Enhanced Thermoelectric Performance in Li Doped SnS via Carrier Concentration Optimization

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Abstract. Tin sulfide (SnS) has attracted increasing attentions due to its similar band structure and crystal structure to tin selenide (SnSe). The layered structure and strong anharmonicity of these materials result in an ultralow lattice thermal conductivity, which is advantageous for the thermoelectric performance. Further enhancement in thermoelectric properties is expected to improve the carrier concentration and power factor by band structure optimization. In this work, lithium (Li) is proved to be an efficient dopant for SnS and the carrier concentration is increased to $1.3 \times 10^{18}$ cm$^{-3}$ at room temperature for Sn$^{0.98}$Li$^{0.02}$S. Calculations show that Li doping flattens the edge of the valence band and increases the number of carrier pockets in SnS, which collectively enhance the electronic transport properties. Moreover, the phonon scattering was enhanced by the nano-precipitates and increased boundaries in Sn$_{1-x}$Li$_x$S, resulting in 40% reduction in thermal conductivity at room temperature. Combined with the enhanced power factor (~3 $\mu$W cm$^{-1}$ K$^{-2}$ at 848 K) and low thermal conductivity (0.36 W m$^{-1}$ K$^{-1}$ at 848 K), the maximum ZT of 0.66 is achieved in Sn$_{1-x}$Li$_x$S bulk samples at 848 K.

1. Introduction
Thermoelectric materials provide a simple and eco-friendly solution for direct conversion between heat and electrical energy without any moving parts or greenhouse gasses [1-3]. The efficiency of thermoelectric materials is generally evaluated by the dimensionless figure of merit ZT ($ZT = \alpha^2\sigma T/\kappa$), where $\alpha$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $T$ is absolute temperature, and $\kappa$ is the thermal conductivity consisting of electronic thermal conductivity ($\kappa_e$) and lattice thermal conductivity ($\kappa_L$) [4]. High power factor $PF = \alpha^2\sigma$ and low thermal conductivity are required to achieve high ZT values from the perspective of formulas. Nevertheless, $\alpha$, $\sigma$ and $\kappa_e$ are strongly coupled and conflict with each other through the transport properties of electrons, which leads to poor ZT values and difficult optimization [5, 6]. For example, increasing the electrical conductivity, usually realized by increasing the carrier concentration, but leads to a reduced Seebeck coefficient and increased electronic thermal conductivity [7, 8]. In a word, it’s difficult to improve the thermoelectric performance by optimizing one thermoelectric parameter individually. Except for the lattice thermal conductivity [9-11], the only parameter that can be independently regulated, is an effective breakthrough to optimize the thermoelectric performance. The reduction in the lattice thermal conductivity is usually achieved by two approaches: (1) nanostructuring [12, 13], introducing defects [14] and all-scale hierarchical architecturing, [15] (2) looking for intrinsic low thermal conductivity materials with complex crystal conductivity, weak chemical bonds, heavy mass [2, 9, 16] and so on.
Tin selenide (SnSe), one of the most potential thermoelectric materials, owns the intrinsic ultralow thermal conductivity in terms of density functional theory (DFT) and calculated large Grüneisen parameters due to its strong anharmonic bonding [16, 17]. Recently, a record high ZT of ~2.8 ± 0.5 out of plane at 773 K was achieved in SnSe single crystal [18]. However, due to the long duration of synthesis, expensive preparation cost and poor mechanical properties for single crystalline [19], polycrystalline materials with similar structure have been widely studied. As an analogue of SnSe, tin sulfide (SnS) shows the similar crystal and band structure as SnSe, which inspire more research in SnS based materials. The crystal of SnS adopts an orthorhombic structure with double layers of tightly bound Sn-S atoms and the layers pile up mainly with the weak and long Sn-S interactions, [20] resulting in ultralow lattice thermal conductivity close to the predicted amorphous limit (0.26 W m⁻¹ K⁻¹), which has been reported by experiments and calculations [21-23]. However, pure SnS still possesses a poor ZT because of the extremely low carrier concentration (2.47× 10¹⁵ cm⁻³ in this work) [22, 24], therefore targeting enhancement of ZT is achieved successfully by increasing carrier concentration via p-type doping like Ag or Na, [25, 26] and a maximal ZT of 0.8 at 850 K when the carrier concentration is further increased to ~1 × 10²⁰ cm⁻³ has been predicted according to the SPB model in Pei’s work [25].

