# Nanotechnology

# **Conversion Reactions of Solids: From a Surprising Three-Step Mechanism towards Directed Product Formation**

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Dedicated to Professor Henri Brunner on the occasion of his 80th birthday

**Abstract:** Directed conversion reactions from binary to multinary compounds are discovered from the reaction of  $Bi_2S_3$  and  $Bi_2Se_3$  with  $NiCl_2$ ·6 $H_2O$  in polyol media under basic conditions. Control of the synthesis conditions allows the preparation of NiBiSe and superconducting  $Ni_3Bi_2S_2$  and  $Ni_3Bi_2Se_2$ . The formation of  $Ni_3Bi_2S_2$  from  $Bi_2S_3$  is found from an unexpected three-step reaction path with Bi and NiBi as intermediates. In the more complex Ni/Bi/Se system, the

# Introduction

Inorganic chemistry of Bi compounds not only attracts attention because of a fascinating variety of clusters,<sup>[1]</sup> nano,<sup>[2]</sup> and intermetallic structures.<sup>[3,4]</sup> but it also serves as a key element in innovative thermoelectric materials and topological insulators, such as Bi<sub>2</sub>Se<sub>3</sub>, BaBiO<sub>3</sub>, and Bi<sub>14</sub>Rh<sub>3</sub>I<sub>9</sub>.<sup>[5-7]</sup> The latter combines several structural features; to identify these and other Bi compounds, computational chemistry is increasingly applied.<sup>[5-9]</sup> To obtain them experimentally, new methods of synthesis have been developed,<sup>[7,10]</sup> which have even allowed the study of metastable Bi-containing phases, as exemplified for NiBi<sub>x</sub>.<sup>[11]</sup> Related Bi compounds seem thus well suited to further explore and elucidate directed reaction paths and mechanisms.<sup>[12]</sup> Knowledge therein is not only desired in case of competing product formation but also with respect to environmental demands.<sup>[13-14]</sup>

For a long time, mechanisms of formation of inorganic solids remained a "black box". A new decade therein started with upcoming solution-based methods. By the polyol route<sup>[15-16]</sup> or the synthesis in ionic liquids<sup>[17-18]</sup> a number of in-

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Institute of Inorganic Chemistry, University of Regensburg Universitätsstraße 31, 93040 Regensburg (Germany) tion between the competing ternaries and to suppress sideproduct formation. Contrary to solid-state reactions (500– 900 °C) control of product formation is reached at reaction temperatures and times between 166–300 °C and 0.5–10 h, respectively. The formation of different phases is discussed from results of DFT calculations.

mechanism found can be used to selectively direct the reac-

organic solids can be attained at mild conditions and low temperatures.<sup>[10,19]</sup> They were developed as effective methods to produce phase-pure micro- or nanoscale inorganic compounds. To study and direct reaction paths therein, conversion and pseudomorph reactions turn out to be useful.<sup>[9,20-22]</sup> Thereby, precursor particles are transformed into desired compounds and properties can be changed or added. Examples are the conversion of Co nanocrystals into  $Co_3S_4$  and  $Co_9S_8$  nanocrystals in the presence of sulfur in solution by a simple diffusion-based mechanism.<sup>[22]</sup> By multistep paths, also multinary intermetallic compounds are obtained.<sup>[23]</sup>

As part of our ongoing investigations into functional conversions, SnS particles were recently shown to react with NiCl<sub>2</sub>·6H<sub>2</sub>O in alkaline ethylene glycol at 197 °C.<sup>[24]</sup> By adjusting reductive conditions Ni<sub>3</sub>Sn<sub>2</sub>S<sub>2</sub><sup>[25]</sup> and core-shell Ni@SnS particles are obtained. Their formation and binary side products depend on kinetics and equilibriums of dissolution and redox reactions. A diffusion-driven transformation was concluded similar to the conversion of PbS to  $Ni_3Pb_2S_2$ .<sup>[26]</sup> In both cases, binary chalcogenide precursors AX are converted to perovskite-related  $M_3A_2X_2 = M_{1.5}AX$  compounds<sup>[9, 24-27]</sup> by adding the transitionmetal Ni. As from solid-state reactions pyrite-type PtSnS<sup>[28]</sup> is formed from SnS+Pt, hypothetical "NiAX" was computed from total-energy DFT calculations. For A = Sn, Pb and X = S, Se the NiAX phases are predicted to be less stable than the Ni15AX compounds.<sup>[29]</sup> However, the question appeared on directed syntheses of possible metastable or competing products on the path AX + Ni.

