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# Boosting thermoelectric performance of *n*-type PbS through synergistically integrating In resonant level and Cu dynamic doping $\begin{array}{c} \mathsf{HPSTAR} \\ \mathsf{1116-2021} \end{array}$

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#### ABSTRACT

PbS has attracted much attention as an excellent thermoelectric material with high development space at middle temperature scope. The thermoelectric performance for *n*-type PbS was boosted by the cooperative effects of resonance level and Cu dynamic doping in our research. In the first place, In doping improved the electrical transport performance of *n*-type PbS effectively on account of optimal carrier concentration and resonant level effects, and reduced the lattice thermal conductivity by reason of heightened phonon scattering through impurity atoms scattering simultaneously. Secondly, Cu dynamic doping further increased average power factor to ~18.8  $\mu$ W cm<sup>-1</sup> K<sup>-2</sup> at 423 K- 823 K of Pb<sub>0.995</sub>In<sub>0.005</sub>S+3%Cu owing to higher Seebeck coefficients and suppressed electronic thermal transports at vast temperature span. In result, the best thermoelectric figure of merit (*ZT*) of Pb<sub>0.995</sub>In<sub>0.005</sub>S+3%Cu at 723 K reached ~1.1 and a record large average *ZT* (*ZT*<sub>ave</sub>) of Pb<sub>0.995</sub>In<sub>0.005</sub>S+3%Cu was achieved ~ 0.8 at 423 K-823 K, which is vital in the implementation of thermoelectric technology.

#### 1. Introduction

To conquer the severe problems caused by globally growing energy consumption and environmental pollution, the researches of new green energy materials have attracted great attention. Nevertheless, currently the problems of high cost and technical challenges add limits to the large-scale application and further development for many of these materials [1-3]. Among them, thermoelectric materials with unique capability of improving adequately the efficiency of energy conversion are gradually coming into sight [4-8]. The conversion efficiency of thermoelectric materials has positive correlation with figure of merit,  $ZT = (S^2 \sigma T / \kappa_{tot})$ , where S expresses Seebeck coefficients,  $\sigma$  denotes electrical conductivity, T shows absolute temperature and  $\kappa_{tot}$  represents total thermal conductivity [9–12]. The  $\kappa_{tot}$  is composed of  $\kappa_{ele}$  (electronic thermal conductivity) and  $\kappa_{lat}$  (lattice thermal conductivity) [9–11,13, 14]. Researchers have been exploring various means to build up thermoelectric properties such as boosting the power factor ( $PF=S^2\sigma$ ) through adjusting carrier concentration, resonance effect, band transport conductivity via engineering nanostructures, interstitials, dislocations and all-scale hierarchical structures [10,15–32]. PbTe based traditional materials have exhibited high thermoelectric performance in medium temperature range attributed to complex band structure and low thermal conductivity [11,33–35]. However, the scarcity on earth and high price of Te prohibit the wide usage of PbTe based thermoelectric materials. In recent years, lead sulfide (PbS) based materials, which own similar crystalline structure and band structure compared to PbTe, have been

engineering, energy filtering effect and decreasing the total thermal

crystalline structure and band structure compared to PbTe, have been intensively studied as potential alternatives of PbTe due to their outstanding mechanical property and ample resource content of S on earth [15,36]. So far, many valuable scientific achievements have been made in *n*-type PbS thermoelectric materials [15,36–40]. The *ZT* in *n*-type PbS has been raised evidently through carrier concentration optimization, nanostructure, band alignment and resonant level [15,19, 36,40–42]. In particular, the resonance effect induced through Al, Ga and In doping showed great potential in regulating electrical transport

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Fig. 1. (a) Powder XRD patterns of  $Pb_{1,x}In_xS$  (x = 0.002, 0.005, 0.010, 0.15) and (b) function relationship between lattice parameters (a) and In concentration.