In this work, lithium (Li) is selected as a p-type dopant that can lower the Fermi level into valence bands and flatten the top of valence band edge, thus an increased carrier concentration of 1.3 × 10¹⁸ cm⁻³ is achieved in Li doped SnS bulk samples. Even though Li doping increased the electrical conductivity by 1–3 orders of magnitude, the Seebeck coefficient maintains impressively high level of 450 ~ 650 μV K⁻¹ at the entire temperature range. Besides, a remarkably low thermal conductivity of 0.36 W/m/K is obtained at 848 K for SnS-1% Li sample. The resultant optimized carrier concentration and increased nanooinclusions believed to be the key factors to the enhancement of thermoelectric performance.

2. Materials and methods

2.1. Synthesis

Commercial flakes of 99.95% Li, powders of 99.99% Sn and 99.5% S were used as raw materials without further purification. The elements were stoichiometrically weighted of Snₓ,LiₓS (x = 0, 0.005, 0.0075, 0.01, 0.02 and 0.03) and then loaded in stainless steel jars in a purified argon (>99.999%) atmosphere for mechanical alloying (MA) by a high-energy ball milling (SPEX 8000 D) for 15 h. The MA-derived powders were consolidated by hot-pressing at 853 K in vacuum for 6 min under an axial pressure of 75 MPa, results in a highly dense disk-shaped pellets sample with dimension of 13 mm and 2.5 mm thickness.

2.2. Phase structures and microstructures

The phase structures were examined by X-ray diffraction (XRD) using Cu Kα radiation (DX-2700B, HAOYUAN China). The structural and morphological characterizations were obtained with scanning electron microscopy (SEM) using FEI Inspect F and transmission electron microscopy (TEM) at room temperature.

2.3. Thermoelectric properties

The Seebeck coefficient and electrical resistivity were measured with CTA-3. The total thermal conductivity was calculated by relationship κ=αρCp, where ρ is the density of bulk sample, α is the thermal diffusivity, and Cp is the specific heat capacity. Both Cp and α were measured by Netzsch LFA 457, in which the reference sample is Pyroceram 9606. The density of bulk sample was measured by the Archimedes method. The lattice thermal conductivity (κₐ) was obtained by subtracting the electronic thermal conductivity (κₑ) from the total thermal conductivity ((κₑ= κ - κₐ). The electronic conductivity contribution is calculated according to Wiedemann-Franz law κₑ = LσT. Here, L is the Lorenz number denoted by SPB model, ranging from 1.48×10⁻⁸ to 1.49×10⁻⁸ V² K⁻². Hall resistances
(RH) of bulk samples were measured with Ecopia AMP55. Hall coefficient (RH) was measured under a reversible magnetic field (0.8 T) by the Van der Pauw method by using a Hall measurement system (Lake Shore 8400 Series, Model 8404, USA) in a wide temperature range. The hole mobility (μH) and carrier concentration (n) were calculated from μH = σRH and n = 1/eRH, where e is the elementary charge.

2.4. Electronic calculation methods

The electronic structure was calculated by the density-functional theory (DFT) using the projector augmented wave (PAW) method that was implemented in the Vienna ab initio simulation package (VASP). The exchange-correlation function was taken from the generalized gradient approximation (GGA) from the parameterization of Perdew–Burke–Ernzerhof (PBE). A plane-wave basis was adopted for the expansion of the valence electron wave functions and charge densities with kinetic-energy cutoffs of 400 eV. We use a well-converged Monkhorst-Pack k-point grid (9 × 9 × 9) for relaxation and self-consistent calculation in Brillouin zone. Experimental lattice constants and internal atomic coordinates were used throughout the calculations.

