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Enhanced thermoelectric properties of SnSe polycrystals *via* texture control[†]

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We present in this manuscript that enhanced thermoelectric performance can be achieved in polycrystalline SnSe prepared by hydrothermal reaction and spark plasma sintering (SPS). X-ray diffraction (XRD) patterns revealed strong orientation along the [$l \ 0 \ 0$] direction in bulk samples, which was further confirmed by microstructural observation through transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM). It was noticed that the texturing degree of bulk samples could be controlled by sintering temperature during the SPS process. The best electrical transport properties were found in the sample which sintered at 450 °C in the direction vertical to the pressing direction, where the highest texturing degree and mass density were achieved. Coupled with the relatively low thermal conductivity, an average ZT of ~ 0.38, the highest ever reported in pristine polycrystalline SnSe was obtained. This work set up a forceful example that a texture-control approach can be utilized to enhance the thermoelectric performance effectively.

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1. Introduction

Thermoelectric (TE) power generation can directly convert waste heat into electrical power¹⁻³ and thus is deemed as a promising technique to relieve the uprising energy crisis worldwide. The conversion efficiency of a thermoelectric device is characterized by a dimensionless figure of merit (*ZT*) defined as $ZT = [S^2\sigma/(\kappa_e + \kappa_l)]T$, where *S*, σ , κ_e , κ_l , and *T* are the Seebeck coefficient, electrical conductivity, electronic thermal conductivity, lattice thermal conductivity, and operating temperature, respectively. Over the past few decades, lots of materials have been widely investigated as promising thermoelectrics, such as Bi₂Te₃-based materials^{4,5} in a low temperature range, PbTe-based⁶⁻¹² alloys in mediate temperature ranges, and half-Heusler intermetallic compounds,¹³⁻¹⁵ metal oxides,¹⁶⁻²⁰ SiGe alloys,²¹⁻²³ *etc.* in a high temperature range. Wherein IV–VI semiconductor PbQ (Q = Te, Se, S)-based alloys exhibit the most remarkable thermoelectric performance in a moderate temperature range (\sim 300–700 K).^{6–8,24} Approaches developed to date to enhance the *ZT* values can be divided into two parts, *i.e.*, optimization of electrical properties and reduction of thermal conductivity. The former approach includes band convergence,^{1,6} resonant states,⁸ *etc.*, while the latter consists of nanostructuring,²⁵ all-scale hierarchical architecturing,²⁴ *etc.*

Tin selenide (SnSe), consisting of nontoxic and earth-abundant elements, crystallizes in an orthorhombic structure (Pnma space group) at room temperature. As the temperature increases over \sim 800 K, it experiences a phase transition to the higher symmetry orthorhombic structure (Cmcm space group).²⁶ Recently, SnSe was regarded as a very promising thermoelectric material since single crystalline SnSe was reported to exhibit an ultrahigh ZT value of \sim 2.6 at 923 K.²⁷ Moreover, a high ZT plateau, ranging from 0.7 to 2.0 in the temperature interval of 300 K to 773 K, was later realized in Na-doped single crystalline SnSe.²⁸ The exceptionally high ZT value in SnSe single crystals results mainly from its intrinsically ultralow thermal conductivity, which was attributed to strong phonon scattering arising from the layered structure and giant anharmonicity of Sn-Se bonds.29,30 However, considering the poor mechanical properties and the difficulty in mass production for single crystals, we are encouraged to explore polycrystalline SnSe with high thermoelectric performance as a replacement. The biggest shortcoming of polycrystalline SnSe is its low electrical transport properties, resulting from the intrinsic very low carrier concentration of $\sim 10^{17}$ cm⁻³. Recently, trials of adding dopants into SnSe in order to lift up the carrier concentration were frequently conducted. For instance, in p-type Na doped polycrystalline SnSe, researchers achieved an optimized carrier



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Paper

concentration of ~2.7 × 10¹⁹ cm⁻³ and a peak ZT of ~0.8 at 773 K along the hot pressing direction;³¹ the carrier density was significantly increased in the Ag-doped sample which exhibits a peak ZT of 0.6 at 750 K;³² K was also proved to be a decent p-type dopant which simultaneously increases the hole concentration and modifies the microstructure, resulting in a record high ZT of ~ 1.1 at 773 K perpendicular to the pressing direction,³³ etc.

