Nanoparticles

Reaction of Ni^{2+} and SnS as a Way to Form Ni@SnS and $Sn_2Ni_3S_2$ Nanocrystals: Control of Product Formation and Shape

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Dedicated to Professor Manfred Scheer on the occasion of his 60th birthday

Abstract: Reductive diffusion of Ni²⁺ into SnS particles was shown to selectively form Sn₂Ni₃S₂, hybrid, or even core-shell Ni@SnS, Ni_{1.523}Sn, and Ni₃S₂, by tuning the reaction conditions at low temperatures. The mechanism of Ni²⁺ reduction and diffusion into SnS was observed in ethylene glycol, which served both as solvent and reducing agent. Tuning of reaction temperature and duration, morphology of the tem-

products. Their formation was controlled by carefully adjusting redox and equilibrium reactions. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy analysis (EDX).

as shown subsequently. Macro-sized SnS, in contrast, is known as a stable compound that does not easily react with semicon-

ductors or metals. However, at high temperatures it reacts

with transition metals to ternary compounds with totally differ-

ent properties, like Sn₂Co₃S₂ or Sn₂Ni₃S₂, in solid state reactions.

The control of respective reactions at the nanoscale should

provide a way to understand and exploit related extended

Bulk compounds $AM_{3/2}S = A_2[M_3S_2]$ were classified as multimetal-ordered half antiperovskites (HAP) with layered partial

 $[M_3S_2]$ structures.^[10-13] These attracted attention, because the

magnetic and electronic properties can be tuned by substitu-

tion of M = Ni, Co, Rh, Pd and A = In, Tl, Pb, Sn. The properties

and supposed applications are related to intermetallic A-M

and chalcogenide-like behavior and range from small bandgap

semiconductors and thermoelectrics^[14-16] to half-metal ferromagnets^[16,17] and catalysts.^[18-21] Known ways of synthesis pro-

vide indications that transformation of semiconductors, metals,

and intermetallics are possible, as exemplified for semi-metal

 $Sn_2Ni_3S_2$. In the solid state it is obtained from the elements (Ni, Sn, S), or from heazlewoodite (Ni_3S_2) and elemental Sn, or from

SnS and Ni at 900 °C.^[22, 23] Reaction mechanisms are not yet

known, pure samples are hardly obtained, and it is barely pos-

sible to influence the size or to selectively control the morphology of particles under these conditions. However, this be-

plate SnS, and the application of ethylenediamine as sup-

porting chelating agent, influence the formation of the final

Introduction

Small particles with different morphologies facilitate tuning of interesting optical, magnetic, electrical, and chemical properties compared to their bulk counterparts. In recent years, intensive research has been devoted to nano- and microcrystalline metals and chalcogenides.^[1,2] Synthetic concepts are well-developed for transition metal, binary oxide, and chalcogenide nanoparticles.^[3,4] Building on these concepts, the transformation to other binary or ternary compounds is desirable to enhance applications or functionality. However, established methods are poorly transferable for the synthesis of multimetal or intermetallic compounds for enhanced functions, for example, for catalysis.^[5,6] To grow related ternary and multinary systems, improved synthesis strategies have to be developed to control formation, growth mechanisms, and shape.

The concept can be exemplified for the semiconductor SnS. At the nanoscale its electronic gap can be tuned from 1.4 to 2.0 eV. This leads to promising nanoelectronic, optoelectronic, thermoelectric, photocatalytic, solid state battery, photovoltaic, near infrared detector, and biomedical applications.^[7–9] For interfaces, multilayer, or combined functions, the reactivity of SnS nanoparticles becomes decisive. The same applies for interlayer or transformation reactions to multinary compounds

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comes possible at the nanoscale. Subsequently, not only a solution-based route for the morphology-controlled reaction of SnS to nanosized Sn₂Ni₃S₂ at

functionality.

a temperature below 200 °C is shown for the first time, but also an elucidation of the reaction mechanism. A reductive diffusion of Ni²⁺ into SnS is proposed. By varying reaction parameters, the formation of core-shell particles, Sn₂Ni₃S₂, Ni₃S₂, and Ni_{1.523}Sn can be controlled from a modified polyol synthesis for isotypic Pb₂Ni₃S₂.^[24] This study serves as a prototype for the

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formation of similar or completely new phases by carefully adjusting the general method.

