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The thermoelectric performance of anisotropic SnSe Doped with Na

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Lead-free polycrystalline SnSe is a promising thermoelectric compound consisting of earth-abundant elements. However, poor electrical transport property for low intrinsic defect concentration (3×10^{17} cm^{-3}) limits the usage of stoichiometric SnSe compound. In this work, NaSe as acceptors was doped into SnSe compound in order to optimize the electrical transport properties, especially to increase the carrier concentration. As a result, the carrier concentrations increased and saturated at about 1.0×10^{19} cm^{-3} for Na_{0.02}Sn_{0.98}Se at 300K. A maximum power factor of 0.48 mWm^{-1}K^{-2} was obtained. And a maximum zT value of 0.75 was observed for Na_{0.02}Sn_{0.98}Se along the direction perpendicular to the sintering pressure, which is 25% higher than that (0.6) of the undoped SnSe compound.

Introduction

Thermoelectric material is a kind of material that could convert heat to electricity directly, or vice versa. Devices made by thermoelectric material have advantages of no moving parts, quiet operation, low environmental impact and high reliability. The performance of thermoelectric materials can be evaluated by the dimensionless figure of merit, zT = S^2σ/κ where S, σ, κ, T are the Seebeck coefficient, the electrical conductivity, the thermal conductivity and the absolute temperature, respectively. Continuous efforts have been invested into optimizing thermoelectric performance, for example, phonon engineering,2,3 band engineering4-6 and point defect engineering7,8 etc. Binary bismuth and lead chalcogenides such as Bi_{2}Te_{3}, PbTe, and their solid solutions have been intensively studied with above optimizing methods for thermoelectric applications.9,10,11 However, for those thermoelectric materials, in spite of high zT values (>1) obtained, widespread application is restricted for toxic Pb and costly Te, which make SnSe obtain more attention as a potential alternative.

Currently, SnSe crystal draws considerable attentions for its extremely high zT values (2.6 and 2.3 at 950 K along the b and c axes, respectively).12 The extremely high zT values is mainly attributed to its ultralow lattice thermal conductivity for the distinctive anharmonic structure in SnSe. SnSe has a layered orthorhombic structure resembling a distorted NaCl rock-salt structure (shown in Figure 1). Along the b-c plane, two-atom-thick SnSe slabs creating a zig-zag accordion-like projection along the b axis spread within the plane of the slabs. Those two-atom-thick SnSe slabs were linked with weaker Sn-Se bonding along the a-axis direction, and contributed the easy cleavage along (100) plane.13 The distinctive structure results in its outstanding anisotropy. For single crystal, weak bonding between Sn-Se in SnSe slabs leads to poor mechanical properties. And compared with polycrystalline, preparation technology of single crystal is complicated. These all contribute to the study of polycrystalline SnSe. The low intrinsic thermal conductivity values (0.3-0.8 Wm^{-1}K^{-1}) and low intrinsic carrier concentration value (3×10^{17} cm^{-3}) of undoped polycrystalline SnSe were reconfirmed at room temperature.14 One feasible solution toward the poor electrical transport property is increasing the carrier concentrations. Various candidates (Na, Ag, Sr, In, Pb and Tl) as dopants were attempted,15 but only Na and Ag seem to be able to dope and increase the carrier concentrations. Na-doping in polycrystalline SnSe increases carrier concentrations but decreases the band gap. In general, bipolar thermal transport is controlled by the minority carrier partial electrical conductivity and band gap for extrinsic cases.16 As a result, the decreasing band gap and the minority carrier partial electrical conductivity compensate each other for thermal conductivity, especially for bipolar conduction.

