 was calculated to be around 35 $\text{kJ}\cdot\text{mol}^{-1}$. It can be seen that the activation energy clearly increases with increasing Sb content in $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ as displayed in Table 2.

Table 2. Parameters k , n , and t_0 by fitting the formation curves of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ at different reaction temperatures using the Avrami equation, and the activation energy (E_a) of the formation of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ obtained by Arrhenius plots.

$\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$	$x = 0$	$x = 0.5$	$x = 1$	$x = 1.5$	$x = 2$
Temperature (°C)	200	200	200	200	200
k (min^{-1})	23(4)	8.0(1)	3.2(4)	--	--
n	0.39(2)	0.36(2)	0.23(1)	--	--

t_0 (min)	0.14(1)	0.16(2)	0.16(1)	--	--
Temperature (°C)	250	250	250	250	250
k (min ⁻¹)	31(4)	15(4)	8.7(9)	2.1(1)	0.5(1)
n	0.41(2)	0.44(3)	0.36(4)	0.57(6)	0.63(1)
t_0 (min)	0.08(1)	0.01(3)	0.13(1)	0.14(1)	0.20(1)
Temperature (°C)	300	300	300	300	300
k (min ⁻¹)	46(8)	33(3)	15(3)	6(3)	3(2)
n	1.8(2)	0.6(3)	0.8(2)	1.5(7)	1.3(9)
t_0 (min)	0.07(1)	0.08(1)	0.08(2)	0.01(1)	0.01(1)
E_a (kJ·mol ⁻¹)	13(3)	31(5)	35(4)	52(20)	90(30)

3.3. Crystal Growth

The anisotropic size broadening of the SR-PXRD was modeled using a linear combination of spherical harmonics.^{23,35}

$$\beta_h = \frac{\lambda}{D_h \cdot \cos \theta} = \frac{\lambda}{\cos \theta} \sum_{lmp} a_{lmp} \cdot Y_{lmp}(\Theta_h, \Phi_h) \quad (3)$$

where β_h is the size contribution to the integral breadth of reflection h , and $Y_{lmp}(\Theta_h, \Phi_h)$ are normalized real spherical harmonics. The anisotropic sizes were calculated from the refined peak-shape parameters a_{lmp} . Figure 4a and 4b show the crystallite sizes along the a,b -plane and along the c -axis, respectively, for the growth of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ ($x = 0, 0.5, 1, 1.5$, and 2) at 200, 250 and 300 °C at the reaction time of 25 min. $D_{a,b\text{-plane}}$ values are much larger than $D_{c\text{-axis}}$, indicating that $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ crystals have platelet-like nanostructures. It shows that the reaction temperature has little influence on the crystallite size from 200 to 300 °C. However, the crystallite size changes with composition showing a “V”-shaped

dependency with x in $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$. At $T = 250\text{ }^\circ\text{C}$ and $t = 25\text{ min}$, $D_{a,b\text{-plane}}$ values are 14.4(3), 6.4(1) and 17.1(3) nm for Bi_2Te_3 , BiSbTe_3 , and Sb_2Te_3 , respectively, while $D_{c\text{-axis}}$ values are 5.4(1), 3.9(1) and 9.5(2) nm for Bi_2Te_3 , BiSbTe_3 , and Sb_2Te_3 , respectively. Among them, binary compounds Bi_2Te_3 and Sb_2Te_3 have relatively larger crystallite sizes, while ternary BiSbTe_3 has the smallest crystallite sizes.

As shown in Figure S7, the broadening of the (0 1 5) peak is comparable for BiSbTe_3 and Bi_2Te_3 . However, the peak at high 2θ (2 0 5) is obviously larger for BiSbTe_3 than for Bi_2Te_3 , indicating the presence of microstrain in BiSbTe_3 . Depending on θ positions, the microstrain (ε) and the peak broadening FWHM (β) follow the Williamson-Hall equation,

$$\beta\cos\theta = D + 4\varepsilon\sin\theta \quad (4)$$

where D is a parameter relative to the size-dependent effect. Figure S7c plots $\beta\cos\theta$ with respect to $4\sin\theta$ of selected diffraction peaks for Bi_2Te_3 and BiSbTe_3 at $t = 25\text{ min}$ and $T = 250\text{ }^\circ\text{C}$. The plot shows that the change of $\beta\cos\theta$ of Bi_2Te_3 is mainly due to the effect of the anisotropic size, and that the microstrain can be neglected in the Bi_2Te_3 nanoparticles. On the other hand, $\beta\cos\theta$ clearly increases with $4\sin\theta$ for BiSbTe_3 indicating a large effect of microstrain. If we neglect the effect of anisotropic size and assume that the microstrain is isotropic, the microstrain of BiSbTe_3 can be roughly derived from the slope with a value of 6.4×10^{-3} . The significant broadening of diffraction peaks at high 2θ for BiSbTe_3 compared with Bi_2Te_3 suggests that there could be large disorder and/or structure and composition fluctuations in the ternary BiSbTe_3 alloy due to the random distribution of the Bi and Sb in the structure, resulting in large microstrain in the ternary $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ structure.