Results and Discussion

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One-pot reaction of SnS to Sn₂Ni₃S₂

For the optimized synthesis of $Sn_2Ni_3S_2$, $SnS_{spherical}$ was reacted with NiCl₂·6H₂O at 197 °C for 10.5 h with ethylenediamine (en) and NaOH in ethyleneglycol (eg) as reducing agents and solvent. Essentially phase-pure spherical SnS was used as reactive template in the synthesis. Some small reflections of the SnS sample can be attributed to elemental Sn (Figure 1a, marked



Figure 1.

XRD pattern of a) SnS. Almost phase-pure SnS was obtained according to reference [25] and used as template. Elemental Sn as side phase is marked with an asterisk, b) Sn₂Ni₃S₂, which was synthesized at 197 °C for 10.5 h, with a slow heating ramp and stops for half an hour at 50, 100, 150 °C during the heating process.

with an asterisk). During the heating process, the temperature was kept constant for half an hour at 50, 100, and 150 °C, before raising the temperature with a low heating ramp (about 3° C min⁻¹).

XRD data for $Sn_2Ni_3S_2$ (Figure 1 b) confirms the trigonal shandite phase (space group *R*-3*m*, No. 166). No characteristic peaks are observed for impurities, such as SnS, NiS, Ni₆SnS₂, or $Ni_9Sn_2S_2$,^[26] which are apparent in the phase diagram. Further evidence for the quality and the composition of the $Sn_2Ni_3S_2$ sample was obtained by energy dispersive X-ray spectroscopy (see Figure 2). The typical composition of 3:2:2 at.% for Ni, Sn, and S is observed at good agreement (3.17:2.10:2.00 at.%).

The refined lattice constants for the measured sample are a=5.455(3) Å and c=13.188(3) Å, which is in accordance with the previously reported data (a=5.4606(2) Å and c=13.188(1) Å).^[18] An average crystallite size of 21.8 nm was estimated by the Scherrer equation,^[27] based on XRD line widths (calculated at the highest peak, *hkl* 246). Figure 3 a–d shows SEM images of SnS nanospheres and as-prepared Sn₂Ni₃S₂ at different magnifications. It is obvious that the products adopt the same spherical shape as the precursor SnS.



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Figure 2. Energy dispersive X-ray spectrum of the optimized ${\rm Sn}_2{\rm Ni}_3{\rm S}_2$ sample.



Figure 3. SEM images of a,b) SnS and c,d) $Sn_2Ni_3S_2$ at a magnification of 2 and 5 $\mu m,$ respectively.

These results suggest a template-dependent growth mechanism. We suppose that SnS acts as both precursor and reactive template, which is converted into the ternary Sn₂Ni₃S₂. A plausible formation mechanism of the ternary nanostructure involves at least three steps [Eq. (1)-(3)]. When en is added to the reaction mixture, the stable nickel complex $Ni(en)_{x}^{2+}$ is formed immediately,^[28, 29] which is indicated by a change in color of the solution to purple. The formation of this complex is essential for the whole reaction, as free Ni^{2+} tends to form nickel sulfides, which is accompanied by the decomposition of SnS (see below). At higher temperatures of around 140-160°C, the solution turns to black, as $Ni(en)_x^{2+}$ decomposes slowly and Ni^{2+} is reduced to the elemental state. This is associated with the moderate intensity reductive characteristic of en,^[20, 30, 31] and also ethylene glycol itself in strong alkaline solution.^[32,33] The in situ produced Ni is, in theory, highly active, and it can be incorporated immediately in the present SnS under retention of its shape.^[34]

$$Ni^{2+} + x en \rightleftharpoons [Ni(en)_x]^{2+}$$
(1)

$$HOCH_2CH_2OH \rightarrow CH_3CHO + H_2O \tag{2a}$$

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

$$2 \text{ SnS} + 3 \text{ Ni}_{\text{in situ}} \rightarrow \text{Sn}_2 \text{Ni}_3 \text{S}_2 \tag{3}$$

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Interesting results were obtained when the proposed mechanism was studied using different temperatures, morphology of the SnS template, and reducing agents. Therefore, a series of related experiments was designed.