3. Results

3.1. Crystal structure characterization

Figure 1(a) shows the crystal structure of orthorhombic (α-phase) SnS with a Pbmn space group (a = 11.19 ± 0.05 Å, b = 3.98 ± 0.02 Å and c = 4.33 ± 0.02 Å). The double Sn-S planes are linked by van der Waals force and the atoms in each layer are joined with the three nearest neighboring atoms by covalent bonds, forming accordion shaped corrugated slabs. The crystal structures of the as-synthesized Sn1-xLiS (x = 0, 0.005, 0.0075, 0.01, 0.02 and 0.03) bulk samples are determined by X-ray diffraction (XRD), and all of the peaks are well indexed to the orthorhombic structure of SnS (PDF#39-0354) as shown in figure 1(b). However, the peak positions for Li doped samples shift slightly to higher angles relative to the pure SnS due to the substitution of a larger atom Sn (112 pm) by a smaller atom Li (76 pm), as shown in figure 1(c), an enlarged view of figure 1(b) within the angular range of 25–35°. This seems to indicate that Li goes into the SnS lattice and the stress field is generated due to the different atomic radius of Sn and Li, which is characterized by Raman spectra. The pure SnS displays the peaks at 163, 193, 219 and 285 cm⁻¹ [27], while the Raman peaks shift to lower wave number can be observed in Sn0.98Li0.02S as shown in figure 2(a). Further, the Li-S bond and Sn-S bond have been detected by X-ray photoelectron spectroscopy (XPS), in which the spectrum of S 2p shows two peaks at binding energies of 161.97 eV [28] and 160.87 eV [29] as shown in figure 2(b).
Figure 2. (a) Raman spectra of SnS and Sn$_{0.98}$Li$_{0.02}$S, (b) X-ray photoelectron spectrum (XPS) of the 2p orbitals for the S element of Sn$_{0.98}$Li$_{0.02}$S.

Figure 3. Fracture SEM images of bulk samples of (a) pure SnS, (b) Sn$_{0.99}$Li$_{0.01}$S, Sn$_{0.98}$Li$_{0.02}$S, (d) Sn$_{0.97}$Li$_{0.03}$S and (e-g) TEM for Sn$_{0.98}$Li$_{0.02}$S.

Figure 3(a)-(d) exhibit the scanning electron microscopy (SEM) for bulk Sn$_{1-x}$Li$_x$S. Pure SnS exhibits a typical lamellar morphology as shown in figure 3(a) and the strong anisotropy of pure SnS has been studied in our pre-work [30]. As the Li content increases, the grain size gradually decreases and the layered structure gradually disappears, meanwhile some nano-precipitates occur on the surface of SnS matrix, as marked in figure 3. To further clarify the composition and structure of doped samples, the microstructures for Sn$_{0.98}$Li$_{0.02}$S are investigated by transmission electron microscope (TEM) and shown in figure 2(e)-(g). The regular parallel fringes spacing of about 0.271 nm is obtained for the nano-precipitates, corresponding to (2 0 0) lattice plane of Li$_2$S. The increased grain boundaries and the nanoinclusions of Li$_2$S in Li-doped samples play an important role in the enhancement of thermoelectric performance, which will be described in details below.