Figure 4c and 4d show the time-dependent crystallite sizes along a,b -plane ($D_{a,b\text{-plane}}$) and along c -axis ($D_{c\text{-axis}}$), respectively, for the crystallite growth of Bi_2Te_3 , BiSbTe_3 and Sb_2Te_3 at $250\text{ }^\circ\text{C}$. For clarity, only the data before 10 min are plotted in Figure 4 since the growth processes of the crystallites

to the maximum values are very fast. Due to the limited time resolution of the experiments and the fast growth of Bi_2Te_3 , the initial crystallites detected are already very large. Thus, the initial crystals are a consequence of both nucleation and growth as they contain many atoms. The fast formation and growth of Bi_2Te_3 crystals could be due to the increase in the concentration of reduced tellurium species such that the system becomes supersaturated, followed by "burst" nucleation throughout the solution. The subsequent growth may be due to the continued formation of reduced tellurium species for a continuous nucleation. There are two common mechanisms to describe the crystal growth, Ostwald ripening and oriented attachment.⁴⁴ In comparing the growth curves (Figure 4c and 4d) with the formation curves (Figure 3a), it can be seen that the crystallite growth almost stopped once the nucleation ceased. More clearly, the formation rate and growth rate (Figure S8) were calculated by differentiating the formation curve and growth curve, respectively, of Bi_2Te_3 at 250 °C. The curves clearly show that both the formation rate and growth rate become zero in about 0.5 min, indicating that grain growth takes place during the formation process, while the Ostwald ripening is very limited. This is quite different from the growth of some oxides such as BiFeO_3 nanoparticles where the Ostwald ripening cannot be neglected.²⁶ The fast growth of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ crystals could be also a combination of agglomeration and growth. However, this is not likely in the present case. If the growth is due to the agglomeration of the initial nanocrystals, one would expect a large number of stacking defects. As discussed above, the microstrain can be neglected in the Bi_2Te_3 nanoparticles indicating limited stacking faults in the formation and growth of Bi_2Te_3 nanoparticles. This also suggests that the microstrain in BiSbTe_3 alloy is due to the random distribution of the Bi and Sb in the structure, rather than the staking faults from the growth of agglomeration. As a result, the growth of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ crystals is mainly caused by addition of monomers to continuously growing nuclei.

Taking into consideration the impeding forces on the grain-boundary movement due to the presence of impurities, pores or precipitates in nanocrystalline samples, a “size-dependent impediment” model has been reported to describe the dynamics of grain growth process of nanocrystalline materials.⁴⁵

$$D(t)^2 = D_{\max}^2 - (D_{\max}^2 - D_0^2)\exp(-k't) \quad (5)$$

where $D_{\max}$ is the maximum crystallite size. k' is a parameter related to the specific interface energy and grain boundary mobility, t is the reaction time, and D_0 is the initial crystallite size, which is fixed to zero in the present study. The solid lines in Figure 4c and 4d are the fits of the growth curves showing that the “size-dependent impediment” model gives a reasonable description of the growth kinetics. By fitting the growth curves, $D_{\max}$ values of 14.4(1), 6.2(1) and 11.4(1) nm, and k' values of 3.7(1), 4.0(1) and 0.3(1) min⁻¹ are obtained for the crystallite growth along a,b -plane of Bi₂Te₃, BiSbTe₃ and Sb₂Te₃, respectively, at the reaction temperature of 250 °C. $D_{\max}$ values of 5.4(1), 2.2(1) and 5.1(1) nm, and k' values of 2.0(1), 3.7(1) and 1.1(1) min⁻¹ are obtained for the crystallite growth along c -axis of Bi₂Te₃, BiSbTe₃ and Sb₂Te₃, respectively, at 250 °C. Bi₂Te₃ has larger k' values than Sb₂Te₃ indicating a faster growth rate of Bi₂Te₃ compared with that of Sb₂Te₃. It should be noted that due to the large disorder in the BiSbTe₃ crystal structure, the crystallite sizes calculated by the PXRD is likely underestimated compared with the real particle size. Therefore, the crystallite growth curves of BiSbTe₃ should be interpreted with care when describing the particle growth mechanisms.