Role of ethylene glycol and ethylenediamine

The solvent medium and reducing agent ethylene glycol has often been used for reduction of metal ions and also as an inhibitor for coagulation.^[32,33] The present studies confirm that NiCl₂·6 H₂O can be reduced to the elemental state by just refluxing in ethylene glycol and NaOH, with or without the addition of ethylenediamine [Eq. (4)]. Nevertheless, without ethylenediamine, larger and agglomerated Ni particles are obtained, which is in accordance with the literature.^[33,35,36] Furthermore, the formation of a certain amount of nickel sulfides is observed when en is not added to the solution. In the present case, NiS^[37] and Ni₃S₂^[38] are then formed, with S^{2–} released from SnS. Intermetallic Ni_{1.523}Sn^[39] is also found, which is assumed to result from a co-reduction of Sn²⁺ and Ni²⁺ [Eq. (5a)–(7b)].

Red :
$$Ni^{2+} + 2e^- \rightarrow Ni$$
 (4)

Sol. eq. : $SnS \rightleftharpoons Sn^{2+} + S^{2-}$ (5a)

Sol. eq. :
$$Ni^{2+} + S^{2-} \rightleftharpoons NiS$$
 (5b)

 ${\rm Red}: \qquad 3\,Ni^{2+}+2\,S^{2-}+2\,e^-\to Ni_3S_2 \eqno(6a)$

$$\operatorname{Red}: \qquad 3\operatorname{NiS}+2\operatorname{e}^{-}\to\operatorname{Ni}_{3}S_{2}+S^{2-} \tag{6b}$$

 $\operatorname{Red}: \qquad 3\operatorname{Ni}+2\operatorname{Sn}^{2+}+4\operatorname{e}^{-}\to\operatorname{Ni}_3\operatorname{Sn}_2 \tag{7a}$

Co-Red :
$$2 \operatorname{Sn}^{2+} + 3 \operatorname{Ni}^{2+} + 10 \operatorname{e}^{-} \rightarrow \operatorname{Ni}_3 \operatorname{Sn}_2$$
 (7b)

 $\mathsf{Red} = \mathsf{reduction}$, Sol. eq. = solution equilibrium, and $\mathsf{Co-Red} = \mathsf{co-reduction}$.

Effect of heating ramp, temperature, and reaction time on products

The temperature-dependent stability of the $[Ni(en)_x]^{2+}$ complex explains the challenging reproducibility and sensitivity of the reaction using different heating ramps and temperatures. With the initially described slow heating ramp, the formation of Sn₂Ni₃S₂ from SnS and Ni²⁺ in eq with en starts at a temperature below 166 °C. In this temperature region the Ni(en)_x²⁺ complex starts to decompose and Ni²⁺ is slowly released to the reaction solution and rapidly reduced. The Ni formed in situ should then be incorporated immediately into SnS to form $Sn_2Ni_3S_2$. At a low Ni^{2+} concentration, reduction is thus preferred. By using a rapid-heating ramp, NiS, Ni₃S₂, and unreacted SnS are found as products in the XRD patterns (see Figure 4a). Clearly, Ni(en) $_{x}^{2+}$ and SnS decompose too quickly under these conditions. The formation of NiS is then related to high concentration of uncomplexed Ni²⁺. This clearly demonstrates the role of the solubility product of NiS, which is reached when Ni²⁺ is not hidden in the en-complex. Furthermore, the con-



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Figure 4. a) Reaction products of a synthesis with a rapid heating ramp. b) Reaction products of a synthesis where all starting materials were injected into the refluxing solution.

centration of S²⁻ in solution is due to the dissolution equilibrium of SnS and increases at high temperature. When S²⁻ is consumed by the formation of NiS, it is recovered by dissolving SnS in accordance with the concept of Le Chatelier [Eq. (5a,b)]. By extending the reaction time and keeping the rapid heating ramp constant, SnS disappears, but the amount of Sn₂Ni₃S₂ does not increase. Instead, the quantity of Ni₃S₂ rises, which is an indicator of progressive reduction of Ni²⁺, which is present in NiS [Eq. (6a,b)]. At long reaction times Ni_{1,523}Sn appears, which is either the product of a co-reduction of Ni²⁺ and Sn²⁺ or a further reductive interdiffusion process of Sn²⁺ on Ni particles [Eq. (7 a,b)].