This question is picked up subsequently for conversion reactions of the binary semiconductors  $Bi_2S_3$  and  $Bi_2Se_3$  with  $NiCl_2 \cdot 6H_2O$  in ethylene glycol (eg) or tetraethylene glycol (TEG). First, the reaction mechanism of the reported transformation<sup>[30]</sup> of  $Bi_2S_3$  to superconducting  $Ni_3Bi_2S_2^{[25,31,32]}$  is studied in ethyl-

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ene glycol. A proposed diffusion mechanism of nickel into Bi<sub>2</sub>S<sub>3</sub> seemed unlikely because of the change in the Bi/S ratio and the unexplained formation of elementary Bi that is ob-

 $Bi_2S_3$  seemed unlikely because of the change in the Bi/S ratio and the unexplained formation of elementary Bi that is observed in the diffraction pattern. Subsequently presented polyol-mediated reactions show a surprising multistep mechanism for the transformation of  $Bi_2S_3$  to  $Ni_3Bi_2S_2$ . Therein, the formation of Bi and  $NiBi^{(11,33)}$  plays an important role. In a next step, knowledge of the mechanism is applied for directed conversions of  $Bi_2Se_3$  with  $Ni^{2+}$ . The aim was to find separate reaction pathways to the competing products  $Ni_3Bi_2Se_2$  and NiBiSeand to suppress other side products. By a similar approach, the synthesis of still unknown NiBiS was attempted. The competing phase stability of the 3:2:2 and 1:1:1 phase was analyzed by total-energy DFT calculations.

The reported results not only serve as an example for directed reactions to adjust the M content along the AX + M pathway, they also show the successful use of binary intermetallic "templates" for the formation of ternary products, which is still a rare method.<sup>[34]</sup> The evaluated multistep reaction mechanism may help to study and direct further reactions of Bi-containing materials in "soft" solid-state chemistry.

# **Results and Discussion**

## Studied reaction paths

The studied compositional and structural transformations are rationalized from the phase diagram (Figure 1). Along the line AX + M, bulk powders of cubic PbS and orthorhombic SnS can be transformed with Ni at elevated temperatures ( $T > 400 \,^{\circ}$ C, path 1) in pure solid-state reactions into trigonal-layered shandite-type Ni<sub>3</sub>Pb<sub>2</sub>S<sub>2</sub> and isotypic Ni<sub>3</sub>Sn<sub>2</sub>S<sub>2</sub>. This path is also used under mild conditions ( $T = 166 - 197 \,^{\circ}$ C) from SnS and PbS nanoparticles in a reductive solution of Ni<sup>2+</sup>.<sup>[24,26]</sup> A diffusion-driven mechanism was proven for the formation of the ternaries, whereas core-shell particles Ni@SnS are formed by a more rapid reduction. A similar mechanism for the conversion of the layered monoclinic superconductor Ni<sub>3</sub>Bi<sub>2</sub>X<sub>2</sub> (X=S, Se), however, requires a change in the Bi:X ratio. For the reaction of Bi<sub>2</sub>Se<sub>3</sub> with Ni<sup>2+</sup>, even two products compete with the known parker-





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Figure 2. Schematic representation of the found reaction pathways from  $Bi_2X_3$  (X = S, Se) to Bi, NiBi, NiBiSe, and  $Ni_3Bi_2X_2$ .

ite  $(Ni_3Bi_2Se_2)$  and pyrite (NiBiSe, Figure 1, paths 2 and 3). Upon a possible transformation of NiBiSe to  $Ni_3Bi_2Se_2$  (=  $Ni_{3/2}BiSe$ ), the Ni content is increased (Figure 1, path 4).

