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Simultaneous enhancement in power factor and thermoelectric performance of copper sulfide by In$_2$S$_3$ doping

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In this work, we demonstrate simultaneously enhanced power factor and thermoelectric performance in Cu$_2$S upon the introduction of In$_2$S$_3$. The evident improvement in electrical conductivity, coupling with less affected Seebeck coefficient, leads to a high power factor of 1361 μW m$^{-1}$ K$^{-1}$ at 850 K, which is much higher than those previously reported values for Cu$_2$S-based thermoelectric materials. Along with moderate thermal conductivity, a high ZT value of 1.23 at 850 K is achieved. Interestingly, the phase transitions and copper segregation of Cu$_2$S are also suppressed by In$_2$S$_3$ doping due to the formation of nanoscale CuInS$_2$ phase. Such a high power factor, together with a decent ZT value and suppressed phase transition and copper segregation, will be beneficial to its practical applications in thermoelectric power generation.

1. Introduction

More than 60% of the world's consumed energy is lost as waste heat,$^1$ and therefore great efforts have been made to develop technologies harvesting the waste heat efficiently. As one of the promising waste heat harvesting technologies, thermoelectric materials and devices have attracted considerable interest in recent decades because they offer a promising route to convert waste heat into electrical power. The efficiency of thermoelectric materials is theoretically quantified by the dimensionless figure of merit (ZT), which is defined as $ZT = (S^2\sigma/\kappa)T$, where $S$, $\sigma$, $\kappa$, and $T$ are the Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature of thermoelectric materials, respectively.

Usually, there are two alternative strategies to achieve high performance (ZT): either by $\kappa$ reduction or by power factor ($PF = S^2\sigma$) enhancement. In recent years, significant achievements have been accomplished to improve ZT by $\kappa$ reduction, such as " rattling" scattering,$^2,3$ grain-boundary scattering,$^4,5$ panoscopic scattering (all length-scale phonon scattering),$^6,7$ anharmonic phonon scattering,$^8,9$ interface scattering in thin films and nanowires.$^{10-12}$ These efforts have successfully reduced $\kappa$ to approach the amorphous limit. There are also several effective approaches to enhance the power factor, like resonant doping,$^{13}$ carrier energy filtering,$^{14,15}$ and band convergence.$^{16}$

Searching for novel materials with excellent performance and without using heavy and toxic elements is the goal for thermoelectric research and practical applications. Among various materials, copper sulfide (Cu$_2$S) is a promising candidate and has received great attention because it is composed of non-toxic and earth-abundant elements, and beneficial for its large-scale practical applications. Additionally, it exhibits high thermoelectric performance due to its exceptionally low thermal conductivity and decent power factor in the moderate and high temperature range.$^{17-20}$ Recently, it has been reported that Cu$_2$S with slightly copper deficiency exhibits excellent thermoelectric performance with high ZT values as high as 1.9 at 973 K.$^{21,22}$ Zhao et al. further enhanced ZT as high as 1.9 at 973 K using a melt-solidification technique.$^{18}$ It is worth noting that ZT is not the only concern for practical applications. The output power density is equally as important as ZT or more important for power generation when the heat source is unlimited or free.$^{23,24}$ The output power density is quantified as $\omega = (T_h - T_c) PF \Delta L$, where $T_h$, $T_c$, and $\Delta L$ are the hot side temperature, cold side temperature, and thermoelectric leg length, respectively.$^{21,22}$ Therefore, it is of great importance to enhance thermoelectric performance for copper sulfide by improving power factor from the viewpoint of power generation.$^{21,22}$ Additionally, the issues regarding segregation of metallic copper and phase transitions of copper sulfide are also primary concerns for practical applications.$^{23,24}$

Herein, we report that the simultaneous enhancement in power factor and thermoelectric performance of Cu$_2$S can be achieved by a simple In$_2$S$_3$ doping approach. The power factor of Cu$_2$S is enhanced significantly up to 1361 μW m$^{-1}$ K$^{-1}$ at about 850 K, which is more than 13 times higher than that of undoped Cu$_2$S and
even higher than those previously reported values for Cu$_2$S-based thermoelectric materials with high ZT. This effective enhancement of power factor is attributed to the greatly improved electrical conductivity along with decent Seebeck coefficient. Due to the improvement of power factor, a ZT value of 1.23 is achieved at 850 K. Additionally, the phase transitions and copper segregation are also suppressed by In$_2$S$_3$ doping. Thus, the simultaneous enhancement in power factor and thermoelectric performance, together with suppressed phase transition and copper segregation, promises its practical applications in thermoelectric power generation.