Nevertheless, the TE properties of pristine polycrystalline SnSe are still poor. Inspired by the report that zone-melting SnSe with a highly textured structure exhibits a good TE performance perpendicular to the pressure direction,³⁴ we hereby synthesized SnSe nano-powder by hydrothermal reaction and then tried to control the texturing degree in bulk samples by spark plasma sintering (SPS) at different sintering temperatures (400 °C, 450 °C and 500 °C). XRD patterns of sintered bulk samples revealed strong orientation in the $\begin{bmatrix} l & 0 \end{bmatrix}$ direction. Besides, we confirmed that the texturing degree of sintered bulk samples could be controlled by the sintering temperature, which was further validated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). On this account, thermoelectric properties were characterized in two directions, i.e., parallel and vertical to the pressing direction, respectively. To express expediently in the text, the parallel and vertical directions are abbreviated as "p" and "v", respectively. The highest texturing degree and mass density were found in the bulk sample which was sintered at 450 $^\circ$ C, leading to the optimal power factor hence the higher average ZT (~0.38) in the "v" direction. Nevertheless, the highest ZT of \sim 0.81 at 773 K was achieved in the "p" direction of the bulk sample sintered at 400 °C, mainly due to its extremely low thermal conductivity. The average ZT value we achieved in this work is among the highest values for pristine polycrystalline SnSe synthesized by hydrothermal reaction; further enhancement can be expected via suitable doping techniques.

2. Experimental section

Reagents

SnCl₂ powder (99%, Aladdin, China), SeO₂ powder (99.4%, Alfa Aesar, US), ethylene glycol (EG) (AR), hydrazine hydrate (>98%), NaOH (AR), and deionized (DI) water were used.

Synthesis

The powder of polycrystalline SnSe was synthesized by hydrothermal reaction. In a typical process, 2 mmol SnCl₂ and 2 g of NaOH were dissolved in 40 ml of DI water after ~10 min stirring to obtain a transparent solution as the Sn source. 1 mmol SeO₂ was dissolved in 20 ml of EG after ~10 min stirring, then 15 ml of hydrazine hydrate was added into the Se solution, resulting in a dark red suspension. After that, SnCl₂ solution was slowly dropped into the Se containing solution; during this process, the dark red suspension gradually became a faint yellow transparent solution and eventually black suspension. The entire solution was then transferred into a 100 ml PTFE (polytetrafluoroethylene)-lined stainless steel autoclave. The autoclave was sealed and heated to 200 $^{\circ}$ C for 12 h, followed by furnace cooling to room temperature. The black SnSe products were collected by centrifugation and then washed with DI water and ethanol several times before drying under vacuum at 50 $^{\circ}$ C. The obtained powders then densified to form both disk-shaped and column-shaped bulk samples by spark plasma sintering (SPS-211Lx, Japan) at an axial pressure of 50 MPa for 5 min at 400 $^{\circ}$ C, 450 $^{\circ}$ C and 500 $^{\circ}$ C, respectively. All samples with high densities >94% of the theoretical density.

X-ray diffraction

The phase structures were investigated by X-ray diffraction (XRD) (Rigaku, Tokyo, Japan) at a scanning rate of 4° min⁻¹.

Electrical properties

The obtained SPS processed samples were cut into bars with dimensions 10 mm \times 2 mm \times 2 mm; the Seebeck coefficient and the electrical resistance were simultaneously measured using an Ulvac Riko ZEM-3 instrument under a helium atmosphere from room temperature to 773 K. The uncertainty of the Seebeck coefficient and electrical resistance measurements is 5%. (To express expediently in the text, the measured direction "parallel" and "vertical" to the pressing direction were abbreviated as the "p" and "v" directions, respectively.)

Thermal conductivity

The thermal conductivity was calculated by $\kappa = DC_{\rm p}\rho$, where the thermal diffusivity coefficient (*D*) was measured using the laser flash diffusivity method in a Netzsch LFA457 (NETZSCH, LFA457, Germany), $C_{\rm p}$ is the specific heat capacity obtained from previous research,²⁷ and the density (ρ) was determined using the Archimedes method. Considering the uncertainties for *D*, $C_{\rm p}$, and ρ , the uncertainty of the thermal conductivity is estimated to be within 8%; the combined uncertainty for all measurements involved in the calculation of *ZT* is less than 15%.

Electron microscopy

Transmission electron microscopy (TEM) investigations were carried out using a FEI Tecnai F30 microscope operated at 300 kV in South University of Science and Technology of China. The thin TEM specimens were prepared using conventional standard methods. The procedures include cutting, grinding, dimpling, polishing and Ar-ion milling in a liquid nitrogen cooling state subsequently. Field emission scanning electron microscopy (FESEM) investigation was carried out using ZEISS with an operation voltage of 5 kV.