The reaction temperature strongly affects the crystallite growth. Figure 4e and 4f show the crystal growth curves of Bi₂Te₃ along a,b -plane ($D_{a,b\text{-plane}}$) and along c -axis ($D_{c\text{-axis}}$), respectively, at the reaction temperatures of 200, 250 and 300 °C. By fitting the “size-dependent impediment” model, $D_{\max}$ values of 14.5(2), 14.4(1) and 16.2(1) nm, and k' values of 1.6(1), 3.7(1) and 4.4(3)min⁻¹ are obtained for the crystallite growth along a,b -plane at 200, 250 and 300 °C, respectively. $D_{\max}$ values of 5.1(1),

5.4(1) and 5.2(1) nm, and k' values of 1.1(1), 2.0(1) and 3.5(3) min^{-1} are obtained for the crystallite growth along c -axis at 200, 250 and 300 $^{\circ}\text{C}$, respectively. The results indicate that the final crystallite size D_{max} is almost unaffected by the reaction temperature. The reaction temperature significantly affects the crystallite growth mechanism as indicated by the kinetic rate parameter k' . The rate parameter k' values are larger along a,b -plane than along c -axis, resulting in anisotropic growth of the Bi_2Te_3 nanoparticles.

Figure 4. (a,b) Crystallite sizes along a,b -plane and along c -axis, respectively, for the growth of

$\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ ($x = 0, 0.5, 1, 1.5, \text{ and } 2$) at 200, 250 and 300 °C at the reaction time of 25 min. (c,d) Time-dependent crystallite sizes along a,b -plane and along c -axis, respectively, for the growth of Bi_2Te_3 , BiSbTe_3 and Sb_2Te_3 at 250 °C. (e,f) Time-dependent crystallite sizes along a,b -plane and along c -axis, respectively, for the growth of Bi_2Te_3 at 200, 250 and 300 °C. The solid lines in (c-f) are the fits using the “size-dependent impediment” growth model.

3.4. Formation Mechanisms

By analyzing the changes in the structural unit cell parameters with reaction time, it is possible to infer changes in the composition during the synthesis, thus to give a deep understanding of the formation mechanisms. Figure 5a and 5b show the time dependences of unit cell parameters a and c , respectively, of Bi_2Te_3 and BiSbTe_3 at reaction temperatures of 200 °C. Note that we can not compare the unit cell parameters obtained from the different sets of the *in situ* experiments directly due to the potential systematic error. However, a single coherent set of *in situ* measurements at each temperature ensures good correspondence between the data points. It can be seen that a decreases (c increases) with reaction time up to about 2 min during the nucleation stage of Bi_2Te_3 at 200 °C. From this it can be inferred that the Bi_2Te_3 is rich in Te in the initial nucleation stage, resulting in a relatively small unit cell parameter a and a larger unit cell parameter c . The unit cell parameters do not change with time after the nucleation stage, showing the stability of the composition of Bi_2Te_3 with prolonged reaction time at 200 °C. It is interesting to see that a decreases (c increases) with reaction time in the initial reaction period and then a continuously decreases (c increases) with time slowly until 25 min for BiSbTe_3 at 200 °C. As discussed above, BiSbTe_3 shows a two-stage nucleation mechanism at 200 °C with an initial fast nucleation stage followed by a second slower nucleation up to 25 min. The changes of unit cell

parameters are in accordance with a nucleation process with two stages. Due to the slow kinetic process of the reaction of the Sb precursor, the two-stage nucleation mechanism of BiSbTe₃ can be understood as an initial fast nucleation stage of primarily Bi₂Te₃ (or Bi-rich Bi_{2-x}Sb_xTe₃) followed by a second stage of slower nucleation and alloying process to the final composition of BiSbTe₃. Note that it may also be possible that Bi rich nanoplatelets form first and then Sb rich nanoplatelets form, resulting in composition fluctuation in the final products. The unit cell can also be changing due to the size-dependence of the nanoparticles, in which the unit cell parameters of nanoparticles normally decrease with decreasing size due to the surface stress. However, in the present study, the change of composition during the reaction should play a major role in the change of unit cells. As can be seen in Figure 5e, Te and BiSbTe₃ crystalline phases coexist during the synthesis at 200 °C. The weight fraction of BiSbTe₃ increases with time accompanied with the depletion of Te. The presence of elementary Te in the synthesis provides a Te excessive environment, which can possibly result in the formation of a Te-rich phase of BiSbTe₃. Meanwhile, the slow kinetic reaction of Sb results in a deficiency of Sb in the BiSbTe₃ phase. The composition approaches the stoichiometric ratio with a continuous increase of Sb content during the reaction at 200 °C corresponding to the continuous changes of the unit cell parameters with reaction time.