Fig. 2. (a) Cross-sectional SEM image of Pb<sub>0.995</sub>In<sub>0.005</sub>S. (b–d) EDX elemental maps showing the homogeneous distribution of (b) Pb, (c) S and (d) In elements in Pb<sub>0.995</sub>In<sub>0.005</sub>S.

property in *n*-type PbS. Recently Luo et al. developed a method of introducing gap state and Fermi level pinning to enhance *ZT* of *n*-type PbS via Ga and In co-doping. The highest *ZT* value achieved 1.0 when *T* = 923 K and the *ZT*<sub>ave</sub> reached 0.74 between 400 K and 923 K for Pb<sub>0.9865</sub>Ga<sub>0.0125</sub>In<sub>0.001</sub>S [40]. Furthermore, in order to obtain a higher *PF* value in a broad temperature region and weaken  $\kappa_{tot}$  concurrently, Zhao et al. optimized the carrier concentration and increased carrier mobility of *n*-type PbS through doping distinctive categories of Cu. The encouraging results of the peak value *ZT* ~1.23 (*T* = 923 K) and *ZT*<sub>ave</sub> ~ 0.62 between 300 and 923 K for Pb<sub>0.95</sub>Sb<sub>0.02</sub>Cu<sub>0.03</sub>S+3%Cu were attained [15]. These valuable works indicate a great potential for future application as well as a fertile ground forehead to explore for the development of *n*-type PbS.

In this research, the  $ZT_{ave}$  in *n*-type PbS matrix was enhanced dramatically by tuning electrical and thermal transport properties stepby-step. Firstly, we found that In doping could optimize the carrier concentration and induce resonance level of *n*-type PbS, which improved the *PF* and reduced the  $\kappa_{lat}$  effectively at the mean while. Secondly, extra Cu atoms were introduced into Pb<sub>0.995</sub>In<sub>0.005</sub>S. Cu doping exhibited a dynamic doping phenomenon in which interstitial Cu atom moved into the Pb sites at high temperature. Cu doping enhanced the power factor of Pb<sub>0.995</sub>In<sub>0.005</sub>S in spacious temperature breadth as a consequence of greater Seebeck coefficients and reduced the electronic thermal conductivity simultaneously. Therefore, the peak *ZT* was enhanced to 1.1 when T = 723 K in Pb<sub>0.995</sub>In<sub>0.005</sub>S+3%Cu. More importantly, a record high  $ZT_{ave} = 0.8$  at 423 K-823 K of Pb<sub>0.995</sub>In<sub>0.005</sub>S+3%Cu was acquired through the synergistic effect of resonant level and Cu dynamic doping.

#### 2. Experimental section

#### 2.1. Synthesis

The bulk thermoelectric materials of PbS,  $Pb_{1,x}In_xS$  (x = 0, 0.002, 0.005, 0.010, 0.015) and  $Pb_{0.995}In_{0.005}S + y\%Cu$  (y = 0, 1, 2, 3, 4) samples were synthesized by high pure chemicals of Pb, S, In and Cu. Melting and sintering methods are used to prepare all the samples. First, the raw materials were weighed and sealed in a quartz ampule under



**Fig. 3.** Temperature dependence of thermoelectric performance of  $Pb_{1,x}In_xS$  (x = 0, 0.002, 0.005, 0.010, 0.015) samples: (a) electrical conductivity, (b) Seebeck coefficients, (c) power factor, (d) the Pisarenko plot of  $Pb_{1,x}In_xS$  at 300 K, (e) band structure of  $Pb_{27}S_{27}$  and  $Pb_{26}InS_{27}$ , (f) projected density of states of  $Pb_{26}InS_{27}$ .

vacuum. The chemicals were gradually warmed up to 723 K by 12 h, followed by a constant heating-up to 1423 K by 7 h before keeping at 1423 K for 6 h and finally natural cooling in a box furnace. The grown ingots were powdered by a mechanical mortar and sieved using 200 mesh sieves. The powder was then densified at 923 K for 5 min in a  $\Phi$ 15 mm diameter graphite die under a compaction pressure of 50 MPa using a spark plasma sintering system (*SPS-211LX, Fuji Electronic Industrial Co., Ltd*). High density cylinder samples in diameter of 15 mm and thickness of 10 mm were manufactured.