In this work, we synthesized a sequence of p-type Na_{x}Sn_{1-x}Se (x=0.0025-0.02) polycrystalline by melting and Spark Plasma Sintering (SPS) methods. And the orientation degree and the transport properties in different directions were investigated for the outstanding anisotropy of the single crystal SnSe. A maximum zT value of 0.75 was observed for Na_{0.02}Sn_{0.98}Se in perpendicular to the pressing direction at 823 K. In parallel to the pressing direction, a maximum zT value of 0.61 was obtained at 823 K.
Results and discussion

Figure 2(a) shows the X-ray diffraction (XRD) patterns of Na$_x$Sn$_{1-x}$Se (x=0, 0.0025, 0.005, 0.0075, 0.01, 0.02) powders grounded from ingots. All diffraction peaks can be well indexed to the orthorhombic SnSe phase ([PDF#48-1224] low temperature phase, Cmcm), suggesting the formation of single phase SnSe-based solid solutions. No impurity phase is observed for all powders. XRD patterns of SnSe bulk sintered by SPS in both parallel and perpendicular to the pressing direction. (c) The sample cut direction for measurements along different directions. (d) A photograph of a bulk sample sintered by SPS. (e) Differential Scanning Calorimeter (DSC) for Na$_0.01$Sn$_{0.99}$Se. The exothermal (endothermal) peak is observed at 803 K.

\[ F = \frac{P - P_0}{P} \]

\[ P_0 = \frac{I(h00)}{\Sigma I(hkl)} \]

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Where P and P$_0$ are the ratios of the integrated intensities of all (h00) planes to those of all (hkl) planes for preferentially and randomly oriented samples, respectively. The orientation factor (F=0.32) in parallel to the pressing direction is much higher than that (F=0) in perpendicular to the pressing direction, which is coincide with the observed results (shown in Figure 2(b)). This could be attributed to the cleavage in (h00) plane. Under the sintering pressure, the cleavage plane tends to the direction perpendicular to the pressing direction, which performs a highly oriented degree in parallel to the pressing direction, namely a stronger (400) peak in parallel to the pressing direction.

Figure 2(e) shows the DSC of the Na-doped Na$_{0.01}$Sn$_{0.99}$Se compound. The exothermal (endothermal) peak of Na$_{0.01}$Sn$_{0.99}$Se is observed around 800 K, indicating the phase transition from the Pnma ($D_{2h}^2$) phase to the Cmcm ($D_{2h}^5$) phase. The temperature of phase transition matches well with the previous reports by Zhao et al.\cite{12}. Figure 3(a) Hall carrier concentration of Na$_x$Sn$_{1-x}$Se as function of Na content at 300K. The measured Hall carrier concentration of the undoped SnSe is around $3 \times 10^{19}$ cm$^{-3}$ at 300K, which is consistent with the prior report\cite{15}. With Na doping, the carrier concentration increases and saturates at about $1.0 \times 10^{19}$ cm$^{-3}$ for Na$_{0.02}$Sn$_{0.98}$Se. Fig. 3(b) shows UV-Vis-NIR spectrums results for all Na$_x$Sn$_{1-x}$Se. The band gap of the undoped SnSe was determined to be 0.84 eV, which matches the past literature well\cite{12}. With increasing Na, the band gap of the Na$_x$Sn$_{1-x}$Se shows decreasing trends.
The electrical transport parameters of Na$_x$Sn$_{1-x}$Se compounds in both parallel and perpendicular to the pressing direction are shown in Fig. 4. The electrical conductivity of undoped SnSe keeps a typical semiconducting behavior, which remains a low level below 573K, then rapidly increases with the temperature. It is noteworthy that the electrical conductivity of Na$_{0.0025}$Sn$_{0.9975}$Se shows a similar trend to that of SnSe, which is related to the low carrier concentration (shown in Figure 3(a)). For the Na$_x$Sn$_{1-x}$Se ($x>0.0025$), the electrical conductivity decreases and turns to increase over 673 K with temperature indicating the thermal excitation of the intrinsic semiconducting carriers. The significant increase of the electrical conductivity is attributed to the improvement of the carrier concentrations. With Na doping, the carrier concentration increases from $3\times10^{17}$ cm$^{-3}$ to $1.0\times10^{19}$ cm$^{-3}$. A maximum electrical conductivity of 49.55 S cm$^{-1}$ is obtained for Na$_{0.01}$Sn$_{0.99}$Se at 823K in perpendicular to the pressing direction.