When the reaction temperature is increased to 250 °C as shown in Figure 5c and 5d, the formation processes seem different from those at 200 °C. For the synthesis of Bi₂Te₃ at 250 °C, due to the fast reaction kinetics, Bi and Te in the precursors are consumed almost simultaneously to form Bi₂Te₃ with the stoichiometric composition. As a result, the unit cell parameters of Bi₂Te₃ at 250 °C are almost constant with reaction time. For the synthesis of BiSbTe₃ at 250 °C, *a* decreases whereas *c* increases with time up to 3 min and then both *a* and *c* become almost constant with reaction time. The unit cell

parameters change distinctly in the nucleation stage from $a = 4.4802(9) \text{ \AA}$ and $c = 30.891(9) \text{ \AA}$ at 0.17 min to $a = 4.4304(4) \text{ \AA}$ and $c = 31.233(3) \text{ \AA}$ at 3 min. This can be attributed to the transformation process from the Te-rich and Sb deficient BiSbTe_3 to a more stoichiometric BiSbTe_3 . As shown in Figure 5f, elementary Te is absent after the reaction time of 2 min. Since the same Te precursors are used for the formation of different $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$, the initial step in the all reactions should be the reduction of TeO_3^{2-} to more reduced tellurium species which can be elemental Te and/or polytelluride anions. During the reaction, the concentration of TeO_3^{2-} decreases and the concentration of more reduced tellurium species increases. It seems that elemental Te forms before making a series of different polytelluride anions, and the formation of tellurides proceeds by the reaction of the metal cations with the polytelluride anions. Thus, the formation kinetics of different $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ should be controlled by the reaction of the metal cations (Bi^{3+} and Sb^{3+}) with the polytelluride anions, i.e., the nucleation of the crystalline phase. It is suggested that the reaction of Bi^{3+} (or Bi complex cations) with polytelluride anions is very fast which promotes the transformation from elemental Te to polytellurides so that Te is absent during the formation of Bi_2Te_3 under the current experimental time resolution. However, the reaction of Sb^{3+} (or Sb complex cations) with polytelluride anions is much slower resulting in the slow nucleation of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$. Note that the metal cations exist in different complexes, and the reactivity of the Bi and Sb complexes with polytelluride anions are likely to be different which affects the formation kinetics of different $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$.

Separate *ex situ* experiments for the synthesis of Bi_2Te_3 , BiSbTe_3 and Sb_2Te_3 were performed in a custom-designed coil autoclave under the reaction temperature of 250 °C with a reaction time of 30 min. Figure 6 shows the STEM images and EDS elemental mapping analysis of the element distributions for Bi_2Te_3 , BiSbTe_3 and Sb_2Te_3 . The STEM image shows that the Bi_2Te_3 sample consists

of small nanoplatelets with typical diameters of about 30 nm and thicknesses of about 10 nm. Larger nanostrings consisting of nanoplatelets are formed for BiSbTe_3 and Sb_2Te_3 . As discussed above, elemental Te is present as intermediate product for the synthesis of BiSbTe_3 and Sb_2Te_3 . The presence of Te intermediate products plays a critical role in the formation of the distinct nanostring structures of BiSbTe_3 and Sb_2Te_3 . It agrees well with the previous studies that the intermediate product of Te nanowires serves as templates for the formation of Bi_2Te_3 nanostrings using alginic acid as reductant.⁴⁶ The EDS elemental mapping analysis confirms the formation of Bi_2Te_3 , BiSbTe_3 and Sb_2Te_3 with homogeneous elemental distribution.

Figure 5. (a,b) Time evolutions of unit cell parameters of Bi_2Te_3 and $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_3$ at 200 °C. (c,d) Time evolutions of unit cell parameters of Bi_2Te_3 and $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_3$ at 250 °C. (e,f) Time evolutions of weight fractions for different crystalline phases in the synthesis of BiSbTe_3 at reaction temperatures of 200 and 250 °C, respectively.

The overall formation mechanisms of different $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ are illustrated in Figure 7. As discussed above, the synthesis processes of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ depend strongly on the composition and reaction temperature. Taking the reaction temperature of 250 °C for example, the initial step in the all reactions

is the reduction of TeO_3^{2-} to more reduced tellurium species. Elemental Te is absent for the formation of Bi_2Te_3 due to the fast reaction of the metal cations with the polytelluride anions. Nanoplatelets are formed as a result of the anisotropic growth due to the layered structure of Bi_2Te_3 (Figure 7a). With the increase of Sb content in the composition, the presence of intermediate product of Te nanorods forms and serves as a template for the synthesis of special hierarchical structure of nanostrings composed of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ nanoplatelets (Figure 7b).