3.2. Electronic structure calculations

Figure 4 shows the electronic band structure and density of states (DOS) of pure and doped SnS, which indicates that the DOS near the Fermi level is mainly derived from Sn and S, and
the contribution of Li is negligible (inset Figure 4(d)). But the band structure of SnS is modified significantly by Li doping in two aspects like alkali elements doped SnSe samples [31, 32]. Firstly, the number of carrier pockets are increased because the Fermi level \( (E_F) \) of Li doped SnS is shifted into the two main valence bands VB1 and VB2, and approached VB3. Secondly, flating the top of the valence band, resulting in an enhanced effective mass. Therefore, an enhanced Seebeck coefficient by the increment of the local DOS near the Fermi level via Mott expression as shown in the following.

\[
\frac{1}{\hbar^2} \left( \frac{\partial^2 E}{\partial k^2} \right)_{k=k_i} = \frac{1}{m^*}
\]

\[
\alpha = \frac{\pi^2 k_B^2 T}{3q} \left( \frac{dn(E)}{nE} + \frac{d\mu(E)}{\mu E} \right)_{E=E_F}
\]

With \( n[E] = g[E]f[E] \)

where \( \hbar \) is the Planck constant and \( k_i \) is the wave vector of the i-th carrier pocket, \( k_B \) is the Boltzmann constant, \( f(E) \) is the Fermi function, \( q \) is the carrier charge, \( n(E) \) is the carrier mobility, and \( g(E) \) is the density of states (DOS).

![Figure 4](image)

Figure 4. Electronic band structure (a) and density of states (DOS) (b) of pure SnS, electronic band structure (c) DOS (d) of Li-doped SnS. The Fermi energy was set to 0.

### 3.3. Thermoelectric properties

Thermoelectric properties for all samples are measured below the phase transition temperature (around 878 K), shown in figure 5. The pure SnS exhibits typical semiconducting thermally activated transport behavior and owns an extreme low electrical conductivity due to the low
carrier concentration. After introducing Li, the electrical conductivity dramatically enhanced from $3.98 \times 10^{-4}$ S cm$^{-1}$ to 0.4 S cm$^{-1}$ at room temperature as the carrier concentration increased from almost $2.47 \times 10^{15}$ cm$^{-3}$ to $1.32 \times 10^{18}$ cm$^{-3}$, as shown in figure 5(a) and (c). The electrical conductivities of all doped samples show the same trend, and the upturn when $T > 598$ K can be attributed to the thermal excitation of minority carriers like Ag doped SnS [26] and Pb, Zn co-doped SnSe [33] samples. Figure 5(b) shows the temperature dependent Seebeck coefficient of Sn$_{1-x}$Li$_x$S. Pure SnS has a high Seebeck coefficient between $562 \mu$V K$^{-1}$ and 816
μV K\(^{-1}\) at the whole testing range, consistent with a p-type semiconductor. Even though Li doping increased the electrical conductivity by 1~3 orders of magnitude, the Seebeck coefficient maintains impressively high level (above 400 μV K\(^{-1}\)) due to the increased effective mass, as described in figure 4. The Seebeck coefficient of doped samples increase as a function of temperature, showing the peak of Seebeck coefficient appears at 598 ~ 648 K, and then decrease due to the intrinsic excitation of carriers, which is consistent with electrical conductivity. According to the Goldsmid method [34, 35], the effective bandgap could be determined by the Seebeck coefficient measurement for a simple band structure such as SnS via \(E_g = 2eS_{\text{max}}T_{\text{max}}\), where \(S_{\text{max}}\) and \(T_{\text{max}}\) are the maximum Seebeck coefficient and the temperature at which \(S_{\text{max}}\) occurs. This yields band gap of 0.7 ~ 0.8 eV for Li doped SnS samples, which is highly consistent with the calculated band gap of pure SnS and Sn\(_{0.98}\)Li\(_{0.02}\)S as shown in figure 4. Although the doped samples show a lower Seebeck coefficient than that of the undoped SnS, the much higher electrical conductivity of the former yields larger PF as shown in figure 5(d). The highest power factor of doped samples reaches ~3 μW cm\(^{-1}\) K\(^{-2}\) at 848 K for Sn\(_{0.995}\)Li\(_{0.005}\)S, which is significantly higher than pure SnS (1.9 μW cm\(^{-1}\) K\(^{-2}\) at 848 K).

