Bottom-up processing and low temperature transport properties of polycrystalline SnSe

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Abstract:

A hydrothermal approach was employed to efficiently synthesize SnSe nanorods. The nanorods were consolidated into polycrystalline SnSe by spark plasma sintering for low temperature electrical and thermal properties characterization. The low temperature transport properties indicate semiconducting behavior with a typical dielectric temperature dependence of the thermal conductivity. The transport properties are discussed in light of the recent interest in this material for thermoelectric applications. The nanorod growth mechanism is also discussed in detail.

Key words: SnSe nanorod, hydrothermal, transport properties

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Introduction

Tin(II) selenide is an important binary IV–VI semiconductor compound with a layered orthorhombic crystal structure (*Pnma* space group, #62) .[1] SnSe is of interest for a wide range of potential applications such as for memory switching devices,[2, 3] infrared optoelectronic devices,[4, 5] solar cells[6, 7] and anode materials for rechargeable lithium batteries.[8] Zhao and co-workers [1] recently reported that single-crystal SnSe exhibited a low thermal conductivity above room temperature resulting in a high thermoelectric figure of merit, ZT , of 2.6 at 923 K along the b axis ($ZT = S^2\sigma T/\kappa$ where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity and T is the absolute temperature). Single crystals typically have better electrical properties but higher thermal conductivity and poorer mechanical properties than polycrystalline materials, [9] therefore, a simple cost-effective synthetic technique for the synthesis of polycrystalline SnSe is of interest.

Chen et.al [10] prepared SnSe powders by melt quenching followed by annealing. Baumgardner et.al [11] synthesized SnSe nanocrystals by injection of bis[bis(trimethylsilyl)amino]tin(II) into hot triethylphosphine selenium in the presence of oleylamine. SnSe nanowires with a mean diameter of 20 nm were obtained by a colloidal synthesis approach using $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ and trioctylphosphine selenide as the Sn source and Se source, respectively.[12] Li et al. reported that bulk single crystals with a length of 0.8 to 1.5 cm and a radius of 60 to 100 μm can be obtained by hydrothermal synthesis.[13] Here we describe a simple and efficient hydrothermal approach for the synthesis of SnSe. By introducing NaOH as the pH balancing agent, SnSe nanorods were obtained. After spark plasma sintering (SPS) densification, the low temperature transport properties of dense polycrystalline SnSe are reported and discussed. This approach can also be employed for the synthesis and densification of other binary chalcogenides such as SnS, SnTe, CdS and CdSe.

Experimental section

The chemical reagents used in this study were of analytical grade and purchased from Fisher Scientific¹. SnCl_2 was used as the Sn source and SeO_2 was used as the Se source. In a typical process, 1 mmol SeO_2 was dissolved in 20 ml ethylene glycol (EG) and stirred for 30 min before 5 ml hydrazine was added to the SeO_2 /EG solution. 2 mmol SnCl_2 and 2 g NaOH were dissolved in 40 ml deionized (DI) water for 10 min to obtain the SnCl_2 solution. This SnCl_2 solution was then slowly dropped into the Se solution and stirred for another 10 min. The entire solution was then transferred into a PTFE-lined stainless steel autoclave with a 100 ml capacity before it was sealed and maintained at 180°C for 12 h. The final black solid product was filtered and then washed with DI water and ethanol three times before drying under vacuum at room temperature. Each synthesis yielded ≈ 0.4 g of pure SnSe powder. The as-synthesized products were characterized by powder X-ray diffraction (XRD, Bruker AXS D8), scanning electron microscopy (SEM, JEOL JSM 6390 LV), and transmission electron microscopy (TEM, JEOL 2100). The reaction conditions and products for all powder specimens (numbered TS-1 to TS-6) are listed in Table 1.

SPS densification (Thermal Technology LLC, 25-10) of SnSe was carried out at 45 MPa and 400 °C for 15 min. A density of 97% of the theoretical density was achieved after densification, as determined by the dimensions and mass of the pellet. Temperature dependent four-probe ρ , S (gradient sweep method) and steady-state κ measurements between 12 K and 300 K were performed on the polycrystalline SnSe specimen. The measurements were conducted in a custom designed radiation-shielded vacuum probe with uncertainties of 4, 6, and 8% for ρ , S , and κ measurements, respectively [14], on 2 x 2 x 5 mm³ parallelepipeds cut by a wire saw. Temperature dependent four-probe Hall measurements were conducted on a nitrogen-jacketed PPMS (Quantum Design) with

¹ Certain commercial equipment or materials are identified in this document and does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purpose.

the AC Transport option on $0.5 \times 2 \times 5 \text{ mm}^3$ parallelepipeds at multiple positive and negative magnetic fields in order to mitigate voltage probe misalignment effects ($\pm 5\%$ uncertainty).