#### 2.2. Thermoelectric properties measurements

The obtained cylinder pellets were incised and abraded into bars (10 mm × 3 mm × 3 mm) for  $\sigma$  and *S* tests with *Ulvac Riko ZEM-3* system at 300–823 K. The system errors of  $\sigma$  and *S* are about 5%. The thermal diffusion coefficient (*D*) measurement was accomplished by laser flash diffusion coefficient method using *Netzsch LFA457* and analyzed by the Cohen model with pulse correction. The cylinder samples with the dimension of 6 mm diameter and 1 mm thickness are used in thermal diffusion coefficient measurements. The heat capacity (*C*<sub>*p*</sub>) was calculated according to Dulong-Petit law with using the Debye temperature

[43]. The mass density ( $\rho$ ) was determined by volume and mass. The densities of all samples are all around 7.2 g/cm<sup>3</sup>. The  $\kappa_{tot}$  was calculated using  $\kappa_{tot} = DC_p\rho$  [44]. The deviation of the  $\kappa_{tot}$  is about 8%. Taking account of the uncertainties of various parameters, the error of *ZT* value is generally less than 15%. The Hall coefficient ( $R_{\rm H}$ ) test was conducted on *Lake Shore 8400* system using magnetic field of 0.9 T. The equation of  $n_{\rm H} = 1/(eR_{\rm H})$  was used to calculated carrier concentration ( $n_{\rm H}$ ), where *e* represents electron charge and *R*H denotes Hall coefficient. The carrier mobility ( $\mu_{\rm H}$ ) was obtained by  $\mu_{\rm H} = \sigma R_{\rm H}$ . The square samples used in Hall coefficient test are in 8 mm × 8 mm × 0.8 mm sizes. The  $\sigma$ , *S*, *D*,  $n_{\rm H}$  and  $\mu_{\rm H}$  were all obtained by experiment test.

#### 2.3. Characterization

The powder X-ray diffraction (XRD) measurement was performed using a *D/MAX2200pc* system (*Rigaku, Japan*) with CuK $\alpha$  at 40 kV and 40 mA at  $2\theta = 20-80^{\circ}$ . The scanning speed and step size are  $6^{\circ}$  min<sup>-1</sup> and 0.02° respectively. The microstructure and element distribution were characterized using a field-emission scanning electron microscope (SEM) that equipped with an energy dispersive X-ray spectroscopy (EDX) detector (*JSM-7900F*).



**Fig. 4.** The temperature dependent thermal transport properties of  $Pb_{1,x}In_xS$  (x = 0, 0.002, 0.005, 0.010, 0.015): (a) total thermal conductivity, (b) electronic thermal conductivity, (c) lattice thermal conductivity, (d) comparison between  $\kappa_{lat}$  calculated by Callaway model and experimental  $\kappa_{lat}$  as a function of In content (x).



Fig. 5. The temperature dependent ZT of  $Pb_{1,x}In_xS$  (x = 0, 0.002, 0.005, 0.010, 0.015).

#### 2.4. Density functional theory (DFT) calculations

First-principles calculations within density functional theory was performed using the projector-augmented wave (PAW) method [45], as implemented in the Vienna Ab-initio Simulation Package (VASP) [46]. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [47] was adopted to describe the exchange-correlation interactions. The plane-waves cutoff energy was set to 450 eV for all the calculations. A  $3 \times 3 \times 3$  (Pb<sub>27</sub>S<sub>27</sub>) supercell was constructed and one Pb substituted by In was adopted for the 3.7% In doped PbS (Pb<sub>26</sub>InS<sub>27</sub>). A Monkhorst-Pack  $\Gamma$ -centered  $5 \times 5 \times 5$  *k*-point



Fig. 6. Powder XRD patterns of  $Pb_{0.995}In_{0.005}S + y\%Cu$  (y = 0, 1, 2, 3, 4).

mesh was used for Brillouin zone sampling. The atomic positions were fully relaxed until the maximum residual ionic force is below 0.01 eV  $\text{\AA}^{-1}$ , and the total energy difference is converged to within  $10^{-7}$  eV.