Thermal conductivities for all samples are below 2 W m\(^{-1}\) K\(^{-1}\) and decreases as temperature increases as shown in figure 5(e). Obviously, the κ comes mainly from the lattice thermal conductivity (inset, figure 5(e)) because of the negligible electronic contribution. It is found that Umklapp processes dominate the scattering of phonons in all of the samples because κ\(_{\text{L}}\) decreases with increase in temperature via a T\(^{-1}\). Moreover, the doped samples own a thermal conductivity as low as 0.36 W m\(^{-1}\) K\(^{-1}\) for Sn\(_{0.98}\)Li\(_{0.02}\)S at 848 K, even lower than that of Ag and Na doped SnS samples, which is attributed to the larger atomic size difference between Li and Sn and therefore a stronger effect on the scattering of phonons. Moreover, the extremely low thermal conductivity benefits from the grain boundaries and nano inclusions introduced by Li doping, as shown in Fig. 3.

ZT values of Sn\(_{1-x}\)Li\(_x\)S samples are calculated and compared with Na and Ag doped SnS samples, which is shown in figure 5(f). All samples show poor thermoelectric performance at low temperature because of the poor electrical conductivity and increase with increasing testing temperature. The highest ZT value of 0.66 is obtained for Sn\(_{0.98}\)Li\(_{0.02}\)S at 848 K, which is about 100% higher than that of pure SnS. The maximum value is comparable to that of Na doped SnS [25] and slightly higher than that of Ag doped SnS [26] samples. According to the present work, lithium is an efficient dopant for SnS, leading to an increased carrier concentration, strongly phonon scattering and optimized band structure. Therefore, the enhanced ZT values are obtained due to the increased PF and decreased thermal conductivity through decoupling and simultaneous optimizing each thermoelectric parameter.

4. Conclusions

SnS is one of the promising thermoelectric materials like SnSe because of the strong lattice anharmonicity. However, the ZT values of SnS are suppressed by the poor electrical conductivity caused by the low carrier concentration. In this work, Li doped SnS bulk samples are obtained successfully by mechanical alloying method. Calculations show that the Fermi level enters into valence band and the valence band edge is flattened after Li doping, both the two effects have a positive influence on the thermoelectric performance enhancement. The highest ZT value of 0.66 is obtained for Sn\(_{0.98}\)Li\(_{0.02}\)S at 848 K contributed by the carrier concentration optimization and reduced thermal conductivity. The thermoelectric performance could be further improved by continuously increasing carrier concentration, but the solid solubility may be a stumbling block. Besides, microstructure and band structure regulating, compositional optimization, solid solution are also efficient approaches for the further improvement of SnS.
References

[1] Yang L, Chen Z G, Dargusch M S and Zou J 2018 Adv. Energy Mater. 8 1701797.

[2] Wang C, Niu Y, Jiang J, Chen Y D, Tian H Q, Zhang R, Zhou T, Xia J F, Pan Y and Wang S Y 2018 Nano Energy 45 432-38.

[3] Bell L E 2008 Science 321 1457-61.

[4] He J and Tritt T M 2017 Science 357 eaak9997.

[5] Snyder G F and Toberer E S 2008 Nat. Mater. 7 105-14.

[6] Tan G J, Zhao L D and Kanatzidis M G 2016 Chem Rev. 116 12123-49.

[7] Wu R N, Li Z L, Li Y B, You L, Luo P F, Yang J and Luo J 2019 Journal of Materiomics 5 489-95.

[8] Zhu T J, Liu Y T, Fu C G, Heremans J P, Snyder J G and Zhao X B 2017 Adv. Mater. 29 1605884.

[9] Chen Z W, Zhang X Y and Pei Y Z 2018 Adv. Mater. 30 e1705617.

[10] Hanus R, Agne M T, Rettie A J E, Chen Z W, Tan G J, Chung D Y, Kanatzidis M G, Pei Y Z, Voorhees P W and Snyder G F 2019 Adv. Mater. 1900108.

