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Thermoelectric properties of n-type transition metal-doped PbSe

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ABSTRACT

Thermoelectric properties of transition metal (Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, or W)-doped PbSe were studied. Peak *ZT*~1.1, ~1.15, and ~1.2 at about 873 K has been achieved in $Ti_{0.015}Pb_{0.985}Se$, $Zr_{0.005}Pb_{0.995}Se$, and $Nb_{0.01}Pb_{0.99}Se$, respectively, with increased room temperature Hall carrier concentration to ~10^{19}–10^{20} cm^{-3}. However, the lower temperature *ZT* (<600 K) is not favorable compared with other transition metal (V, Cr, Mo, or W)-doped PbSe with lower doping concentration. Higher room temperature *ZT* contributes to the higher average *ZT* despite lower peak *ZT*. First-principles calculation found resonant states created in n-type PbSe doped by Ti, V, Zr, Nb, Mo, Hf, Ta, or W similar to Cr-doped PbSe, while Pisarenko plots show absence of resonant states due to the deep residence of the states and the limited doping concentration confirmed by the calculations.

Introduction

Pb chalcogenides are important mid-temperature (500 °C-600 °C) thermoelectric materials with high dimensionless figure of merit $ZT = [S^2\sigma/(\kappa_L+\kappa_e)]T$, where S is the Seebeck coefficient, σ the electrical conductivity, κ_L the lattice thermal conductivity, κ_e the electronic thermal conductivity, and T the absolute temperature [1–13]. Increasing the power factor ($S^2\sigma$) and reducing the thermal conductivity can both improve *ZT*. Compared with PbTe, PbSe has been widely investigated due to the abundant Se and decent *ZT*. With narrow band gap and complex band structure, PbSe is easy to be optimized by doping [14–18]. For p-type PbSe, Na [19] and K [4] are usually heavily doped to converge the two hole valence bands for high valley degeneracy and then increased Seebeck coefficient. N-type PbSe has only single non-parabolic band and limited valley degeneracy [14] but having resonant states when doped by Al [20], which also contributes to the high Seebeck coefficient. In addition, a weak electron-phonon coupling was proved beneficial to the high Hall mobility in n-type Br-doped PbSe [14]. Extensive nanoscale precipitates were found to be effective for decreasing the lattice thermal conductivity in n-type Sb-doped PbSe [21]. Actually, increased *ZT* has been achieved in n-type PbSe doped with most group IIIA elements (B, Al, Ga, and In) [20,22,23], group VA elements (Sb [21] and Bi [24]), and group VIIA elements (Cl [25,26], Br [14], and I [27,28]). However, the *ZT* curve generally increases steeply from room temperature to high temperature, resulting in only high peak *ZT*, but low average *ZT* and low device efficiency (η), which depends on the average *ZT* of the TE materials over the temperature range, $\eta_{max} = [(T_H\text{-}T_C)/T_H]\ [(1+ZT_{average})^{1/2}-1]/[(1+ZT_{average})^{1/2}+T_C/T_H]$, where T_H is the temperature at the hot junction, and T_C is the temperature at the cold junction [29–32]. In our previous study, we found that some transition metals [33,34] (Ti, V, Cr, Nb, and Mo) can enhance the lower temperature (below 600 K) thermoelectric properties of n-type PbSe. Specifically, Cr-doped PbSe [33,34] has both higher room temperature *ZT* ~0.4 and peak *ZT* ~1.0 between 573 K and 773 K, causing the increased average *ZT* and efficiency of n-type PbSe over a wide temperature range (300 K–873 K) [27,35–39].

In this article, we systematically study the thermoelectric properties of n-type transition metal (TM: Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, or W)-doped PbSe. Hopefully, we can find the origin for the high

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average *ZT* in Cr-doped PbSe [33,34]. Peak *ZT* values ~0.9 to 1.2 at about 873 K were achieved in Ti-, Zr-, Nb-, and Hf-doped PbSe with, however, lower room temperature $ZT < 0.1$. Higher average *ZT* was mostly obtained in samples with higher room temperature *ZT*, which was the result of the lower carrier concentration confined by the limited doping concentration. First-principles band structure calculations indicated the untouchable extra electronic states in conduction band bottom (CBB) of PbSe introduced by all the transition elements.

