



Regular Article

Enhanced thermoelectric performance of p-type SnSe doped with Zn

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ABSTRACT

In this study, we have synthesized SnSe doped with zinc (Zn) and investigated the effect of Zn doping on the thermoelectric properties of SnSe. The results demonstrate that a high thermoelectric figure of merit (ZT) of 0.96 at 873 K is obtained for $\text{Zn}_{0.01}\text{Sn}_{0.99}\text{Se}$, which is 41% higher than that of pure SnSe ($ZT = 0.68$). The value is the highest value reported for p-type polycrystalline doped SnSe materials, which arises from the increased power factor coming from a high electrical conductivity and an enhanced Seebeck coefficient.

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1. Introduction

Thermoelectric materials could provide a clean and efficient way to solve the global energy and environmental crisis, thanks to their ability to direct conversion between thermal and electrical energy, which enable reprocessing of waste energy [1]. The conversion efficiency of thermoelectric materials can be assessed with the dimensionless figure of merit, $ZT = S^2\sigma T/\kappa$, where Z is figure of merit and T is absolute temperature, S , σ and κ are Seebeck coefficient, electrical conductivity, and thermal conductivity [2]. However, the development of highly efficient thermoelectric materials is still a great challenge because it requires decoupling of σ , S and κ , which are often unfavorably interdependent according to the Wiedemann–Franz law [3].

Because of energy efficiency, management and conservation, the search for high-performance thermoelectric materials with low cost and earth abundant elements is attracting significant attention. Recently, the surprising high record $ZT \approx 2.6$ and 2.3 at 923 K along the b and c -axis were reported by Zhao et al. in p-type SnSe single crystal [4], which arose from the intrinsically ultralow thermal conductivity due to strong anharmonicity of the chemical bonds. High ZT ranging from 0.7 to 2.0 was realized in sodium doped SnSe single crystals in a wide temperature range of 300–773 K [5]. However, due to the long duration of synthesis and expensive preparation cost for single-crystalline SnSe, thermoelectric properties for polycrystalline SnSe-based samples have been studied [6–12]. The maximum ZT of 0.5 at 820 K was reported for p-type polycrystalline SnSe by Sassi [6]. Doping is an efficient way in improving its thermoelectric performance. For instance, peak ZT of

0.6 was observed separately in p-type Ag-doped and Tl-doped polycrystalline SnSe [7–8]. Peak ZT for Cu-doped SnSe and Na-doped SnSe are 0.7 and 0.75, respectively [9–10]. ZT for n-type $\text{SnSe}_{0.95}\text{-BiCl}_3$ and $\text{SnS}_{0.1}\text{Se}_{0.8}\text{I}_{0.03}$ reaches 0.7 and 1.0, respectively [11–12].

The highest thermoelectric figure of merit for p-type polycrystalline doped SnSe materials is not larger than 0.75. In this paper, Zn-doped SnSe samples are prepared and the effects of Zn doping on the thermoelectric properties are investigated. Our results indicate that a high thermoelectric figure of merit ZT of 0.96 at 873 K is obtained for $\text{Zn}_{0.01}\text{Sn}_{0.99}\text{Se}$, which is 41% higher than that of pure SnSe ($ZT = 0.68$). The highest ZT value reported for polycrystalline p-type doped SnSe arises from the increased power factor, which comes from a high electrical conductivity and an enhanced Seebeck coefficient.

2. Experimental

Elemental Sn shot (99.999%, Alfa Aesar), Zn powders (99.999%, Alfa Aesar) and Se (99.999%, Alfa Aesar) powders were weighed according to the atomic ratio of $\text{Zn}_x\text{Sn}_{1-x}\text{Se}$. The mixture was loaded into quartz ampoule sealed under vacuum at 10^{-3} Pa, and then heated to 1223 K over 10 h, soaking at that temperature for 24 h, followed by furnace-cooling to room temperature. The obtained ingot was ground into powders with an agate mortar. Then hot-pressed at 673 K under the pressure of 600 MPa in a diameter of 15 mm tungsten carbide die in vacuum for 1 h. The heating rate was 7 K/min.

The samples were characterized by X-ray diffraction (XRD) using Philips X'Pert PRO X-ray diffractometer equipped with graphite monochromatic Cu K_α radiation ($\lambda = 1.54056$ Å). The operation voltage and current were kept at 40 kV and 40 mA, respectively. The microstructure was characterized by field emission scanning electron microscopy (FESEM; SU8020).