#### 3. Results and discussion

In this paper, the designing strategy for improving the thermoelectric performance of PbS via In doping and Cu interstitials is described below as two rational successive steps. First, the electrical transport properties



Fig. 7. (a)–(b) The SEM images and locally enlarged picture of Pb<sub>0.995</sub>In<sub>0.005</sub>S+3%Cu. (c–f) EDX elemental mapping of (c) Pb, (d) S, (e) In and (f) Cu.

were improved effectively and  $\kappa_{\text{lat}}$  was decreased at the same time, which was triggered by the optimized carrier concentration and resonance level through introducing In in *n*-type PbS. Second, Cu dynamic doping was chosen to further improve the Seebeck coefficients and reduce the electron thermal conductivity. The maximum *ZT* and a record high *ZT*<sub>ave</sub> were obtained by the integrated effect of improved power factor and lowered thermal conductivity which was caused by resonant level and Cu dynamic doping.

#### 3.1. Introducing resonant level through In doping

The XRD results for Pb<sub>1-x</sub>In<sub>x</sub>S (x = 0.002, 0.005, 0.010, 0.015) samples, together with the standard data of PbS (PDF#05–0592) for comparison, are depicted in Fig. 1(a). The XRD patterns show that all synthesized samples possess a cubic phase of PbS. Fig. 1(b) demonstrates that the lattice parameters display uniformly a decreasing trend with increasing In content (x), as a result of the smaller atomic radius of In (~1.66 Å) compared to Pb (~1.75 Å). Such a change of lattice parameter indicates that In is successfully integrated into PbS lattice.

Fig. 2 shows the SEM and the corresponding EDX elemental mapping of  $Pb_{1-x}In_xS$  (x = 0.005). It is obvious in the elemental maps that all the

elements are homogeneously distributed within the observed area. The majority of In distributes in PbS homogeneously.

The electrical transport properties of Pb<sub>1.x</sub>In<sub>x</sub>S are presented in Fig. 3. It can be seen from Fig. 3(a), In doping boosts dramatically the  $\sigma$  of *n*-type PbS. The electrical conductivity at 300 K grows from 372 S cm<sup>-1</sup> of original PbS up to a maximum of 3578 S cm<sup>-1</sup> of Pb<sub>0.985</sub>In<sub>0.015</sub>S. The rise of electrical conductivity is mainly due to the increased carrier concentration caused by the donor effect of In doping. The carrier concentration reached 3  $\times 10^{20}$  cm<sup>-3</sup> for Pb<sub>0.985</sub>In<sub>0.015</sub>S, which indicates In has strong doping effect in *n*-type PbS.

The negative value states of Seebeck coefficients suggest that all the compounds exhibit an *n*-type semiconductor transport behavior (Fig. 3 (b)). The absolute values of Seebeck coefficients at 300 K display a decreasing trend from 253  $\mu$ V K<sup>-1</sup> of pristine PbS to 31  $\mu$ V K<sup>-1</sup> of Pb<sub>0.985</sub>In<sub>0.015</sub>S with increasing In content. The Seebeck coefficients correlate with carrier concentration negatively following Equation (1), in which *k*<sub>B</sub> represents Boltzmann constant, *m*<sup>\*</sup> is effective mass, *h* denotes Planck constant and *n* expresses carrier concentration [48,49]. Therefore, the boosted carrier concentration caused the reduction of Seebeck coefficients.



**Fig. 8.** Temperature dependence of electrical transport properties of  $Pb_{0.995}In_{0.005}S + y\%Cu$  (y = 0, 1, 2, 3, 4): (a) electrical conductivity, (b) Seebeck coefficients, (c) power factor, (d) carrier concentration, (e) carrier mobility of  $Pb_{0.995}In_{0.005}S$  and  $Pb_{0.995}In_{0.005}S+3\%Cu$ , and (f) average power factor at 423 K-823 K.

$$S = \frac{8\pi^2 k_B^2 m^* T}{3eh^2} \left(\frac{\pi}{3n}\right)^{2/3}$$
(1)