Experimental section

N-type transition metals (TM: Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, or W)-doped PbSe were prepared by melting, hand milling, and hot pressing. The raw materials with nominal compositions were sealed into a vacuum carbon-coated quartz tube by a Partulab device (MRVS-1002) and melted to an ingot. The detail composition of these transition metal-doped samples are as follows: $Ti_xPb_{1-x}Se$ ($x = 0.005$, 0.01, 0.015, and 0.02), $V_xPb_{1-x}Se$ ($x = 0.01$, 0.0125, and 0.015), $Zr_xPb_{1-x}Se$ ($x = 0.004$, 0.0045, 0.005, 0.006, and 0.01), $Nb_xPb_{1-x}Se$ ($x = 0.005$, 0.01, 0.015, and 0.02), $Mo_xPb_{1-x}Se$ ($x = 0.005$, 0.01, and 0.02), $Hf_xPb_{1-x}Se$ ($x = 0.005$, 0.01, 0.015, and 0.02), $Ta_xPb_{1-x}Se$ ($x = 0.005$, 0.01, and 0.015), and $W_xPb_{1-x}Se$ ($x = 0.005$, 0.01, and 0.015). The obtained ingots were cleaned and hand milled in a glove box. The powder was hot pressed by direct current (dc-HP) press at 600 °C for 2 min under a pressure of 80 MPa to get a half-inch disk. X-ray diffraction spectra analysis was conducted on a Rigaku D/max 2500 PC instrument with Cu K_α ($\lambda = 1.5418$ Å) radiation. All the samples are single phase without any impurity. The electrical resistivity (ρ) and Seebeck coefficient (S) were simultaneously measured on a commercial system (CTA-3). The thermal conductivity κ was calculated using $\kappa = D\alpha C_p$, where D is the volumetric density determined by the Archimedes method, α the thermal diffusivity obtained on a laser flash apparatus (Netzsch LFA 457), and C_p the specific heat measured on a differential scanning calorimetry thermal analyzer (Netzsch DSC 404 F3). All the samples were well compacted with relative density >98%. The Hall coefficient R_H at room temperature was measured using a van de Pauw technique under a reversible magnetic field of 1.5 T. The Hall carrier concentration n_H and Hall mobility μ_H were calculated using $n_H = 1/(eR_H)$ and $\mu_H = \sigma R_H$, respectively. The uncertainty for the electrical conductivity is 3%, the Seebeck coefficient 5%, and the thermal conductivity 7% (comprising uncertainties of 4% for the thermal diffusivity, 5% for the specific heat, and 3% for the density), so the combined uncertainty for the power factor is 10% and that for *ZT* value is 12%.

Computational section

First-principles calculations were performed by the projector augmented wave (PAW) method implemented in the Vienna *ab initio* Simulation Package (VASP) [40,41]. The Perdew-Burke-Ernzerhof generalized gradient approximation for the exchange-correlation potential was used for the calculations [42]. The formation energy and electronic structure calculations for all the transition elements-doped PbSe were carried out based on a 3 × 3 × 3 supercell of PbSe unitcell with fully relaxed structures. The plane-wave cutoff energy was set to be 350 eV. Spin-orbital interactions were considered in the electronic structure calculations.

Results and discussion

Table 1
Ionic radius (r) and Pauling electronegativities (PE) of Pb, Se, Ti, V, Cr Zr, Nb, Mo, Hf, Ta, and W.