Role of the SnS source

In addition to the importance of the reaction temperature and heating ramp we found that the tin sulfide source plays an important role in this modified polyol process. Two kinds of SnS sources (SnS_{spherical}, SnS_{bulk}) were tested for the preparation of $Sn_2Ni_3S_2$. As shown before, it is possible to synthesize the phase-pure shandite phase, when using spherical SnS under optimized conditions. Whereas, when $\mathsf{SnS}_{\mathsf{bulk}}$ (prepared by a solid-state method) is used, only small amounts of the target shandite phase are observed. Prominent side phases Ni₃S₂, and Ni_{1.523}Sn, plus a small unknown phase, are also apparent. Different heating ramps and reaction times did not increase the amount of Sn₂Ni₃S₂. One can conclude that the morphology of the applied SnS precursor plays a key role in the synthesis of Sn₂Ni₃S₂. As diffusion in nanoparticles is much faster than in the bulk materials,^[40] this can possibly lead to facilitated chemical transformation of the particles. The spherical shape of the precursor makes it extremely susceptible to its surroundings and Ni can diffuse into the lattice more easily.

Hydrazine as reducing agent (Ni-coated SnS)

When ethylenediamine is replaced by hydrazine as the additional reducing agent and the temperature is lowered to 70 °C, only a small amount of Sn₂Ni₃S₂ is formed, and the main prod-

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ucts were Ni and SnS according to the X-ray diffraction data (Figure 5). Figure 5 a shows the pristine SnS, whereas Figure 5 b shows the products after reaction with the addition of hydra-



Figure 5. a) Pristine SnS. b) Product after reaction with hydrazine to Ni@SnS core-shell particles. c) Reaction of Ni@SnS to Sn₂Ni₃S₂ in a solid state reaction at 700 °C (5 days).

zine. The reduction of Ni²⁺ seems to be too fast to form $Sn_2Ni_3S_2$ under these conditions, so that elemental Ni is formed on SnS (marked with an asterisk). No consecutive reactions are observed in solution, especially for SnS, which does not dissolve. The washed and dried product reacts to $Sn_2Ni_3S_2$ in a solid state reaction at T=500-700 °C (Figure 5 c, small side phases of Ni₃S₂ and Ni_{1.523}Sn are marked with # and +, respectively). We conclude on the formation of core-shell particles Ni@SnS.

The whole system presented is determined by equilibrium and redox reactions [Eq. (4)–(7b)], which have been summarized in Scheme 1. As shown above, the concentration of free Ni^{2+} is particularly crucial for the competing reduction to Ni^{0} or the formation of NiS.



Scheme 1. Equilibrium and redox reactions in the SnS, [Ni(en)]²⁺ system.

Discussion of the mechanism of formation for Sn₂Ni₃S₂

To exclude any other mechanisms of formation for the $Sn_2Ni_3S_2$ phase, like a dissolution-precipitation process, which proceeds over chemical intermediates like Ni_3S_2 or NiS, the following tests were conducted. In one approach all starting materials were injected into refluxing ethylene glycol, which resulted in NiS, Ni_3S_2 , and $Ni_{1.523}Sn$ (Figure 4b). Further experiments were all conducted at the optimized slow-heating ramp for $Sn_2Ni_3S_2$,

described before, and refluxed at 197 °C for 10.5 h; by using Ni₃S_{2,bulk} and SnCl₂·2H₂O as starting materials, the reaction stopped at Ni₃S₂, with a small NiS side phase. NiCl₂·6H₂O, SnCl₂·2H₂O, and Na₂S/S also resulted in Ni₃S₂ and NiS, with the addition of Ni_{1.523}Sn, when Na₂S was applied. These results altogether underline that one challenging point of the synthesis is the integrity of SnS. After dissolution of SnS it is not possible to get to the Sn₂Ni₃S₂ phase. With careful adjustments, the method should be applicable to other M+AX systems too, including compounds with varying M content like PtSnS^[41] or Pd₅InSe.^[42]