By introducing In, the power factor ( $PF=S^2\sigma$ ) is evidently enhanced as presented in Fig. 3(c). The PF of  $Pb_{0.995}In_{0.005}S$  sample first rises with increased temperature, followed by a maximum when T = 523 K, and then keeps a high value in the subsequent temperature range. The outstanding  $PF \sim 12.3 \ \mu\text{W cm}^{-1} \ \text{K}^{-2}$  is gained in  $Pb_{0.995}In_{0.005}S$  when T reaches 823 K. The relation between Seebeck coefficients and carrier concentration of PbS at 300 K is depicted by the Pisarenko plot (Fig. 3 (d)). It can be seen that data points of experimental Seebeck coefficients distribute above the Pisarenko line, indicating the resonance state induced by In doping effectively improves the effective mass and leads to enhancement of Seebeck coefficients [40]. In doping introduces a new band cross the Fermi level (Fig. 3(e)), which effectively increases the carrier concentration and the electrical properties. This new band mainly results from the resonant level of the In atom, as shown in (Fig. 3 (f)). Therefore, the excellent PF of In doped PbS can be attributed to both carrier concentration optimization and resonant level effect.

Fig. 4(a) depicts the temperature dependent  $\kappa_{tot}$ . The growing chemometrics content of In triggers a gradual increase of  $\kappa_{tot}$  at room

temperature, rising from 2.4 W  $m^{-1}$  K<sup>-1</sup> of PbS to 4.4 W  $m^{-1}$  K<sup>-1</sup> of Pb<sub>0.985</sub>In<sub>0.015</sub>S. The  $\kappa_{lat}$  can be calculated by  $\kappa_{lat} = \kappa_{tot} - \kappa_{ele}$  [18,27]. The  $\kappa_{\rm ele}$  is computed utilizing  $\kappa_{\rm ele} = L\sigma T$  in which L represents Lorenz parameter. It is evident that the  $\kappa_{ele}$  is directly proportional to additive amount of In. The possible reason for this phenomenon is that the  $\sigma$  has been dramatically elevated. Specifically, the  $\kappa_{ele}$  of Pb<sub>0.985</sub>In<sub>0.015</sub>S at 300 K is dramatically increased to 2.5 W  $\ensuremath{\text{m}^{-1}}\xspace$  K  $\ensuremath{\text{m}^{-1}}\xspace$  k is dramatically increased to 2.5 W  $\ensuremath{m}^{-1}\xspace$  K is dramatically increased 0.2 W  $m^{-1}~\text{K}^{-1}$  of pure PbS. While the  $\kappa_{lat}$  of PbS is significantly suppressed by In doping (Fig. 4(c)). The  $\kappa_{lat}$  at 300 K decreases from 2.3 W m<sup>-1</sup> K<sup>-1</sup> of PbS to 1.8 W m<sup>-1</sup> K<sup>-1</sup> of Pb<sub>0.995</sub>In<sub>0.005</sub>S. The  $\kappa_{lat}$  decreases with growing temperature can be attributed to Umklapp rule and the  $Pb_{0.985}In_{0.015}S$  displays a poor  $\kappa_{lat}$  of 0.6 W m<sup>-1</sup> K<sup>-1</sup> when T = 823 K. To gain further insights into the mechanism, theoretical calculation was carried out based on Callaway model (Fig. 4(d)). The phonon scattering by point defects is generally caused by mass and strain field variations [50,51]. It is noticeable that the experimental  $\kappa_{lat}$  is smaller than that calculated by Callaway model. The result implies nanostructure precipitates may exist in  $Pb_{1-x}In_xS$  which give rise to the phonon scattering in addition to point defect.

The temperature dependent *ZT* of  $Pb_{1,x}In_xS$  (x = 0, 0.002, 0.005, 0.010, 0.015) is presented in Fig. 5. The *ZT* of *n*-type PbS is enlarged



Fig. 9. Schematic pictures of (a) PbS, (b)  $Pb_{1-x}In_xS$ , (c)  $Pb_{0.995}In_{0.005}S + y\%Cu$  at low temperature (below 450 K) and (d)  $Pb_{0.995}In_{0.005}S + y\%Cu$  at high temperature (above 450 K).

appreciably through In doping owing to resonant level effect and decreased  $\kappa_{\text{lat}}$ . At 823 K, the remarkable *ZT* can reach 0.7 in Pb<sub>0.995</sub>In<sub>0.005</sub>S and increases over 57% compared to the peak *ZT* of 0.4 for pristine PbS.