At the same temperature, the electrical conductivity in perpendicular to pressing direction is higher than that in another measuring direction, (as shown in Figure 3(b)). The difference in both measuring directions for electrical conductivity mainly comes from the outstanding anisotropy of the effective mass. Based on the Fermi surface shape, the effective mass possesses the highest value along a-axis direction (corresponding to perpendicular to the SnSe layers) meaning a higher effective mass in parallel to pressing direction$^{17}$. High effective band mass results in a low mobility. Because the mobility ($\mu = e\tau/\hbar m^*_{\text{eff}}$) is inversely proportional to inertial mass $m^*$, the scattering time $\tau$ decreases with $m^*$. Simultaneously, the Seebeck coefficient of Na$_x$Sn$_{1-x}$Se ($x=0, 0.0025, 0.005, 0.0075, 0.01, 0.02$) measured along perpendicular and parallel to the sintering pressure. (a)(b), the electrical conductivity. (c)(d), the Seebeck coefficient. (e)(f), the power factor.

Figure 4 The electrical transport properties as a function of temperature for Na$_x$Sn$_{1-x}$Se ($x=0, 0.0025, 0.005, 0.0075, 0.01, 0.02$) measured along perpendicular and parallel to the sintering pressure. (a)(b), the electrical conductivity. (c)(d), the Seebeck coefficient. (e)(f), the power factor.

for the thermal excitation corresponding to the change in electrical conductivity. With increasing Na, the temperature of the maximum Seebeck coefficient demonstrates an increasing trend while the band gap gradually decreases. This mainly results from the elevation in carrier concentrations. Different from the electrical conductivity, the Seebeck coefficient of Na$_x$Sn$_{1-x}$Se shows scarcely difference in both parallel and perpendicular to the pressing direction.

Figure 3(e) and 3(f) show the power factor of Na$_x$Sn$_{1-x}$Se as function of temperature in both parallel and perpendicular to the pressing direction. The maximum power factor of the undoped SnSe is 0.29 mW m$^{-1}$K$^{-2}$. With Na doping, the maximum power factor of 0.48 mW m$^{-1}$K$^{-2}$ is obtained for Na$_{0.02}$Sn$_{0.98}$Se at 823K in the direction perpendicular to the sintering pressure, which is 39.58% higher than that for the SnSe. The power factor maximum in parallel to pressing direction is 0.32 mW m$^{-1}$K$^{-2}$ which is 33.33% lower than that in another measuring direction. The outstanding anisotropy in power factor is observed.

Fig. 5(a) and 5(b) show the temperature dependence of the thermal conductivity of all the samples in both perpendicular and parallel to the sintering pressure. The thermal conductivity of all samples decreases with temperature below 773K due to the increased phonon-scattering. When the temperature is over 773K, a turn happens to the thermal conductivity, which is related to the phase transition from Pnma space group to Cmcm space group at around 800 K (as shown in Figure 2(c)). Derived from the strong anharmonicity in bonding, low temperature Pnma phase SnSe possesses lower thermal conductivity values than high temperature Cmcm phase SnSe$^{18}$.
improvement of thermal conductivity is mainly attributed to the phonon conduction component, not the electronic thermal conductivity. For Na$_x$Sn$_{1-x}$Se ($x=0$), the higher phonon conduction could be related to the fluctuation of soft lattice caused by the change in the strain field which mainly depends on bond polarity. The larger electronegativity difference between cations and anions is, the higher intensity of bond polarity is. The enormous difference between Sn–Se and Na–Se (the electronegativity of Na and Sn are 0.93 and 1.96) could rigidify the soft lattice, which results in a slight improvement in the phonon conduction.