All compounds under consideration are summarized in Figure 2 to point out the structural differences of educts and products. Contrary to the two-dimensional Bi–X (X = S, Se) structures in Bi<sub>2</sub>S<sub>3</sub> and Bi<sub>2</sub>Se<sub>3</sub>, Bi and Se form Bi–Se dumbbells in pyrite related NiSbS-type NiBiSe.<sup>[9,28]</sup> Ni atoms are found in octahedrons NiBi<sub>3</sub>Se<sub>3</sub>. The Ni<sub>3</sub>Bi<sub>2</sub>X<sub>2</sub> compounds exhibit CsCl-like BiX substructures with Ni atoms in half of the available tetragonal bipyramides X<sub>2</sub>Bi<sub>4</sub>. Because of the structural relations to O-deficite perovskites, the monoclinic parkerites (*C*2/*m*) and trigonal shandites (*R*3*m*) were classified as half antiperovskites.<sup>[27]</sup> They differ in Ni-site occupation and contain low-dimensional [Ni<sub>3</sub>X<sub>2</sub>] substructures related to P and As<sup>[9c]</sup> with the rare situation of Ni<sup>0</sup> in linear X–Ni–X coordination.

#### Conversion chemistry in the Bi-NiBi-Ni<sub>3</sub>Bi<sub>2</sub>S<sub>2</sub> system

The unknown mechanism for path 2 with X = S is studied first and compared to the results of Shao and co-workers who proposed a simple diffusion-driven reaction of nickel into Bi<sub>2</sub>S<sub>3</sub>.<sup>[30]</sup> However, the formation of Ni<sub>3</sub>Bi<sub>2</sub>S<sub>2</sub> thereby seems strange as not only an element (here Ni) is added but also one must be lost (expected: S). A different mechanism is indicated by the occurrence of elementary Bi as a side product that is observed in the diffraction pattern, but not commented. Based on this ambiguity, our first aim was to clarify a more probable mechanism of the reaction.

The reported (one-pot) low-temperature self-template route to Ni<sub>3</sub>Bi<sub>2</sub>S<sub>2</sub> starts with Bi<sub>2</sub>S<sub>3</sub>/NiCl<sub>2</sub>·6 H<sub>2</sub>O (molar ratio 1:3) in an ethylene glycol (eg)/ethylenediamine (en) mixture and additional NaOH to increase the reduction potential of the solution.<sup>[30]</sup> By a reproduction of the one-pot approach under slightly modified conditions, the starting material Bi<sub>2</sub>S<sub>3</sub> is already entirely converted to Ni<sub>3</sub>Bi<sub>2</sub>S<sub>2</sub> and Bi as a side phase after 30 min at 166 °C (Figure S1a and S1b, Supporting Information). This shows that the reaction already starts at even lower temperatures than thought before. After extending the reaction



time to 10.5 h at 197 °C, Bi cannot be detected anymore in the XRD. It seems that the excess Bi was dissolved and washed out. In principle one could conclude on a self-template mechanism as proposed by Shao and co-workers. The ribbon-shaped structure of the reactant  $Bi_2S_3$  and the obtained product  $Ni_3Bi_2S_2$  can be seen in Figure S2, Supporting Information. However, after sintering the product in an evacuated ampoule at 300–500 °C,  $Bi_2S_3$  and Bi are still found as side phases, which were not crystalline enough to be detected before. One must conclude that the reaction is not just nickel diffusion into  $Bi_2S_3$ , but proceeds over multiple, different steps.<sup>[33]</sup> Therefore  $Bi_2S_3$  might not act as the template during the reaction.