Results and discussion

SnSe possesses an orthorhombic layered structure with the *Pnma* space group at room temperature (PDF #48-1224). Fig. 1(a) shows the XRD pattern of the SnSe powders after the hydrothermal reaction process; all characteristic peaks can be well indexed as the low temperature phase, indicating the



Fig. 1 (a) Powder XRD patterns of SnSe. (b) SEM image and (c) low-magnification TEM micrograph of SnSe powders. (The inset (a) is the image of the bulk sample cutted for the measurement along different directions.)

formation of the SnSe single phase. It is noticeable that the XRD pattern of powders shows a much stronger intensity in the $(4\ 0\ 0)$ plane, indicating preferential orientation along the $[l\ 0\ 0]$ direction. SEM and TEM observations were used hereby to obtain the microstructure of SnSe powders. The SEM image shown in Fig. 1(b) clearly revealed the plate-like features of SnSe powders with a thickness of about 150 nm and a width of about 1-5 µm. Fig. 1(c) shows the low-magnification TEM micrograph with an insert of the electron diffraction pattern along the [1 0 0] zone axis for SnSe powders, the plate-like shape is consistent with the observation in the SEM image. The selected area electron diffraction (SAED) pattern of the pointed area contains the dots for the $(0 \ 0 \ 2)$ and $(0 \ 2 \ 0)$ planes, suggesting that the surface of the plate-like grain is the $(1 \ 0 \ 0)$ plane. Moreover, the natural arrangement of the plate-like grains shows [1 0 0] preferred orientations, leading to stronger intensities in the $(l \ 0 \ 0)$ Bragg directions, which is consistent with the XRD results of powders.

To investigate the influence of sintering temperature during the SPS process on the TE performance, SnSe powders synthesized by hydrothermal reaction were densified at 400 $^{\circ}$ C, 450 $^{\circ}$ C and 500 $^{\circ}$ C, respectively. Fig. 2(a) and (b) show the XRD

patterns of bulk SnSe samples taken in the plane vertical and parallel to the pressing direction at different sintering temperatures. All patterns can also be indexed as the low temperature SnSe phase with an orthorhombic structure without any second phase detected. It is worth noting that the diffraction intensity shows a significant difference in the two directions, where the diffraction intensity in the (4 0 0) plane in the direction vertical to the pressing direction is much stronger. Typically, the strongest diffraction peak changes from (4 0 0) in the direction vertical to the pressing direction to (1 1 1) in the direction parallel to the pressing direction, indicating anisotropy features of the bulk samples and the preferred orientation along the $(l \ 0 \ 0)$ plane. Thus we drew a scheme to interpret the anisotropy during the SPS process as shown in Fig. 3. Under pressure, the plate-like grains are preferentially oriented with their b-c plane perpendicular to the pressing direction and form highly textured bulk samples. As the surface of the plate-like grain is the (1 0 0) plane, the bulk samples stacked by plate-like grains thus have strong orientation along the $[l \ 0 \ 0]$ direction. The texturing degree can be estimated by the typical formula $F = (P - P_0)/(1 - P_0)$ from the XRD results, 35 in this work, *P* is the ratio of the ($l \ 0 \ 0$) intensity and the overall intensity of the measured sample, while P_0 is the ratio



Fig. 2 XRD patterns of bulk samples SnSe (SPSed in 400 °C, 450 °C and 500 °C): (a) vertical to the pressing direction and (b) parallel to the pressing direction.



of the (l 0 0) intensity and the overall intensity of the JCPDS card. As a result, the highest texturing degree ~0.55 is achieved in a 450 °C sintered sample, while 400 °C and 500 °C sintered are ~0.52 and ~0.53, respectively. The texturing degree is closely related to the TE properties, which will be discussed later.