Figure 6. STEM images and EDS elemental mapping analysis of the element distributions for the samples prepared in the custom-designed coil autoclave under the reaction temperature of 250 °C with the reaction time of 30 min. (a-c) Bi_2Te_3 , (d-g) BiSbTe_3 , and (h-j) Sb_2Te_3 .

Figure 7. Schematic illustration of the formation mechanisms of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$.

4. CONCLUSIONS

High intensity *in situ* SR-PXRD is a powerful method to obtain detailed information about the formation and growth processes of nanoparticles in hydrothermal/solvothermal synthesis, which makes possible controllable synthesis of nanomaterials with tailored structures and properties. The *in situ* study reveals a fast nucleation process of Bi_2Te_3 . The nucleation process is slower when the Sb content increases in $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$. It is found that the formation of BiSbTe_3 at 200 °C involves an initial nucleation stage of Bi_2Te_3 and a second stage of slower nucleation and alloying process to BiSbTe_3 , accompanying with the composition evolution with reaction time. The crystallization kinetics is different from the bulk or surface nucleation mechanism due to the impeding effect of the solvent in the synthesis. Fitting the formation curves with an Arrhenius model, the activation energies are obtained, and the activation energy increases with increasing Sb content in $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$. Anisotropic dimensions

are found for $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ nanoparticles with larger crystallite sizes along the a,b -plane than along the c -axis. The “size-dependent impediment” model provides good fits to the growth curves of the $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ nanoplatelets. The microstrain can be neglected in Bi_2Te_3 , while distinct microstrain is found in the ternary BiSbTe_3 structure. The presence of intermediate product of Te is required to serve as a template for the synthesis of special hierarchical structure of nanostrings composed of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ nanoplatelets.

ASSOCIATED CONTENT

Supporting Information

Pictures of the coil autoclave, additional SR-PXRD patterns, weight fractions of Sb_2Te_3 at 250 °C, diffraction peaks broadening analysis of Bi_2Te_3 and BiSbTe_3 at $t = 25$ min and $T = 250$ °C, TEM image of Bi_2Te_3 prepared at $T = 250$ °C. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: jlmi@ujs.edu.cn

*E-mail: bo@chem.au.dk

Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the beamtime obtained at beamline I711, MAX-lab synchrotron radiation source, Lund University, Sweden. Dr. Per S. Christensen is thanked for technical assistance with the *ex-situ* syntheses using the custom-designed coil reactor. This work was supported by the National Natural Science Foundation of China (Grant 51401089), the Natural Science Foundation of Jiangsu Province (Grant BK20140552), the Scientific Research Foundation of Jiangsu University (Grant 14JDG013), the Specialized Research Fund for Cultivating Academic Leader of Jiangsu University, the Danish National Research Foundation (Center for Materials Crystallography, DNRF93), and the European Commission under the Seventh Framework Programme CALIPSO (Grant 312284).

REFERENCES

- (1) Kim, S. I.; Lee, K. H.; Mun, H. A.; Kim, H. S.; Hwang, S. W.; Roh, J. W.; Yang, D. J.; Shin, W. H.; Li, X. S.; Lee, Y. H.; Snyder, G. J.; Kim, S. W. Dense Dislocation Arrays Embedded in Grain Boundaries for High-Performance Bulk Thermoelectrics. *Science* **2015**, *348*, 109-114.
- (2) Zhang, H.; Liu, C. X.; Qi, X. L.; Dai, X.; Fang, Z.; Zhang, S. C. Topological Insulators in Bi₂Se₃, Bi₂Te₃ and Sb₂Te₃ with a Single Dirac Cone on the Surface. *Nat. Phys.* **2009**, *5*, 438-442.
- (3) Dresselhaus, M. S.; Chen, G.; Tang, M. Y.; Yang, R.; Lee, H.; Wang, D.; Ren, Z.; Fleurial, J.-P.; Gogna, P. New Directions for Low-Dimensional Thermoelectric Materials. *Adv. Mater.* **2007**, *19*, 1043-1053.
- (4) Zhao, X. B.; Ji, X. H.; Zhang, Y. H.; Zhu, T. J.; Tu, J. P.; Zhang, X. B. Bismuth Telluride Nanotubes and the Effects on the Thermoelectric Properties of Nanotube-Containing Nanocomposites. *Appl. Phys. Lett.* **2005**, *86*, 062111.
- (5) Zhang, H. T.; Luo, X. G.; Wang, C. H.; Xiong, Y. M.; Li, S. Y.; Chen, X. H. Characterization of