To elucidate the questioned mechanism of formation, the reevaluated one-pot synthesis was split into three parts (Figure 3). The exact amount of solvents and reagents that deviate from the standard one-pot synthesis, described in the experimental part, are summarized in the Supporting Information



**Figure 3.** XRD patterns of the decoupled one-pot reaction a) SR1: Collected Bi after reduction of Bi<sub>2</sub>S<sub>3</sub> in an eg/en/NaOH mixture b) SR2: NiBi after reaction of Bi with Ni<sup>2+</sup> in an eg/en/NaOH mixture c) SR3: Ni<sub>3</sub>Bi<sub>2</sub>S<sub>2</sub>+Bi after reaction of NiBi with S or Na<sub>2</sub>S at 197 °C in an eg/en/NaOH mixture (molar ratio 1:1 or 3:2).

(SR1–SR8; they are referenced with SRn with n as the number of the reaction in the Supporting Information). In a first step, Bi<sub>2</sub>S<sub>3</sub> was reacted at 197 °C without the addition of NiCl<sub>2</sub>·6H<sub>2</sub>O, which led to elementary Bi as the only product after a short time (SR1, Supporting Information and Figure 3a). This is due to the temperature-dependent reduction potential of basic ethylene glycol. It is known that Bi<sub>2</sub>S<sub>3</sub> can be reduced in ethylene glycol at temperatures above 150°C and S<sup>2-</sup> ions are evolved.[10,35] Surprisingly, intermetallic NiBi is obtained when reacting the obtained Bi particles with NiCl<sub>2</sub>·6H<sub>2</sub>O at 197 °C in an eg/en/NaOH mixture for more than 10 h (SR2, Supporting Information, Figure 3b). This step is very sensitive to the synthesis conditions, as NiBi is often contaminated with NiBi<sub>3</sub>, possibly due to agglomerated Bi particles derived from the first reductive step. Reaction of the collected NiBi with Na2S or S (molar ratio 1:1 or 3:2) in an eg/en/NaOH solution leads to Ni<sub>3</sub>Bi<sub>2</sub>S<sub>2</sub> and the obligatory Bi (SR3; Figure 3 c and Scheme 1 a). During the whole process no other possible binary or ternary compounds like Ni<sub>3</sub>S<sub>2</sub> or NiBiS occurred. Trials to convert NiBi<sub>3</sub> into ternaries were not successful. We suggest that the mecha-



 $\label{eq:scheme1} \begin{array}{l} \mbox{Scheme1. Multistep mechanisms to different ternaries in the evaluated} \\ \mbox{Ni-Bi-S/Se system.} \end{array}$ 

nism of the one-pot synthesis most probably takes the same route over NiBi as the intermediate and reactive template, as the occurring Bi side phase can be explained hereby. This is underlined as NiBi and NiBi3 compounds also occur in the onepot synthesis under large Ni excess (SR4). The morphologies of the Bi-NiBi-Ni<sub>3</sub>Bi<sub>2</sub>S<sub>2</sub> particles are shown in Figure S3, Supporting Information. No rodlike structure, as observed during the one-pot synthesis can be seen. The particles seem to be more roundish and agglomerated. This can most likely be attributed to the fact that the elemental Bi had to be ground after the first reaction step as it clumped together to one big glob. During the one-pot reaction, the transformations seem to be fast enough, so that no pronounced agglomeration occurs and the rodlike morphology is not destroyed. However, there is considerable morphology retention between NiBi and Ni<sub>3</sub>Bi<sub>2</sub>S<sub>2</sub>. This proves that intermetallic NiBi can possibly not only act as a reactive but also as a morphological template in the production of ternary chalcogenides. This will be the work of future studies.