In general, the significant improvement of the carrier concentration tends to contribute to the bipolar thermal conductivity. However, it is interesting that distinctive difference in thermal conductivity is not observed between SnSe and Na-doped SnSe at high temperature range. The barely difference in the trends of thermal conductivity could be attributed to the drop of gap band ($E_g$). For a single parabolic band and acoustic phonon scattering ($\lambda = -1/2$), bipolar thermal conductivity in semiconductors can be expressed as:

$$\kappa = \frac{k_B^0}{e^2} \left( \frac{E_g}{k_B T} \right)^{2/3} \left( \frac{2F(\xi)}{F(\xi)} \right)^2 \frac{T}{g} = \frac{1}{\sigma_n} + \frac{1}{\sigma_p}. \quad (4)$$

Where $k_B$ is the Boltzmann constant, $e$ the free electron charge, $F$ the Fermi integral of the order of $x$. Therefore $\xi_n = -E_g/k_B T$, where $E_g$ is the band gap. In general, bipolar thermal transport is controlled by the minority carrier partial electrical conductivity for extrinsic cases. With increasing Na, the band gap of the Na$_x$Sn$_{1-x}$Se shows a decreasing trend which weakens the effects of the carrier concentration on bipolar thermal conductivity. The thermal conductivity shows anisotropy in different measuring directions.

Figure 6 Temperature dependence of (a)(b) electrical conductivity, (c)(d) Seebeck coefficient, (e)(f) total thermal conductivity, for sample SnSe and Na$_{0.01}$Sn$_{0.99}$Se respectively with measurements from room temperature to 823 K (closed green circles squares), then back to room temperature (open green circles), then increased again to 823 K (closed pink squares), and then decreased to room temperature (open pink squares).

Figure 5(c) and 5(d) show the temperature dependence of $zT$ values for Na$_{1-x}$Sn$_x$Se. The $zT$ value of the undoped SnSe increases with temperature and a maximum $zT$ of 0.6 is obtained at 823 K, which is higher than the previous reports. The maximum $zT$ value of 0.75 is obtained for Na$_{0.01}$Sn$_{0.99}$Se at 823 K in perpendicular to the pressing direction. In parallel to the pressing direction, the maximum $zT$ of 0.61 is obtained for Na$_{0.01}$Sn$_{0.99}$Se. The enhancement of $zT$ for Na-doped SnSe is mainly attributed to the optimization of electrical transport performance.

Compared with Ag-doped SnSe, the increase of $zT$ values in Na$_{1-x}$Sn$_x$Se and Ag$_{1-x}$Sn$_x$Se is attributed to the rise of electrical transport properties (shown in ESI). It is worth noting that the extremum values of Na$_{1-x}$Sn$_x$Se emerge at higher temperature than that of Ag$_{1-x}$Sn$_x$Se in both resistivity and Seebeck coefficient. This could be derived from the effects of different dopants to different extents on band gap.

Experimental

The weighted elemental tin (Sn, 99.999%), Selenium (Se, 99.999%), Na$_2$Se (99.99%) were loaded into graphite crucible, then loaded into quartz ampoules. The ampoules were evacuated to $7.5 \times 10^{-5}$ Pa, sealed, and slowly heated up to 1253 K over 12 h, then kept that temperature for 24 h followed by water quench. The obtained ingots were annealed at 973 K for 7 days followed by another water quench. The annealed ingots were ground into powders with an agate mortar, the powders were loaded into graphite mould with 13 mm diameter and sintered in Spark Plasma Sintering (SPS) under 50 MPa pressure and 873 K for 5 min. The cylinders (Figure 1d) were cut into Bar- and coin-shaped samples (Figure 1c) along different directions for electrical and thermal transport measurements. The parallel (perpendicular) to pressing direction was defined as electrical and thermal properties test direction was parallel (perpendicular) to SPS pressing direction.

The phase composition was analyzed by powder X-ray diffraction (XRD) with X-ray diffract-meter (Cu Ka radiation $\lambda=0.154$ nm, Bruker, German). The temperature dependence of electrical conductivity, Seebeck coefficient was tested by LSR-3 (Linseis) under static Helium atmosphere. The thermal conductivity was measured using the Physical Property Measurement System (PPMS-14, Quantum
Notes and references