- Nanocrystalline Bismuth Telluride (Bi_2Te_3) Synthesized by a Hydrothermal Method. *J. Cryst. Growth* **2004**, *265*, 558-562.
- (6) Feng, H. Q.; Wu, C. Y.; Zhang, P.; Mi, J. L.; Dong, M. D. Facile Hydrothermal Synthesis and Formation Mechanisms of Bi_2Te_3 , Sb_2Te_3 and $\text{Bi}_2\text{Te}_3\text{-Sb}_2\text{Te}_3$ Nanowires. *RSC Adv.* **2015**, *5*, 100309-100315.
- (7) Zhang, Y.; Hu, L. P.; Zhu, T. J.; Xie, J.; Zhao, X. B. High Yield Bi_2Te_3 Single Crystal Nanosheets with Uniform Morphology via a Solvothermal Synthesis. *Cryst. Growth Des.* **2013**, *13*, 645-651.
- (8) Zhu, H. T.; Luo, J.; Fan, H. M.; Zhang, H.; Liang, J. K.; Rao, G. H.; Li, J. B.; Liu, G. Y.; Du, Z. M. Tri-Wing Bismuth Telluride Nanoribbons with Quasi-Periodic Rough Surfaces. *J. Mater. Chem.* **2011**, *21*, 12375-12380.
- (9) Ge, Z. H.; Nolas, G. S. Controllable Synthesis of Bismuth Chalcogenide Core-Shell Nanorods. *Cryst. Growth Des.* **2014**, *14*, 533-536.
- (10) Bøjesen, E. D.; Iversen, B. B. The Chemistry of Nucleation, *CrystEngComm* **2016**, *18*, 8332-8353.
- (11) Alayoglu, S.; Zavalij, P.; Eichhorn, B.; Wang, Q.; Frenkel, A. I.; Chupas, P. Structural and Architectural Evaluation of Bimetallic Nanoparticles: A Case Study of Pt-Ru Core-Shell and Alloy Nanoparticles. *ACS Nano* **2009**, *3*, 3127-3137.
- (12) Liang, L.X.; Deng, Y.; Wang, Y.; Gao, H. L. Epitaxial Formation of Core-Shell Heterostructured $\text{Bi}_2\text{Te}_3\text{@Sb}_2\text{Te}_3$ hexagonal nanoplates. *J. Nanopart. Res.* **2014**, *16*, 2138.
- (13) Fei, F.; Wei, Z.; Wang, Q.; Lu, P.; Wang, S.; Qin, Y.; Pan, D.; Zhao, B.; Wang, X.; Sun, J.; Wang, X.; Wang, P.; Wan, J.; Zhou, J.; Han, M.; Song, F.; Wang, B.; Wang, G. Solvothermal Synthesis of Lateral Heterojunction $\text{Sb}_2\text{Te}_3/\text{Bi}_2\text{Te}_3$ Nanoplates. *Nano Lett.* **2015**, *15*, 5905-5911.
- (14) Thanh, N. T. K.; Maclean, N.; Mahiddine, S. Mechanisms of Nucleation and Growth of

- Nanoparticles in Solution. *Chem. Rev.* **2014**, *114*, 7610-7630.
- (15) Zheng, H.; Smith, R. K.; Jun, Y.; Kisielowski, C.; Dahmen, U.; Alivisatos, A. P. Observation of Single Colloidal Platinum Nanocrystal Growth Trajectories. *Science* **2009**, *324*, 1309-1312.
- (16) Polte, J.; Ahner, T.; Delissen, F.; Sokolov, S.; Emmerling, F.; Thünemann, A. F.; Kraehnert, R. Mechanism of Gold Nanoparticle Formation in the Classical Citrate Synthesis Method Derived from Coupled in situ XANES and SAXS Evaluation. *J. Am. Chem. Soc.* **2010**, *132*, 1296-1301.
- (17) Yao, T.; Sun, Z.; Li, Y.; Pan, Z.; Wei, H.; Xie, Y.; Nomura, M.; Niwa, Y.; Yan, W.; Wu, Z.; Jiang, Y.; Liu, Q.; Wei, S. Insights into Initial Kinetic Nucleation of Gold Nanocrystals. *J. Am. Chem. Soc.* **2010**, *132*, 7696-7701.
- (18) Harada, M.; Kizaki, S. Formation Mechanism of Gold Nanoparticles Synthesized by Photoreduction in Aqueous Ethanol Solutions of Polymers Using In Situ Quick Scanning X-ray Absorption Fine Structure and Small-Angle X-ray Scattering. *Cryst. Growth Des.* **2016**, *16*, 1200-1212.
- (19) Agthe, M.; Plivelic, T. S.; Labrador, A.; Bergström, L.; Salazar-Alvarez, G. Following in Real Time the Two-Step Assembly of Nanoparticles into Mesocrystals in Levitating Drops. *Nano Lett.* **2016**, *16*, 6838-6843.
- (20) Chen, S.; Yang, Q.; Wang, H.; Zhang, S.; Li, J.; Wang, Y.; Chu, W.; Ye, Q.; Song, L. Initial Reaction Mechanism of Platinum Nanoparticle in Methanol-Water System and the Anomalous Catalytic Effect of Water. *Nano Lett.* **2015**, *15*, 5961-5968.
- (21) Uehara, A.; Booth, S. G.; Chang, S. Y.; Schroeder, S. L. M.; Imai, T.; Hashimoto, T.; Mosselmans, J. F. W.; Dryfe, R. A. W. Electrochemical Insight into the Brust-Schiffrin Synthesis of Au Nanoparticles. *J. Am. Chem. Soc.* **2015**, *137*, 15135-15144.