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The Seebeck coefficient and electrical resistivity were measured by commercial equipment (ZEM-3(M10), Ulvac Riko, Inc.) in a low pressure helium environment with samples of about $2\text{ mm} \times 3\text{ mm} \times 10\text{ mm}$. The thermal conductivity was calculated from $\kappa = dC_pD$. The density d was measured by Archimedes' method. The specific heat C_p was determined by using differential scanning calorimetry (Netzsch DSC 404F3). The thermal diffusivity D was measured by the laser flash method (Netzsch, LFA-457). The Hall coefficient (R_H) was measured using Van Der Pauw method under a reversible magnetic field of 1.5 T. The Hall carrier concentration (p) and hall mobility (μ) of the charge carriers were calculated from the relations $p = 1/(R_H e)$ and $\mu = R_H/\rho$, where e was the electric charge. The uncertainty for the electrical conductivity was 3%, the Seebeck coefficient 5%, the thermal conductivity 7%, so the combined uncertainty for the power factor was 10% and that for ZT value is 12%. Error bars were not shown in the figures to increase the readability of the curves.

3. Results and discussion

Fig. 1(a) shows the XRD pattern for $\text{Zn}_x\text{Sn}_{1-x}\text{Se}$ samples ($x = 0, 0.01, 0.02, 0.03$), almost all diffraction peaks can be indexed to the phase of SnSe (JCPDS No. 89-0233), belonging to the orthorhombic structure, indicating that the specimens have the same crystallographic structure as that of SnSe. However, a small amount of ZnSe with JCPDS No. 01-0690 as impurity phase existed in Zn-doped compound $\text{Zn}_{0.03}\text{Sn}_{0.97}\text{Se}$. The values of the lattice parameters a , b and c for all samples have been calculated from the XRD data, as shown in Fig. 1(b). It can be seen that the lattice parameters both a and c decrease with increasing Zn content x from 0 to 0.03, which may be result from that the ionic radius of Zn^{2+} (0.88 Å) is smaller than that of Sn^{2+} (0.93 Å). In comparison, lattice parameter b decreases with Zn content, then increases with further increasing Zn content. The decrease in b may be due to the substitution of the smaller ionic radius of Zn^{2+} (0.88 Å) for Sn^{2+} (0.93 Å). The increase in b may attribute to the substitution of Zn into the position of Sn defect.

The scanning electron microscopy is employed to study the surface morphology of fractured surface of $\text{Zn}_{0.02}\text{Sn}_{0.98}\text{Se}$, as shown in Fig. 2. The obvious layered structures with sizes of 0.5–1 μm are observed in Fig. 2(a&b), indicating the oriented structures in polycrystalline $\text{Zn}_{0.02}\text{Sn}_{0.98}\text{Se}$ sample. Energy-dispersive X-ray spectroscopy (EDXS) analyses (Fig. 2(c)) indicate Zn, Sn and Se are distributed in the sample and there are ZnSe at the grain boundaries.

The electrical properties of $\text{Zn}_x\text{Sn}_{1-x}\text{Se}$ samples ($x = 0, 0.01, 0.02, 0.03$) is shown in Fig. 3. Fig. 3(a) gives the temperature dependence of the electrical conductivity σ of $\text{Zn}_x\text{Sn}_{1-x}\text{Se}$ ($x = 0, 0.01, 0.02, 0.03$). One can see that σ for pure SnSe monotonously increases from 0.46 Scm^{-1} at room temperature to 65.05 Scm^{-1} at 873 K, showing typical semiconductor transport behavior. In the case of the Zn-doped samples, all samples show the same temperature-dependent trend: as

temperature increases from 300 to 700 K, the electrical conductivity increases slowly; then increases rapidly to the maximum at a certain temperature; and above that, decreasing σ is observed with increasing temperature. A good linear relationship between $\ln\sigma$ and $1/T$ for $\text{Zn}_x\text{Sn}_{1-x}\text{Se}$ samples ($x = 0, 0.01, 0.02, 0.03$) exists in the low temperature range of 300–550 K and high temperature range of 600–775 K, as shown in the inset of Fig. 3(a). By using a thermally activated expression (Arrhenius plot) in the corresponding temperature regime, written as:

$$\ln\sigma = C + \frac{E_a}{2k_B T} \quad (1)$$

where C , k_B and E_g is a constant, Boltzmann constant and band gap, respectively. By the best fit of the experimental data with formula (1), one can obtain two activation energies $E_{a1} = 0.14\text{ eV}$, 0.18 eV , 0.17 eV and 0.16 eV in low temperature and $E_{a2} = 0.89\text{ eV}$, 0.85 eV , 0.84 eV and 0.85 eV in high temperature for $\text{Zn}_x\text{Sn}_{1-x}\text{Se}$ ($x = 0, 0.01, 0.02, 0.03$), respectively. The second activation energy E_{a2} are almost equal to the energy gap $E_g = 0.86\text{ eV}$ for SnSe reported in high temperature [5], which indicates intrinsic excitation occurs in the temperature range of 600–775 K. In addition, the electrical conductivity is significantly influenced by Zn doping above 800 K. For instance, σ for Zn substituted samples is larger than that of pure SnSe in the whole temperature range investigated. In order to examine the effect of Zn doping on the electrical conductivity of SnSe, the carrier concentration p as a function of temperature is given in Fig. 3(b). Seen from Fig. 3(b), p for $\text{Zn}_x\text{Sn}_{1-x}\text{Se}$ ($x = 0, 0.01, 0.02, 0.03$) increases over the measured temperature range, which is caused by the thermal excitation of majority carriers. p for $\text{Zn}_{0.01}\text{Sn}_{0.99}\text{Se}$ is larger than that of SnSe in the whole temperature range investigated. Since ionic radii of Zn^{2+} (0.88 Å) and Sn^{2+} (0.93 Å) is similar to that of Sn^{2+} (0.93 Å), Zn doping in SnSe can present two kinds of valence state Zn^+ and Zn^{2+} . Obviously, substitution of Zn^+ for Sn^{2+} will introduce acceptor level into the gap of the host, while the substitution of Zn^{2+} for Sn^{2+} will not introduce directly donor or acceptor levels into the gap. Therefore, if Sn^{2+} are replaced by Zn^+ the carrier concentration (holes) will increase, which would explain why the electrical conductivity of $\text{Zn}_{0.01}\text{Sn}_{0.99}\text{Se}$ is larger than that of SnSe. p for $\text{Zn}_x\text{Sn}_{1-x}\text{Se}$ ($x = 0.02$ and 0.03) is larger than that of SnSe, while smaller than that of $\text{Zn}_{0.01}\text{Sn}_{0.99}\text{Se}$. From the results of XRD and SEM, one can see as increasing Zn content, part of Zn substitutes Sn, the other Zn reacts with Se, forming ZnSe. This leads to the decrease in defect of Se, causing decrease in hole concentration. Combined with the data of electrical conductivity and carrier concentration, carrier mobility μ is calculated as shown in Fig. 3(c). It can be seen that the carrier mobility decreases after Zn substitution. For example, at 300 K, μ for SnSe is $56\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, in the case of Zn substituted samples $\text{Zn}_x\text{Sn}_{1-x}\text{Se}$ ($x = 0.01, 0.02$ and 0.03) μ are in the range of $25\text{--}30\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$. Hole mobility as a function of temperature is fitted by using $\ln\mu \sim \alpha \ln T$ as shown in the inset of Fig. 3(c). α increases from -1.5 to -1.0 as

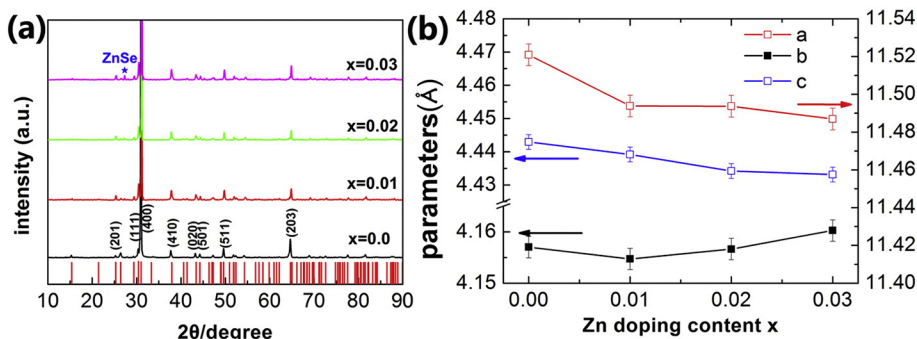


Fig. 1. XRD patterns for $\text{Zn}_x\text{Sn}_{1-x}\text{Se}$ ($x = 0, 0.01, 0.02, 0.03$) (a); lattice parameters for $\text{Zn}_x\text{Sn}_{1-x}\text{Se}$ ($x = 0, 0.01, 0.02, 0.03$) (b).

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