Fig. 4 shows the SEM image on a fresh fractured surface of bulk SnSe samples, which sintered at 400 °C, 450 °C and 500 °C in the planes vertical and parallel to the pressing direction, respectively. The textured features are clearly revealed and are in great agreement with the scheme in Fig. 3. As shown in Fig. 4(a) and (b), the plate-like feature of powders is somehow maintained in a 400 °C sintered sample, the relatively low sintering temperature results in a lower texturing degree, and a lower relative density of ~96%. While 450 °C seems a more appropriate sintering temperature for SnSe powders after a hydrothermal reaction process, leading to the highest texturing degree and the most dense sample with a relative density of

Pressure direction pressu

Fig. 4 SEM images of bulk SnSe sintered at (a) and (b) 400 $^\circ C;$ (c) and (d) 450 $^\circ C$ and (e) and (f) 500 $^\circ C.$

over 97%, Fig. 4(c) and (d). The higher texturing degree and higher density are favorable to the electrical transport properties in the direction vertical to the pressing direction. As shown in Fig. 4(e), the local fusion and grain coarsening are clearly observed in a 500 °C sintered sample, then a lower texturing degree was obtained. Moreover, the potential volatilization in high sintering temperature leads to a low relative density of \sim 94%. Thus, the 450 °C sintered sample is expected to have better TE performance.

To obtain more details of the microstructure, the 450 $^\circ C$ sintered sample was further examined by the TEM view along the "v" direction. The low-magnification TEM image shown in Fig. 5(a) reveals the lamellar structure of the grains, which is consistent with the scheme shown in Fig. 3, indicating strong orientation of the bulk sample. Fig. 5(b) shows a highresolution TEM image; the corresponding electron diffraction pattern (inset) can be easily indexed as the [0 1 1] direction of the SnSe sample. As shown, the layered structure of SnSe is clearly revealed in the lattice image. It is known that phonons could be confined in layers and scattered at the interfaces,³⁶ the in-layer and interlayer off-phase atomic motions are expected due to the intrinsic layered structure which significantly increases the possibility of scattering the propagation of in-plane phonons,³⁷ thus the intrinsic layered structure is responsible for the ultralow lattice thermal conductivity in SnSe. Moreover, due to the lamellar microstructure of the bulk sample, anisotropic transport properties could be expected.

Fig. 6 shows the electrical transport properties ranging from 323 to 773 K of all the bulk SnSe samples in both the "p"



Fig. 5 (a) Low magnification TEM image of the 450 $^{\circ}$ C sintered sample view along the direction vertical to the press direction; (b) high-resolution TEM image of the 450 $^{\circ}$ C sintered sample along the [0 1 1] direction; the inset is the corresponding electron diffraction.

Paper



Fig. 6 Electrical transport properties of SnSe at different SPS temperatures: (a) electrical conductivity; (b) Seebeck coefficient; (c) power factor; (d) carrier concentration and Hall mobility.

direction and "v" directions; the schematic of the measured direction is inserted in Fig. 6(c). Fig. 6(a) shows the temperature dependent electrical conductivity of SnSe sintered at 400 °C, 450 $\,^\circ \mathrm{C}$ and 500 $\,^\circ \mathrm{C}$ in two directions. It is obvious that the electrical conductivity in the "v" direction is generally higher than that in the "p" direction, because the "p" direction is the preferred orientation, *i.e.*, the [l 0 0] direction, which leads to transport property features closer to the *a* direction in single crystals, that is, lower electrical conductivity. With increasing temperature, the electrical conductivity of all the samples shows a similar trend, firstly, increases with temperature from room temperature to \sim 473 K, then decreases rapidly to \sim 673 K, and finally shows an upturn at high temperature; this trend related to the carrier concentration and mobility will be discussed later. Benefiting from the higher texturing degree and higher density, the 450v sample achieved higher mobility and carrier concentration, as shown in Fig. 6(d), leading to extremely high electrical conductivity especially from 350 to 650 K; a maximum electrical conductivity of \sim 73.11 S cm⁻¹ was obtained at 423 K.

As seen in Fig. 6(b), the sign of the Seebeck coefficient of the bulk samples is positive over the entire temperature range, indicating p-type semiconductor behavior and the dominant charge carrier is hole, which may be caused by the volatilization of Sn during the sintering process. The analysis of the existence of Sn vacancies is shown in Fig. S1 and S2 (ESI†). The Seebeck coefficient of all the bulk samples shows an increasing trend from room temperature to 600–700 K, and a slight decrease at high temperature, which may be attributed to the onset of

thermal excitation of minority carriers, *i.e.*, bipolar effect, consisting with the increased carrier concentration at high temperature shown in Fig. 6(d). It is noticeable that the Seebeck coefficient tends to be a constant value at high temperature, which may be related to the phase transition occurring at ~ 800 K, and the texture effect does not exist at high temperature due to phase transition.