From the obtained results, one must conclude the reactions as summarized in Equations (1–4). Bi<sub>2</sub>S<sub>3</sub> decomposes in the eg/en/NaOH mixture, Bi<sup>3+</sup> is reduced by the polyol and S<sup>2-</sup> is complexed by en, leading to formal [S(en)<sub>x</sub>]. In a second step Ni<sup>2+</sup> is reduced to Ni<sup>[36,37]</sup> to form NiBi with the previously emerged Bi. Finally, NiBi reacts with [S(en)<sub>x</sub>] to Ni<sub>3</sub>Bi<sub>2</sub>S<sub>2</sub> and Bi is evolved. Excess [S(en)<sub>x</sub>] can just be washed out. Elemental sulfur can also be applied, as the reductive power of the polyol solution is reported to be strong enough to reduce it to S<sup>2-,[38]</sup> Consequently, the observed reaction from Bi<sub>2</sub>S<sub>3</sub> to Ni<sub>3</sub>Bi<sub>2</sub>S<sub>2</sub> is also related to a multistep process involving the formation of Bi and NiBi.

$Bi_2S_3 + 3x en \rightarrow 2Bi + 3$	$S[S(en)_x]$	(1)
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$$HOCH_2CH_2OH \rightarrow CH_3CHO + H_2O$$
(2a)

$$2 \operatorname{Ni}^{2+} + 2 \operatorname{CH}_3 \operatorname{CHO} \rightarrow 2 \operatorname{Ni}_{\text{in situ}} + \operatorname{CH}_3 \operatorname{COCOCH}_3 + 2 \operatorname{H}^+$$
(2b)

$$Ni_{in \, situ} + Bi \rightarrow NiBi$$
 (3)

$$3 \operatorname{NiBi} + 3 [S(en)_x] \to \operatorname{Ni}_3 \operatorname{Bi}_2 S_2 + \operatorname{Bi} + [S(en)_x]$$
(4)

# Conversion chemistry in the Bi–NiBi–NiBiSe–Ni $_3$ Bi $_2$ Se $_2$ system

One-pot attempts to synthesize the related  $Ni_3Bi_2Se_2$  compound starting from  $Bi_2Se_3$  and  $NiCl_2 \cdot 6H_2O$  in an eg/en/NaOH mixture resulted in a blend of NiSe, BiSe, NiBiSe, and  $Ni_3Bi_2Se_2$ 

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(SR5). This joint appearance speaks for a close stability of binaries and ternaries with 1:1, 1:1:1, and 3:2:2 stoichiometries. The binary phases cannot be eliminated by a change in temperature and reaction time, which indicates an equilibrium situation that is not easily shifted completely towards one of the ternary products under these conditions.

After a successful application and identification of NiBi as a reactive template for the synthesis of ternary Ni<sub>3</sub>Bi<sub>2</sub>S<sub>2</sub>, it was now used for directed synthesis of its selenium homologues. Starting the reaction from NiBi, the controlled synthesis of ternary compounds is possible and no binary nickel or bismuth selenides occur in the end products. Interestingly, the 1:1:1 and 3:2:2 phases still occur as competing phases. At temperatures around 197°C and moderate alkalinity both phases are detected (SR6). Our attempts to obtain phase pure NiBiSe remained difficult, as for all evaluated conditions (no matter if 3:2 or 1:1 stoichiometry) small amounts of Ni<sub>3</sub>Bi<sub>2</sub>Se<sub>2</sub> and Bi were present. Nevertheless, by working without NaOH and at lower temperatures of 190 °C, NiBiSe is nearly the sole product (SR7, Figure 4a, Scheme 1c). Increasing the pH, temperature, and reaction time (SR8, Figure 4b, Scheme 1b) to 300 °C for 14.5 h completely suppressed the formation of the 1:1:1 phase. In general, shorter reaction times, lower temperatures, and/or less NaOH led to an increase of the NiBiSe phase. Additionally, the once-formed 1:1:1 phase can be completely transformed



**Figure 4.** a) XRD results of SR7; synthesis of NiBiSe, starting from NiBi at 190 °C without NaOH (small side phase of Ni<sub>3</sub>Bi<sub>2</sub>Se<sub>2</sub> marked with + nd Bi marked with #). b) XRD results of SR8; synthesis of Ni<sub>3</sub>Bi<sub>2</sub>Se<sub>2</sub> and Bi, starting from NiBi at 300 °C in tetraethylene glycol (TEG), (Bi is marked with #).

to  $Ni_3Bi_2Se_2$  under the mentioned harsh conditions which suppress the 1:1:1 phase (SR9). We suppose that there is a narrow stability range for NiBiSe.