- (22) Abécassis, B.; Testard, F.; Spalla, O.; Barboux, P. Probing in situ the Nucleation and Growth of Gold Nanoparticles by Small-Angle X-ray Scattering. *Nano Lett.* **2007**, *7*, 1723-1727.
- (23) Bremholm, M.; Becker-Christensen, J.; Iversen, B. B. High-Pressure, High-Temperature Formation of Phase-Pure Monoclinic Zirconia Nanocrystals Studied by Time-Resolved in situ Synchrotron X-Ray Diffraction. *Adv. Mater.* **2009**, *21*, 3572-3575.
- (24) Jensen, K. M.; Christensen, M.; Bremholm, M.; Iversen, B. B. Structure, Size, and Morphology Control of Nanocrystalline Lithium Cobalt Oxide. *Cryst. Growth Des.* **2011**, *11*, 753-758.
- (25) Mi, J. L.; Clausen, C.; Bremholm, M.; Lock, N.; Jensen, K. M. Ø.; Christensen, M.; Iversen, B. B. Rapid Hydrothermal Preparation of Rutile TiO₂ Nanoparticles by Simultaneous Transformation of Primary Brookite and Anatase: An in Situ Synchrotron PXRD Study. *Cryst. Growth Des.* **2012**, *12*, 6092-6097.
- (26) Mi, J. L.; Jensen, T. N.; Christensen, M.; Tyrsted, C.; Jørgensen, J. E.; Iversen, B. B. High-Temperature and High-Pressure Aqueous Solution Formation, Growth, Crystal Structure, and Magnetic Properties of BiFeO₃ Nanocrystals. *Chem. Mater.* **2011**, *23*, 1158-1165.
- (27) Jensen, K. M. Ø.; Tyrsted, C.; Bremholm, M.; Iversen, B. B. In Situ Studies of Solvothermal Synthesis of Energy Materials. *ChemSusChem.* **2014**, *7*, 1594-1611.
- (28) Mi, J. L.; Clausen, H. F.; Bremholm, M.; Schmøkel, M. S.; Hernández-Fernández, P.; Becker, J.; Iversen, B. B. Pulsed-Flow Near-Critical and Supercritical Synthesis of Carbon-Supported Platinum Nanoparticles and in Situ X-Ray Diffraction Study of Their Formation and Growth. *Chem. Mater.* **2015**, *27*, 450-456.
- (29) Nørby, P.; Roelsgaard, M.; Søndergaard, M.; Iversen, B. B. Hydrothermal Synthesis of CoSb₂O₄: In Situ Powder X-ray Diffraction, Crystal Structure, and Electrochemical Properties. *Cryst. Growth*

Des. **2016**, *16*, 834-841.