Combining the high electrical conductivity and the moderate Seebeck coefficient, bulk samples in the "v" direction achieve a higher power factor compared with the "p" direction shown in Fig. 6(c), and the high Seebeck coefficient ranging from 373 to 673 K is favorable to the average *ZT* values at moderate temperature. In this system, the 450v sample shows the highest power factor over the entire temperature range, and the peak value of ~581 μ W m⁻¹ K⁻² is obtained at 473 K.

To further investigate the electrical transport properties of the bulk samples sintered at 400 °C, 450 °C and 500 °C, the carrier concentration and hall mobility of these three samples are measured using the van der Pauw method shown in Fig. 6(d). As can be seen, the carrier concentration changes slightly with temperature, and at room temperature, the hall carrier concentration is 3.4×10^{19} cm⁻³ for the 400 °C sintered sample, 8.0×10^{19} cm⁻³ for the 450 °C sintered sample and 6.3×10^{19} cm⁻³ for the 500 °C sintered sample, which are much higher than those reported pristine SnSe samples,^{32,38} leading to higher electrical conductivity but a lower Seebeck coefficient. However, hall mobility changes obviously with temperature; with increasing temperature, hall mobility firstly increases from room temperature to ~523 K and then decreases from

Fig. 7 (a) Thermal conductivity and (b) ZT values of SnSe at different SPS temperatures.

523 to 723 K, and upturns at high temperature, indicating a similar tendency to electrical conductivity. This trend is well explained in previous reports that carrier transport is mainly dominated by grain boundary potential barrier scattering from room temperature to ~523 K and the phonon scattering mechanism dominates the transport above 523 K.^{32,38-40}

Fig. 7(a) shows the total thermal conductivity (κ_{tot}) as a function of temperature of all the bulk samples measured along the two directions. It is seen that κ_{tot} exhibits a decreasing trend over the entire temperature range in all samples. Generally, total thermal conductivity consists of electronic thermal conductivity $(\kappa_{\rm e})$ and lattice thermal conductivity $(\kappa_{\rm l})$, the electronic thermal conductivity is calculated by the Wiedemann-Franz relation, $\kappa_{\rm e} = L\sigma T$, where L is the Lorenz number, σ is the electrical conductivity, and lattice thermal conductivity is estimated by subtracting κ_e from κ_{tot} . In this work, the electrical conductivity is relatively low, thus the total thermal conductivity is mainly dependent on the lattice thermal conductivity. Due to the texture features, the transport properties of the "p" direction, which is the preferred orientation direction, *i.e.*, [l 0 0] direction, are closer to those of the *a* direction in single crystals.²⁷ Thus, the "v" direction samples show a higher thermal conductivity than the "p" direction over the entire temperature range. It is notable that the 400p sample achieves an extremely low thermal conductivity of ~ 0.23 W m⁻¹ K⁻¹, which is comparable to the single crystal along the b direction and favorable to its TE performance.

The calculated figure of merit, *ZT*, as a function of temperature is shown in Fig. 7(b). Benefiting from the high texturing degree and high mass density, SnSe sintered at 450 °C shows the best electrical transport properties and the highest average *ZT* (~0.38) values in the "v" direction. Compared with previous reports, what we achieved in this work is the highest average *ZT* value in pristine polycrystalline SnSe as shown in Fig. 8. The details are shown in Table S1 (ES†). Further enhancement can be expected *via* proper hole-doping during hydrothermal reaction. Moreover, attributed to the extremely low thermal conductivity at high temperature, the sample sintered at 400 °C exhibits the highest peak *ZT* value of ~0.81 at 773 K in the "p" direction. Our results demonstrate that the thermoelectric performance of SnSe polycrystals can be enhanced significantly by sole texture-control;

Fig. 8 Comparison of the average ZT values of pristine polycrystalline SnSe.^{26,32–34,38,41}

this technique could also be applied to other layered thermoelectric systems.

4. Conclusions

In summary, we investigated the relationship between the texture and TE properties in polycrystalline SnSe samples, which were synthesized by hydrothermal reaction followed by the SPS process. These bulk samples all show a strong orientation along the $[l \ 0 \ 0]$ direction, and structural anisotropy was further confirmed by TEM and SEM observations. We noticed that the texturing degree can be effectively controlled by the sintering temperature. The highest texturing degree was achieved in SnSe samples sintered at 450 °C, resulting in the highest power factor and the best thermoelectric properties in the vertical direction in the moderate temperature range. Our studies of the texturing degree of SnSe may guide the further synthesis process of polycrystalline SnSe. Furthermore, the texture-control approach is highly applicable to other thermoelectric systems.

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