Results and Discussion

Phase pure SnSe was synthesized by an efficient hydrothermal method using SnCl_2 as the Sn source and SeO_2 as the Se source with a Sn-to-Se ratio of 2:1, DI water and EG as the solvents and NaOH as the pH adjusting agent. SnCl_2 not only acted as the Sn source but also the reducing agent. Figure 1 shows the XRD patterns of the products prepared at different temperatures for 12 h. All four XRD patterns match that of SnSe and the crystallographic planes are indexed on Figure 1d. The formation mechanism can be explained by the following equation [15,16]:

As shown in Equation 1, SeO_2 was reduced to Se when hydrazine was added to the SeO_2/EG solution. Selenium was then further reduced to Se^{2-} when Sn^{2+} was added. Finally, Sn^{2+} reacted with Se^{2-} to form SnSe. We note that when using a Sn-to-Se ratio of 1:1 with the same procedure no SnSe was detected in the final product.

Figure 2 shows TEM images of SnSe synthesized at different hydrothermal temperatures. The SnSe was flower-like in appearance, consisting of nanorods 100 to 400 nm in diameter and 1 to 2 μm in length when the hydrothermal temperature was 120°C , as shown in Figures 2a-c. When the temperature was increased, the SnSe “flowers” began to disassemble, as shown in Figures 2d-i. At 180°C nanorods with sizes ranging from 100 to 400 nm in diameter and 0.5 to 2 μm in length, as

shown in Figures 2j-l, were obtained.

Figure 3 shows XRD patterns of the powder with different NaOH content. As shown in Figure 3a two phases were detected when NaOH was not used, SnO (marked by green stars) and SnSe₂ (marked by yellow stars). Clearly SnSe cannot be obtained without the presence of NaOH. This indicates that when the pH value is much less than 7 the reaction described by Equation 3 cannot proceed. The Sn⁴⁺ ions will react with Se²⁻ to form SnSe₂ with the residual Sn²⁺ forming SnO. NaOH has an important role in suppressing the production of SnO and SnO₂.

When NaOH was added to the solution, phase pure SnSe was obtained, as shown in Figures 3b and c. The different line widths between Figures 3b and c indicate that the grain size of SnSe increases with increasing NaOH contents, as expected since NaOH is also a mineralizing agent thus enabling the formation of larger crystals.[17] XRD analyses of the products after different reaction times indicated a mixture of Se and SnSe, with a decreasing Se-to-SnSe ratio with increasing reaction time.

Figure 4 shows TEM images of SnSe prepared with different NaOH content. As shown in Figures 4a two different morphologies exist in the product, the larger grains are from SnSe₂ and the smaller grains are from SnO as indicated by XRD (Figure 3a). The morphologies are all flower-like for the specimens prepared using 2 g NaOH (Figures 4 c and d) and 4 g NaOH (Figures 4 e and f). For the specimen with 2 g NaOH, the “flowers” consisted of rods 80 to 300 nm in diameter and 300 to 500 nm in length, smaller than that obtained for the specimens prepared using 4 g NaOH.

Employing SPS dense polycrystalline SnSe was obtained for low temperature transport properties measurements from the SnSe product obtained at 100 °C for 12h with a 2 g NaOH content. SPS processing generates internal localized heating thus allowing

for the rapid, low temperature densification of fine-grain powders.[18] Since only the surface temperature of the nanorods rises rapidly by self-heating, grain growth can be minimized by controlling the current. Optimization of the maximum SPS current prevented the formation of impurities. This resulted in phase-pure polycrystalline SnSe with a density of 97% of the theoretical density. XRD patterns before and after SPS are shown in Figure 5 and indicate phase-pure polycrystalline SnSe after SPS.