	Pb	Se	Dopants (Transition Elements)								
			Ti	V	Cr	Zr	Nb	Mo	Hf	Ta	W
r (Å)	1.20	1.91	0.68	0.74	0.69	0.80	0.70	0.62	0.79	0.69	0.62
PE	2.33	2.55	1.54	1.63	1.66	1.33	1.60	2.16	1.30	1.50	2.36

Nine transition metals with different ionic radius (r) and Pauling electronegativities (PEs) (see Table 1) were selected to dope in PbSe for optimization of the TE properties (Fig. S1–S16). The electrical conductivity increased first and then decreased with increasing doping concentration when doped with any kind of transition metal, resulting in the nine maximum *ZT* values shown in Fig. 1(a). Peak *ZT*s close to or higher than 0.9 at 873 K were achieved in Ti-, Zr-, Nb-, Hf-, or Ta-doped PbSe (see red box). The highest *ZT* value is ~1.2 at 873 K for $Nb_{0.01}Pb_{0.99}Se$. However, the room temperature *ZT*s of all these samples are lower than 0.1. While the room temperature *ZT*s were optimized to ~0.4–0.5 by other dopants (V, Mo, W, or Cr) [33,34] (see blue box). Although with lower maximum *ZT*s, V-, Mo-, W-, or Cr-doped PbSe has higher average *ZT* (>0.6) than Ti-, Zr-, Hf-, or Ta-doped PbSe as presented in Fig. 1(b). Especially for Cr-doped PbSe, the average *ZT* is higher than 0.8 due to both higher room temperature *ZT* (~0.4) and higher temperature *ZT* (~1.0 at 573–773 K) [28]. So, two categories are clearly separated. The ionic radius of all the transition metals are closer to Pb, indicating the substitution of Pb for n-type doping, consistent with the negative Seebeck coefficient (Figs. S1, S3, S5, S7, S9, S11, S13, and S15). The solubility of TM is determined by the difference of electronegativity between the anion (Se^{2-}) and average cations (Pb^{2+} together with TM^{3+}) after doping. Larger difference results in higher solubility. When transition metal (TM^{3+}) substitutes Pb^{2+} in Pb-Se system, all the substitutions will reduce the PE of cationic sites. Lower average cation electronegativity enlarges the electronegativity difference between anions and cations. This is the reason why Ti (1.54), Zr (1.33), Nb (1.6), Hf (1.3), and Ta (1.5) could have higher solubility than V (1.63), Mo (2.16), W (2.36), and Cr (1.66) in Pb-Se, which possibly separated nine dopants. W (2.36) has higher PE than Pb and lower PE than Se, resulting in the smallest electronegativity difference between anions and cations when doped. The assumption was also confirmed by the calculation of the formation enthalpy of $(TM)_{0.04}Pb_{0.96}Se$ (shown in Fig. 1(c)) defined as

$$\Delta H = 0.04E_{Pb} + E_{(TM)_{0.04}Pb_{0.96}Se} - 0.04E_{TM} - E_{PbSe} \tag{1}$$

which is correspondent to the reaction

$$0.04(TM) + PbSe \rightarrow 0.04Pb + (TM)_{0.04}Pb_{0.96}Se \tag{2}$$

Here, E_{Pb}, $E_{(TM)0.04Pb0.96Se}$, E_{TM}, and E_{PbSe} are the total energies of Pb, $(TM)_{0.04}Pb_{0.96}Se$, TM, and PbSe at their most stable states, respectively. V-, Mo-, W-, or Cr-doped PbSe has higher formation enthalpy than that of Ti-, Zr-, Nb-, Hf-, or Ta-doped PbSe, indicating the difficulty for doping with V, Mo, W, or Cr. Room temperature carrier concentration of these nine doped samples are presented in Fig. 1(d). Higher formation enthalpy resulted in the lower carrier concentration due to the lower solubility.

We can also divide (a) electrical conductivity, (b) Seebeck coefficient, and (c) power factor for TM-doped PbSe into two categories. The electrical conductivity of all the samples decreased with increasing temperature, showing typical degenerated semiconductor behavior (Fig. 2(a)). The electrical conductivity of Ti-, Zr-, Nb-, Hf-, and Ta-doped PbSe in the red box is higher than that of V-, Cr- [33], Mo- [33], and W-doped PbSe in the blue box due to the higher carrier concentration. Room temperature electrical conductivity increased from 9×10^4 S m^{-1} for $Mo_{0.01}Pb_{0.99}Se$ to