Again one must conclude on a series of reactions [Eq. (5-10)]. During the one-pot reaction,  $Bi_2Se_3$  decomposes,  $Bi^{3+}$  is reduced, and  $Se^{2-}$  is complexed to  $[Se(en)_x]$ . As a consequence, the binary NiSe and BiSe side phases are formed due to a strong affinity of  $Se^{2-}$  to the metal ions. One part of the available  $Bi^{3+}$  is reduced to  $Bi^{2+}$ , which reacts further to BiSe; the other part is reduced to the elemental state, which is able to form NiBi in a second step. NiBi can afterwards either form NiBiSe or Ni<sub>3</sub>Bi<sub>2</sub>Se<sub>2</sub>, depending on the harshness of the reaction conditions. The key to the reaction is found in intact NiBi. By these means, no  $\mathrm{Ni}^{2+}$  and  $\mathrm{Bi}^{3+}$  are available in the reaction medium and binaries can be avoided. The exact mechanism of the activation of the elemental selenium during the reaction could not be determined in this work. It is known that elemental selenium in ethylenediamine is able to react with elemental or ionic metals at room temperature or at least under solvothermal conditions, but no intermediate reaction products are known.<sup>[38,39]</sup> Xie and co-workers propose a nucleophilic reaction between en and selenium and show that selenium is dissolved in ethylenediamine under solvothermal conditions.<sup>[40]</sup> This brown solution is shown to be a suitable selenium feed stock. Furthermore, en probably also activates the metal surface of Bi and NiBi.<sup>[39]</sup> In our case, the proposed activation of selenium with en is additionally supported by the reductive power of the polyol solution [Eq. (2a-b)].

$$\operatorname{Bi}_2\operatorname{Se}_3 + 3x \operatorname{en} \to 2\operatorname{Bi} + 3\left[\operatorname{Se}(\operatorname{en})_x\right] \tag{5}$$

$$Ni^{2+} + x en \rightleftharpoons [Ni(en)_x]^{2+}; Ni^{2+} + [Se(en)_x] \rightarrow NiSe + x en$$
 (6)

$$Bi^{2+} + [Se(en)_x] \rightarrow BiSe + x en$$
 (7)

$$Ni_{in situ} + Bi \rightarrow NiBi$$
 (8)

 $3 \operatorname{NiBi} + 3 [\operatorname{Se}(\operatorname{en})_x] \rightarrow \operatorname{NiBiSe} + x \operatorname{en}$  (9)

 $NiBiSe + x en \rightarrow Ni_3Bi_2Se_2 + Bi + [Se(en)_x]$ (10)

#### Quantum chemical calculations

For an interpretation of the experimental results, the conducted reactions were simulated in terms of energetic classifications of the educts and the products by quantum chemical calculations. As only elemental and metallic reactants have been used with NiBi as the starting material, the idea of our recently developed scheme to systematically evaluate phase stabilities of competing systems with different compositions<sup>[9,29,9c]</sup> is applied. Therein, the total electronic energy for educts and possible products is calculated under stoichiometric conditions, that is, the number of atoms is maintained according to paths (1) and (2). The present calculations are, however, restricted to the formation of the 1:1:1 and 3:2:2 phases from NiBi. A full approach that will take into account all possible side products will be published elsewhere. It is noteworthy, that although our approach does not require any experimental preinformation, the calculations reflect the experimental results, which

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**Figure 5.** Energetic classification of educts and products for path (1):  $3 \text{ NiBi} + 2X \rightarrow \text{Ni}_3\text{Bi}_2X_2 + \text{Bi}$  and path (2):  $\text{NiBi} + X \rightarrow \text{NiBi}X$ .