Figure 6 shows the low temperature transport properties of polycrystalline SnSe and Figure 7 shows ρ versus $1/T$ as well as the temperature dependent Hall measurement data. From the low temperature ρ measurements shown in Figure 6(a), the ρ values decrease with increasing temperature indicating thermally activated semiconductor behavior. The solid line in Figure 7 is an unconstrained fit to the highest temperature data using $\rho = \rho_0 \exp(E_a / k_B T)$, where E_a is the activation energy and k_B is the Boltzmann constant, and results in an E_a value of 0.26 eV implying a band-gap ($E_g \approx 2E_a$) of 0.52 eV. This estimated activation energy is in general agreement with previously reported values.[1,10] Figure 6(b) shows the temperature dependence of S . Over the entire temperature range S increases linearly with increasing temperature indicating a more metallic-like, or degenerate semiconductor, temperature dependence. The positive values of S implies that holes are the dominant carriers (p-type conduction) as also indicated by the temperature dependent carrier concentration shown in the inset of Figure 7. The change in hole concentration is relatively small over the measuring temperature range (5 K to 300 K) indicating a constant Hall resistance, as has also been observed above room temperature.[1]

The dominant contribution to κ is presumably from the lattice given the relatively large ρ values

shown in Figure 6(c). The temperature dependence of κ is typical of a dielectric solid. At room temperature κ for our polycrystalline specimen is similar to that of the recently reported bulk polycrystalline SnSe synthesized by direct reaction of the elements,[19] and intermediate between the reported values measured from two pieces cut along different pressing directions of a cylindrically shaped polycrystalline SnSe specimen.[10] The dotted-dashed line is for a calculated grain size of $0.8\ \mu\text{m}$ and indicates that grain-boundary scattering is the dominant phonon scattering mechanism at low temperatures. This grain size corroborates our SEM analyses that indicated an average grain size of $\approx 0.9\ \mu\text{m}$ for our polycrystalline SnSe specimen.

Conclusion

SnSe nanorods were synthesized and, after SPS densification, the low temperature transport properties of polycrystalline SnSe were measured for the first time. By employing a hydrothermal approach with a Sn-to-Se source ratio of 2:1, and SnCl_2 not only used as a Sn source but also a reducing agent, SnSe nanorods forming flower-like arrangements were obtained when the reaction temperature was below 180°C and nanorods were obtained at a reaction temperature of 180°C , the “flowers” changing to rods with increasing hydrothermal temperature. The size of these nanorods was affected by the NaOH content. SnSe_2 and SnO were obtained when NaOH was absent. SPS densification of the SnSe nanorods allowed for low temperature transport properties measurements that indicated degenerate semiconducting behavior.

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Table 1. Reaction conditions and products of different specimens.

Sample Number	Reaction Temperature (°C)	Reaction Time (h)	NaOH Content (g)	Product
TS-1	120	12	4	SnSe
TS-2	140	12	4	SnSe
TS-3	160	12	4	SnSe
TS-4	180	12	4	SnSe
TS-5	180	12	2	SnSe
TS-6	180	12	0	SnSe ₂ +SnO

Figure captions

Figure 1. XRD patterns of the products prepared under different hydrothermal temperatures for 12 h: (a) 120°C, (b) 140°C, (c) 160°C, (d) 180°C.

Figure 2. TEM images and sketches of the products prepared under different hydrothermal temperatures for 12 h: (a), (b) and (c) at 120°C, (d), (e) and (f) at 140°C, (g), (h) and (i) at 160°C, and (j), (k) and (l) at 180°C.

Figure 3. XRD patterns of the products prepared with different NaOH content at 120°C for 12 h: (a) 0 g NaOH, (b) 2 g NaOH and (c) 4 g NaOH. Diamonds indicate the diffraction peaks of SnO and asterisks indicate the diffraction peaks of SnSe₂.

Figure 4. TEM images of the products prepared with different NaOH content at 120°C for 12 h: (a) and (b) 0 g NaOH, (c) and (d) 2 g NaOH and (e) and (f) 4 g NaOH.

Figure 5. XRD patterns of (a) powder SnSe before SPS and (b) polycrystalline SnSe densified by SPS.

Figure 6. Low temperature transport properties of SnSe nanocrystals: (a) ρ , (b) S , and (c) κ (the dotted-dashed line refers to a calculation for 0.8 μm grain size).

Figure 7. ρ versus 1000/T where the dashed line is a fit of the form $\rho = \rho_0 \exp(E_a/k_B T)$ to the highest temperature data. Inset: temperature dependent carrier concentration.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

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SnSe nanorods were synthesized by a simple hydrothermal method through a bottom-up approach. Micron sized flower-like crystals changed to nanorods with increasing hydrothermal temperature. Low temperature transport properties of polycrystalline SnSe, after SPS densification, were reported for the first time. This bottom-up synthetic approach can be used to produce phase-pure dense polycrystalline materials for thermoelectrics applications.

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