## 3.2. Enhancing thermoelectric performance of n-type PbS by Cu dynamic doping

To improve further the thermoelectric properties, we attempted to enhance Seebeck coefficients and reduce  $\kappa_{ele}$  with co-doping In and Cu in *n*-type PbS matrix. Pb<sub>0.995</sub>In<sub>0.005</sub>S is selected for the subsequent investigation because the sample exhibits the best thermoelectric performance overall.

Fig. 6 shows the XRD patterns of  $Pb_{0.995}In_{0.005}S + y\%Cu (y = 0, 1, 2, 3, 4)$ . All samples keep single cubic PbS phase. The SEM and EDX characterization were carried out for the  $Pb_{0.995}In_{0.005}S+3\%Cu$  compound with high performance, as shown in Fig. 7. From Fig. 7(a) and (b), the approximate pictures of the sample surface with different magnification can be observed. The EDX elemental mapping across relatively a large area reveals a homogeneous distribution of all elements.

The electrical properties of Pb<sub>0.995</sub>In<sub>0.005</sub>S + *y*%Cu was systematically studied. Fig. 8(a) shows a decrease of  $\sigma$  with regard to increasing temperature. The  $\sigma$  decreases significantly by introducing extra Cu, as a result of reduced carrier concentration (*n*<sub>H</sub>) (Fig. 8(d)). Specifically the  $\sigma$  decreases from 3639 S cm<sup>-1</sup> of Pb<sub>0.995</sub>In<sub>0.005</sub>S to 1577 S cm<sup>-1</sup> of Pb<sub>0.995</sub>In<sub>0.005</sub>S+3%Cu at 300 K.

Fig. 8(b) shows the temperature dependence of Seebeck coefficients of Pb<sub>0.995</sub>In<sub>0.005</sub>S + *y*%Cu. Introducing Cu enhances the absolute value of Seebeck coefficients which is attributed to smaller carrier concentration. The absolute value of Seebeck coefficients at 300 K is raised up to 79  $\mu$ V K<sup>-1</sup> of Pb<sub>0.995</sub>In<sub>0.005</sub>S+3%Cu from 46  $\mu$ V K<sup>-1</sup> of Pb<sub>0.995</sub>In<sub>0.005</sub>S. The absolute value of Seebeck coefficients in Cu doped Pb<sub>0.995</sub>In<sub>0.005</sub>S increased abruptly above 500 K. With the purpose of uncovering the mechanism, the temperature dependent Hall tests were carried out. Fig. 8(d) shows that the carrier concentration of Pb<sub>0.995</sub>In<sub>0.005</sub>S+3%Cu declines sharply with temperature rising to 500 K, which suggests the existence of a dynamic Cu doping phenomenon. In Cu doped lead chalcogenide, some Cu atoms may occupy interstitial site at low

temperature [11,52]. Fig. 9(a) represents the pure PbS and (b) shows the lattice position of Pb replaced by In. Fig. 9(c) and (d) present a dynamic Cu doping phenomenon. In  $Pb_{0.995}In_{0.005}S + y\%Cu$ , some Cu atoms may occupy interstitial site at low temperature as shown in Fig. 9(c). With temperature rising, a fraction of Cu interstitial atoms may be capable to replace the lattice position of Pb as shown in Fig. 9(d), which would decrease the carrier concentration and enhance the Seebeck coefficients of *n*-type PbS. As shown in Fig. 8(c), the *PF* of Pb<sub>0.995</sub>In<sub>0.005</sub>S is boosted evidently by Cu doping over whole temperature range because of the enhanced Seebeck coefficients. The PF of  $Pb_{0.995}In_{0.005}S+3\%$ Cu reaches a peak value of 21.7  $\mu$ W cm<sup>-1</sup> K<sup>-2</sup> when T = 573 K and maintains a high level over wide temperature range. Fig. 8(f) shows the average power factor ( $PF_{ave}$ ) in  $Pb_{0.995}In_{0.005}S + y\%Cu$  (y = 0, 1, 2, 3, 4) samples between 423 K and 823 K. The  $PF_{ave}$  is calculated by Equation (2) and the  $T_{\rm h}$  and  $T_{\rm c}$  are the temperatures of the hot and cold ends. The  $Pb_{0.995}In_{0.005}S+3\%$ Cu sample possesses a higher maximum  $PF_{ave} \sim 18.8$  $\mu$ W cm<sup>-1</sup> K<sup>-2</sup>, which is 36% higher than that of Pb<sub>0.995</sub>In<sub>0.005</sub>S.