will be shown hereinafter. The zero value in Figure 5 represents the energy of educts, that is, a combination of the values for NiBi and the respective chalcogenide X that equals the utilized stoichiometry. The gain in energy with respect to the products is depicted for X=S, Se by bars according to the following scheme:

 $3 \operatorname{NiBi} + 2 X \rightarrow \operatorname{Ni}_3 \operatorname{Bi}_2 X_2 + \operatorname{Bi}$  path(1)

$$NiBi + X \rightarrow NiBiX$$
 path(2)

In the case of the X=S reaction, path (1) to Ni<sub>3</sub>Bi<sub>2</sub>S<sub>2</sub> is preferred to path (2) to a still unknown NiBiS by more than 120 kJmol<sup>-1</sup>. For X=Se, the formation of Ni<sub>3</sub>Bi<sub>2</sub>Se<sub>2</sub> is also favored over NiBiSe. However, the difference in energy for the 3:2:2 phase is less than 70 kJmol<sup>-1</sup>. From a thermodynamic point of view the calculations give a hint that the difference in energy is related to the observation that both phases can be obtained experimentally for X=Se, but not for X=S and that NiBiSe can be converted to Ni<sub>3</sub>Bi<sub>2</sub>Se<sub>2</sub> under more harsh conditions. In case of X=S, only the more stable product is directly obtained (Ni<sub>3</sub>Bi<sub>2</sub>S<sub>2</sub>) by the present approach. However, a final answer on the question if NiBiS can be obtained or not will be given from subsequent detailed calculations on the entire energy landscape with all possible side products<sup>[8,9]</sup> and/or novel experiments.

# Conclusions

In this paper, we identified and tested a plausible multistep reaction pathway that results in the formation of ternary mixed metal chalcogenides in the Ni/Bi/X (X = S, Se) system. Our experiments identified three different pathways that can take place: 1) AX  $\rightarrow$  M<sub>3/2</sub>AX; 2) A<sub>2</sub>X<sub>3</sub> $\rightarrow$  M<sub>3/2</sub>AX; and (3) A<sub>2</sub>X<sub>3</sub> $\rightarrow$  MAX. According to the results found for A = Bi, Bi is formed first when the reaction is started from Bi<sub>2</sub>S<sub>3</sub> or Bi<sub>2</sub>Se<sub>3</sub>. Bi is then converted into intermetallic NiBi that, in turn, can react to ternary compounds Ni<sub>7</sub>BiX with different *z*(Ni).

According to calculated high differences in the energy of formation, the more stable of the competing products is directly obtained ( $Ni_3Bi_2S_2$ , Scheme 1a). No binaries are formed, independent from which reactant is applied ( $Bi_2S_3$  or NiBi). In

the case of smaller differences between different binaries and ternaries, control of conversion to different stoichiometry is only possible by applying NiBi as an intermetallic precursor, as seen for the selenium system. Intact NiBi avoids reactive Ni<sup>2+</sup> and Bi<sup>3+</sup> ions that otherwise are able to form different binaries. In the selenium system, two different ternaries, Ni<sub>3</sub>Bi<sub>2</sub>Se<sub>2</sub> and NiBiSe appear in the phase diagram. Primarily, NiBiSe is formed when no NaOH is given to the reaction solution and lower temperatures of around 190 °C are applied (Scheme 1 c). Under more harsh conditions of high pH and high temperatures Ni<sub>3</sub>Bi<sub>2</sub>Se<sub>2</sub> can be obtained (Scheme 1 b). Furthermore, the present results also show that the conversion of one ternary compound into the other is possible along the M + AX line in the ternary phase diagram for NiBiSe to Ni<sub>3</sub>Bi<sub>2</sub>Se<sub>2</sub>.

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Elucidation of these reaction pathways provides a view into the steps involved in the formation of solid-state compounds. The present conversion reaction provides methods for the directed synthesis of various intermetallics and novel functional multinary compounds.