Conclusion

Nanocrystalline Sn₂Ni₃S₂ could be directly prepared for the first time under ethylene glycol reflux at a temperature as low as 150-197 °C. It was evident that the supporting chelating and reducing agent ethylenediamine, the reaction temperature, and the morphology of the precursor play an important role in the synthesis. A reductive diffusion-based mechanism with SnS as reactive template was discussed. After rapid reduction of Ni^{2+} with hydrazine at 70 °C, Ni does not diffuse into SnS, but core-shell-particles are formed. However, they can be transferred to the ternary $Sn_2Ni_3S_2$ by solid-state reactions at T >500 °C. At high concentrations of uncomplexed Ni^{2+} and S^{2-} , the binary sulfides NiS and $\mathrm{Ni}_3\mathrm{S}_2$ are formed and SnS is dissolved. Additionally, under the present reductive conditions Sn^{2+} forms the intermetallic Ni_{1.523}Sn after a long reaction time. The present study shows that binary compounds can indeed be transformed to ternaries with different functions. Thereby, core-shell particles can be designed based on the rate of reduction. The discussed method leads to ways to obtain related compounds and functionalized materials.

Experimental Section

Synthesis

Preparation of spherical SnS (SnS_{spherical}) **particles**: SnS starting material was prepared by a modified solvothermal route described in reference [25]. Sn powder and excess thiourea were added to a glass ampoule that had been filled with the solvent mixture (water/ethylenediamine = 1:1) up to 80% of the total volume. The ampoule was sealed and maintained at 180 °C for 12 h. After cooling down to room temperature the products were washed thoroughly with distilled water and ethanol and dried at 75 °C.

Preparation of spherical Sn₂Ni₃S₂: The particles were prepared from a stoichiometric mixture of NiCl₂·6H₂O (0.1676 g, 0.71 mmol) and SnS_{spherical} (0.0709 g, 0.47 mmol) in a 250 mL round-bottom flask. SnS_{spherical} was added to the flask, which was then filled with 70–100 mL ethylene glycol (eg) and magnetically stirred. After half an hour, NiCl₂·6H₂O was added under continuous stirring. Lastly, ethylenediamine (en, 4.75 mL) and NaOH (0.5126 g, 12.8 mmol) were introduced to the reaction mixture. Following further stirring for half an hour, the flask was heated to 166–197 °C at different heating ramps. After refluxing for 0.5 h–10.5 h, the mixture was naturally cooled to room temperature. The products were filtered

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and washed several times with distilled water and alcohol and dried at 75 $^\circ\text{C}$ overnight.

Preparation of Ni-coated SnS particle and transformation to Sn₂Ni₃S₂: The synthesis of Ni@SnS follows the same procedure as described for spherical Sn₂Ni₃S₂, with the exception that ethylenediamine is replaced by hydrazine. The mixture is kept at 60–70 °C for 3 h under stirring. After cooling to room temperature, the products were filtered and washed several times with distilled water and alcohol and dried at 75 °C overnight.

Analysis

The structure of the products was characterized by X-ray powder diffraction, using a Huber G670 diffractometer equipped with an imaging plate with monochromatic Cu_{Ka1} radiation ($\lambda = 1.54060$ Å, Ge-monochromator). Lattice parameters were refined with the software WinXPOW (version 1.08). X-ray energy dispersive spectroscopy analysis was performed on a SEM 5900 LV (JEOL) with an operating voltage of 15 kV. Morphologies of the as-prepared samples were investigated with scanning electron microscopy using a Zeiss Digital Scanning Microscope DSM 950.

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