$$PF_{ave} = \frac{1}{T_h - T_c} \int_{T_c}^{T_h} PF dT$$
<sup>(2)</sup>

Fig. 10(a) shows the  $\kappa_{tot}$  of Pb<sub>0.995</sub>In<sub>0.005</sub>S + y%Cu (y = 0, 1, 2, 3, 4) as function of temperature. The  $\kappa_{tot}$  diminishes remarkably through adding Cu. At 300 K, the  $\kappa_{\rm tot}$  drastically reduces to 3.5 W  $\rm m^{-1}~\rm K^{-1}$  for  $Pb_{0.995}In_{0.005}S+3\%Cu$  from 4.3 W m<sup>-1</sup> K<sup>-1</sup> for  $Pb_{0.995}In_{0.005}S$ . The  $\kappa_{ele}$  is decreased effectively in the whole temperature region by adding Cu and reduces sharply above 500 K (Fig. 10(b)) The reason is that the Cu doping can reduce effectively the carrier concentration (Fig. 8(d)). In detail, the  $\kappa_{ele}$  at 300 K of Pb<sub>0.995</sub>In<sub>0.005</sub>S significantly declines from 2.4 W m<sup>-1</sup> K<sup>-1</sup> to 1.0 W m<sup>-1</sup> K<sup>-1</sup> of Pb<sub>0.995</sub>In<sub>0.005</sub>S+3%Cu. The  $\kappa_{ele}$  in  $Pb_{0.995}In_{0.005}S{+}3\%Cu$  at 823 K degrades to 0.4 W  $m^{-1}$  K  $^{-1}.$  The relation tionship between electronic thermal conductivity, carrier concentration and mobility are described in Equations (3) and (4) where L is the Lorenz number. It is clear to find the  $\kappa_{ele}$  decreases significantly on account of reduced carrier concentration  $(n_{\rm H})$  by introducing extra Cu. The Umklapp process is followed by  $\kappa_{lat}$  of all samples and the  $\kappa_{lat}$  also has a declining trend with temperature rising [53]. As shown in Fig. 10(c), Cu dynamic doping also reduces the *k*<sub>lat</sub> in high temperature range owing to enhanced phonon scattering. The *k*<sub>lat</sub> in Pb<sub>0.995</sub>In<sub>0.005</sub>S+3%Cu is



**Fig. 10.** The temperature dependent thermal transport properties and thermoelectric performance of  $Pb_{0.995}In_{0.005}S + y\%Cu$  (y = 0, 1, 2, 3, 4): (a) total thermal conductivity, (b) electronic thermal conductivity, (c) lattice thermal conductivity, (d) *ZT*, (e) average *ZT* at 423 K-823 K, (f) comparation of average *ZT* between  $Pb_{0.995}In_{0.005}S+3\%Cu$  in this work, *n*-type  $PbS+1\%Bi_2S_3+1\%PbCl_2$ ,  $Pb_{0.9855}Ga_{0.0125}In_{0.001}S$  and  $PbS_{0.97}Te_{0.03}+0.1\%PbCl_2$  in previous literature [39–41].

diminished to 0.7 W m<sup>-1</sup> K<sup>-1</sup>, which decreases nearly 17% compared to that of  $Pb_{0.995}In_{0.005}S$  at 823 K.