# **Experimental Section**

#### General

The following chemicals have been used without further purification: Bismuth(III)nitrate (Merck), thiourea (Aldrich), ethylene glycol (Fluka, > 99.5%), tetraethylene glycol (Aldrich, 99%), ethylenediamine (Aldrich, >99%), nickel(II)chloride hexahydrate (Alfa Aesar, 98%), selenium black (Merck, 99.5%), sulfur powder (Aldrich, 99.998%), Sodium hydroxide pellets (Merck, 99%), bismuth pieces (ChemPur, 99.999%).

#### Synthesis of Bi<sub>2</sub>S<sub>3</sub> nanorods:

The Bi<sub>2</sub>S<sub>3</sub> nanorods were synthesized according to ref. [41].

#### Synthesis of Bi<sub>2</sub>Se<sub>3</sub>

Elemental Bismuth powder (0.522 g) and Se black powder (0.296 g) were stirred in ethylenediamine (6 mL) overnight. The resulting precipitate was washed with water and ethanol and dried at 80 °C in a drying cabinet. To increase crystallinity, the obtained powder was annealed at 250 °C for 3 h under flowing argon according to Li.<sup>[39]</sup>

#### Reproduction of the one-pot synthesis of Ni<sub>3</sub>Bi<sub>2</sub>S<sub>2</sub>

The one-pot synthesis of the ternary Ni<sub>3</sub>Bi<sub>2</sub>S<sub>2</sub> was performed according to a slightly modified report of Shao.<sup>[30]</sup> A mixture of Bi<sub>2</sub>S<sub>3</sub> (0.129 g) and NiCl<sub>2</sub>·6 H<sub>2</sub>O (0.178 g, molar ratio 1:3) in ethylene glycol (70 mL) was added to a 100 mL round-bottomed flask, magnetically stirred, and treated with ultrasound. Then NaOH (0.545 g) and ethylenediamine (5.05 mL) were added. After the NaOH had completely dissolved the flask was heated and the mixture was refluxed at 197 °C for 0.5–10.5 h in air. After cooling to room temperature, the products were centrifuged and washed several times with water and ethanol and dried at 60 °C.

All other modifications of the synthesis conditions can be found in the Supporting Information. They are referenced with SRn (*n* corresponds to the number of the respective reaction.

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#### Analysis

**X-ray powder diffraction**: XRD was performed with a Huber G670 diffractometer equipped with an imaging plate with monochromatic Cu<sub>Ka1</sub> radiation ( $\lambda = 1.54060$  Å, Ge-monochromator, increment  $\Delta \theta = 0.005^{\circ}$ , Bragg angular range 4°  $\leq$  100°). Morphologies of the as-prepared samples were investigated with SEM using a Zeiss Digital Scanning Microscope DSM 950.

Quantum chemical calculations: The first-principles calculations were carried out within the framework of DFT with exchange-correlation functionals in the generalized gradient approximation (GGA) according to Perdew-Burke-Ernzerhof (PBE).<sup>[42]</sup> Full geometry optimizations were executed with the Vienna Ab initio Simulation Package (VASP),<sup>[43]</sup> atomic site parameters and cell constants were, therefore, allowed to fully relax with the conjugant gradient algorithm. The interactions between the ions and the electrons are described by the projector-augmented-wave (PAW) method with scalar-relativistic potentials and a cutoff energy of 500 eV. All structure optimizations were performed in three subsequent steps with an initial k-grid mesh of  $4 \times 4 \times 4$  rising to  $8 \times 8 \times 8$  and  $12 \times 12 \times 12$ to reach sufficient accuracy. Particularly for large unit cells, this offers an additional verification of the performed calculations. A structure optimization was considered to be converged with a difference in total energy of less than  $1\!\times\!10^{-6}\,\text{eV}$  and a maximum Hellmann-Feynmann force of  $1 \times 10^{-4}$  eV Å<sup>-1</sup>. The final values of the total energies of the investigated systems were obtained with energy differences (between last and second to last step) of less than  $1 \times 10^{-3}$  eV per formula unit.

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**Keywords:** formation mechanism · nanoparticles · polyol process · synthetic methods · ternary chalcogenide

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