[11] Zhou T, Mao J, Jiang J, Song S W, Zhu H T, Zhu Q, Zhang Q Y, Ren W Y, Wang Z M, Wang C and Ren Z F 2019 J. Mater. Chem. C, 7 4334.

[12] Huang K F, Loo S, Guo F, Chen W, Dyck J S, Uher C, Tim H, Polychroniadis E K, Kanatzidis M G 2004 Science 303 1457-61.

[13] Li J F, Liu W S, Zhao L D and Zhou M 2010 NPG Asia Mater. 2 152-58.

[14] Zhou C J, Lee Y K, Cha J, Yoo B, Cho S P, Hyeon T and Chung I 2018 J Am. Chem. Soc. 140 9282-90.

[15] Biswas K, He J Q, Blum I D, Hogan T P, Seidman D N, Dravid V P, Kanatzidi M G 2012 Nature 489 414-18.

[16] Zhao L D, Lo S H, Zhang Y S, Sun H, Tan G J, Uher C, Wolverton C, Dravid V P and Kanatzidis M G 2014 Nature 508 373-77.

[17] Chen Y X, Ge Z H, Yin M J, Feng D, Huang X Q, Zhao W Y and He J Q 2016 Adv. Funct. Mater. 26 6836-45.

[18] Chang C, Wu M H, He D S, Pei Y L, Wu C F, Wu X F, Yu H L, Zhu F Y, Wang K D, Chen Y, Huang L, Li J F, He J Q and Zhao L D 2018 Science 360 778-83.

[19] Lee Y K, Luo Z Z, Cho S P, Kanatzidis M G, Chung I 2019 Joule 3 1-13.

[20] Li S, Li X F, Ren Z F and Zhang Q 2018 J. Mater. Chem. A 6 2432-48.

[21] Parker D and Singh D J 2010 J. Appl. Phys. 108 083712.

[22] Tan Q and Li J F 2014 J. Electron. Mater. 43 2435-39.

[23] Sun B Z, Ma Z J, He C and Wu K C 2015 RSC Adv. 5 56382-90.

[24] Tan Q, Wu C F, Sun W and Li J F 2016 RSC Adv. 6 43985-88.

[25] Zhou B Q, Li S, Li W, Li J, Zhang X Y, Lin S Q, Chen Z W and Pei Y Z 2017 ACS Appl. Mater. Interfaces 9 34033-41.

[26] Tan Q, Zhao L D, Li J F, Wu C F, Wei T R, Xing Z B and Kanatzidis M G 2014 J. Mater. Chem. A 2 17302-06.

[27] Kamar M, Patel M, Kim J, Kim J and Kim B S 2018 Mater. Lett. 213 122-25.

[28] Abraham K M and Chaudhri S M 1986 J. Electrochem. Soc. 133 1307-11.

[29] Snyder G F and Toberer E S 2008 Nat. Mater. 7 105-14.

[30] Wang C, Chen Y D, Jiang J, Zhang R, Niu Y, Zhou T, Xia J F, Tian H Q, Hu J and Yang P 2017 RSC Adv. 7 16795-800.

[31] Ge Z H, Song D S, Chong X Y, Zheng F S, Jin L, Qian X, Zheng L, Dunin-Borkowski R E, Qin P, Feng J and Zhao L D 2017 J. Am. Chem. Soc. 139 9714-20.

[32] Peng K L, Lu X, Zhan H, Hui S, Tang X D, Wang G W, Dai J Y, Uher C, Wang G Y and Zhou X Y Energy Environ. Sci. 9 454-60.

[33] Liu J, Wang P, Wang M Y, Xu R, Zhang J, Liu J Z, Li D, Liang N N, Du Y W, Chen G and Tang G D 2018 Nano Energy 53 683-89.

[34] Pei Y Z, Heimz N A and Snyder G J 2011 J. Mater. Chem. 21 18256.