$$\kappa_{ele} = L\sigma T \tag{3}$$

$$\sigma = nq\mu \tag{4}$$

The thermoelectric properties of *n*-type PbS is improved via modulating electrical and thermal transports synergistically (Fig. 10(d) and (e)). Cu dynamic doping can increase *ZT* obviously which is account of heightened power factor and the dramatical reduction of  $\kappa_{ele}$ . The *ZT*<sub>ave</sub> is calculated by Equation (5) and the thermoelectric efficiency of Pb<sub>0.995</sub>In<sub>0.005</sub>S + *y*%Cu (*y* = 0, 1, 2, 3, 4) at 423 K - 823 K are 5.5%, 8.5%, 8.7%, 9.0% and 8.4% respectively. The maximum *ZT* of Pb<sub>0.995</sub>In<sub>0.005</sub>S+3%Cu achieves 1.1 at 723 K. In particularly, Pb<sub>0.995</sub>In<sub>0.005</sub>S+3%Cu exhibits a record high *ZT*<sub>ave</sub> = 0.8 at 423 K - 823 K, which is larger than the *ZT*<sub>ave</sub> = 0.4 at 423 K - 823 K of Pb<sub>0.995</sub>In<sub>0.005</sub>S and that reported in previous references as shown in Fig. 10(f) [39–41]. These important foundations reveal that synergistic effect of resonant

level and Cu dynamic doping is a remarkable strategy of improving the *ZT* in *n*-type PbS over broad temperature range.

$$ZT_{ave} = \frac{1}{T_h - T_c} \int_{T_c}^{T_h} ZT dT$$
<sup>(5)</sup>

#### 4. Conclusions

In our research, In and Cu co-doping remarkably improved the *ZT* of *n*-type PbS over a broad temperature region. In doping boosted the *PF* and decreased the  $\kappa_{\text{lat}}$  for *n*-type PbS instantaneously on account of resonant level and scattering phonon. The maximum *ZT* for Pb<sub>0.995</sub>In<sub>0.005</sub>S achieved 0.7 at 823 K. Cu dynamic doping further heightened the average *PF* to ~18.8  $\mu$ W cm<sup>-1</sup> K<sup>-2</sup> thanks to better Seebeck coefficients through optimized carrier concentration, decreased  $\kappa_{\text{ele}}$  and  $\kappa_{\text{lat}}$  simultaneously. The maximum *ZT* value in Pb<sub>0.995</sub>In<sub>0.005</sub>S+3%Cu achieved 1.1 at 723 K. Especially, a record large *ZT*<sub>ave</sub> = 0.8 between 423 K and 823 K was attained for

 $Pb_{0.995}In_{0.005}S+3\%Cu$ . This investigation exploits an outstanding method of promoting *ZT* in *n*-type PbS by synergistic effect of resonant level and Cu dynamic doping.

#### Prime novelty statement

In this work, the thermoelectric performance of *n*-type PbS is enhanced by synergistically integrating In resonant level and Cu dynamic doping. We firstly dope In in *n*-type PbS to enhance the electrical transport properties by optimizing the carrier concentration and induce resonance level, and the lattice thermal conductivity is reduced through improved phonon scattering by impurity atoms. Furthermore, Cu dynamic doping increased average power factor to ~18.8  $\mu$ W cm<sup>-1</sup> K<sup>-2</sup> at 423 K-823 K of Pb<sub>0.995</sub>In<sub>0.005</sub>S+3%Cu owing to higher Seebeck coefficients and suppress the electronic thermal conductivity over broad temperature range. Finally, the maximum thermoelectric figure of merit (*ZT*) of Pb<sub>0.995</sub>In<sub>0.005</sub>S+3%Cu reached ~1.1 at 723 K and a record large average *ZT* (*ZT*<sub>ave</sub>) of Pb<sub>0.995</sub>In<sub>0.005</sub>S+3%Cu is achieved ~ 0.8 at 423 K-823 K. This investigation develops an outstanding method to enhance *ZT* of *n*-type PbS by synergistic effects of In resonant level and Cu dynamic doping.

#### CRediT authorship contribution statement

Zhenghao Hou: Formal analysis, Conceptualization, Writing - review & editing. Dongyang Wang: Methodology. Tao Hong: Methodology. Yongxin Qin: Formal analysis, Conceptualization, Writing review & editing. Shang Peng: Methodology. Guangtao Wang: Methodology. Jinfeng Wang: Methodology. Xiang Gao: Formal analysis, Conceptualization, Writing - review & editing. Zhiwei Huang: Formal analysis, Conceptualization, Writing - review & editing. Li-Dong Zhao: Formal analysis, Conceptualization, Writing - review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Z. Hou et al.

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