- (30) Becker, J.; Bremholm, M.; Tyrsted, C.; Pauw, B.; Jensen, K. M. Ø.; Eltzholt, J.; Christensen, M.; Iversen, B. B. Experimental Setup for in Situ X-Ray SAXS/WAXS/PDF Studies of the Formation and Growth of Nanoparticles in Near-and Supercritical Fluids. *J. Appl. Cryst.* **2010**, *43*, 729-736.
- (31) Mi, J. L.; Christensen, M.; Tyrsted, C.; Jensen, K. Ø.; Becker, J.; Hald, P.; Iversen, B. B. Formation and Growth of Bi₂Te₃ in Biomolecule-Assisted Near-Critical Water: In Situ Synchrotron Radiation Study. *J. Phys. Chem. C* **2010**, *114*, 12133-12138.
- (32) Song, J.; Xia, F.; Zhao, M.; Zhong, Y. L.; Li, W.; Loh, K. P.; Caruso, R. A.; Bao, Q. Solvothermal Growth of Bismuth Chalcogenide Nanoplatelets by the Oriented Attachment Mechanism: An in Situ PXRD Study. *Chem. Mater.* **2015**, *27*, 3471-3482.
- (33) Hammersley, A. P.; Svensson, S. O.; Hanfland, M.; Fitch, A. N.; Hausermann, D. Two-Dimensional Detector Software: from Real Detector to Idealised Image or Two-Theta Scan. *High Pressure Res.* **1996**, *14*, 235-248.
- (34) Rodriguez-Carvajal, J. Recent Advances in Magnetic Structure Determination by Neutron Powder Diffraction. *Physica B*, **1993**, *192*, 55-69.
- (35) Jarvinen, M. Application of Symmetrized Harmonics Expansion to Correction of the Preferred Orientation Effect. *J. Appl. Crystallogr.* **1993**, *26*, 525-531.
- (36) Avrami, M. Kinetics of Phase Change. I General Theory. *J. Chem. Phys.* **1939**, *7*, 1103-1112.
- (37) Zhang, H.; Banfield, J. F. Kinetics of Crystallization and Crystal Growth of Nanocrystalline Anatase in Nanometer-Sized Amorphous Titania. *Chem. Mater.* **2002**, *14*, 4145-4154.
- (38) Matusita, K.; Sakka, S. Kinetic Study of Crystallization of Glass by Differential Thermal Analysis--Criterion on Application of Kissinger Plot. *J. Non-Cryst. Solids* **1980**, *38*, 741-746.

- (39) Fernández-García, M.; Wang, X.; Belver, C.; Hanson, J. C.; Rodriguez, J. A. Anatase-TiO₂ Nanomaterials: Morphological/Size Dependence of the Crystallization and Phase Behavior Phenomena. *J. Phys. Chem. C* **2007**, *111*, 674-682.
- (40) Mi, J. L.; Jensen, K. M. Ø.; Tyrsted, C.; Bremholm, M.; Iversen, B. B. In Situ Total X-Ray Scattering Study of the Formation Mechanism and Structural Defects in Anatase TiO₂ Nanoparticles under Hydrothermal Conditions. *CrystEngComm* **2015**, *17*, 6868-6877.
- (41) Mi, J. L.; Nørby, P.; Bremholm, M.; Becker, J.; Iversen, B. B. The Formation Mechanism of Bimetallic PtRu Alloy Nanoparticles in Solvothermal Synthesis. *Nanoscale* **2015**, *7*, 16170-16174
- (42) Nørby, P.; Johnsen, S.; Iversen, B. B. In Situ X-ray Diffraction Study of the Formation, Growth, and Phase Transition of Colloidal Cu_{2-x}S Nanocrystals. *ACS Nano* **2014**, *8*, 4295-4303.
- (43) Xia, F.; Chen, D.; Scarlett, N. V. Y.; Madsen, I. C.; Lau, D.; Leoni, M.; Ilavsky, J.; Brand, H. E. A.; Caruso, R. A. Understanding Solvothermal Crystallization of Mesoporous Anatase Beads by In Situ Synchrotron PXRD and SAXS. *Chem. Mater.* **2014**, *26*, 4563-4571.
- (44) Li, D.; Nielsen, M. H.; Lee, J. R. I.; Frandsen, C.; Banfield, J. B.; De Yoreo, J. J. Direction-Specific Interactions Control Crystal Growth by Oriented Attachment. *Science* **2012**, *336*, 1014-1018.
- (45) Natter, H.; Schmelzer, M.; Löffler, M. S.; Krill, C. E.; Fitch, A.; Hempelmann, R. Grain-Growth Kinetics of Nanocrystalline Iron Studied in Situ by Synchrotron Real-Time X-Ray Diffraction. *J. Phys. Chem. B* **2000**, *104*, 2467-2476.
- (46) Mi, J. L.; Lock, N.; Sun, T.; Christensen, M.; Søndergaard, M.; Hald, P.; Hng, H. H.; Ma, J.; Iversen, B. B. Biomolecule-Assisted Hydrothermal Synthesis and Self-Assembly of Bi₂Te₃ Nanostring-Cluster Hierarchical Structure. *ACS Nano* **2010**, *4*, 2523-2530.

Table of Contents Graphic