2. Experimental

2.1 Sample preparation

Reagent chemicals were used as obtained: Cu$_2$S (Alfa-Aesar, 99.5%) and In$_2$S$_3$ (Alfa-Aesar, 99.98%). Cu$_2$S and In$_2$S$_3$ were weighted according to the specified molar ratios of Cu$_2$S-xIn$_2$S$_3$ (x=0, 1%, 2%, 5% and 10%), and then the weighted chemicals were fully mixed and ground with agate mortar and pestle for 30 minutes. The mixed fine powders were then densified by spark plasma sintering system (LABOX-650, SINTER LAND) at 873 K under uniaxial pressure of 50 MPa for 5 minutes in a 12.7 mm diameter graphite die.

2.2 Sample characterization

X-ray diffraction (XRD) patterns were performed by a PANalytical EMPYREAN system with Cu Kα radiation (λ=1.542 Å). The measurement was conducted at a 2 theta range of 20°–50° at room temperature with a scanning rate of 13.5 degree/min. Hall measurements were performed with a commercial instrument (HL5500PC). The squared sample with a thickness less than 500 μm was placed in a vacuum with an applied magnetic field (0.51 T) perpendicular to its surface. The resistivity (ρ) and Hall coefficient (R$_H$) were measured by the van de Pauw method. The Hall carrier mobility (μ) was calculated by μ=ρ/R$_H$, and the Hall carrier concentration n$_H$ by n$_H$=1/(eR$_H$). Scanning electron microscopy (SEM) characterization was performed on an FEI QUANTA 200 FEG microscope at 20 KV. Transmission electron microscopy (TEM) characterization was carried out on a JEM-2100 microscope.

2.3 Performance measurement

The electrical transport properties (Seebeck coefficient and electrical conductivity) of Cu$_2$S-xIn$_2$S$_3$ (x=0, 1%, 2%, 5% and 10%) were measured simultaneously using an ULVAC-RIKO ZEM 3 system under low-pressure helium gas. The experiments were repeated twice for each sample. The measurement of thermal diffusivity was performed by the laser flash method (Netzsch, LFA 457, Germany). Before the measurement, the sample was coated with a thin layer of graphite by graphite spray (Graphite33) to avoid errors from the emissivity of the sample. The specific heat capacity was calculated from the differential scanning calorimetric results (Netzsch, STA 449, Germany). The density was measured by the Archimedes method. The thermal conductivity was calculated via the equation κ=ρD Cp (κ is the thermal conductivity, ρ is the density, D is the thermal diffusivity, Cp is the specific heat capacity).

Fig. 1 Powder XRD patterns of Cu$_2$S-xIn$_2$S$_3$ (x=0, 1%, 2%, 5% and 10%). a. Powder XRD patterns. b. Enlarged powder XRD patterns.

3. Results and Discussion

3.1 Sample characterization

Powder x-ray diffraction (XRD) patterns of undoped and doped Cu$_2$S with different nominal compositions are given in Fig. 1. The x-ray diffraction patterns of the undoped Cu$_2$S are well indexed as monoclinic Cu$_2$S (JCPDS No. #00-033-0490). After In$_2$S$_3$ doping, the monoclinic Cu$_2$S phase diminishes gradually and the tetragonal CuInS$_2$ phase (JCPDS No. #01-081-9515) becomes detectable, especially for heavily doped Cu$_2$S as shown in Fig. 1b. Therefore, it can be believed that the doped samples are a two-phase composite, composed of undoped monoclinic Cu$_2$S phase and doped tetragonal CuInS$_2$ phase.

The microstructure features of undoped and doped Cu$_2$S have been investigated by SEM, shown in Fig. 2 and Fig. S1. After doping In$_2$S$_3$, the morphology of Cu$_2$S changes apparently and the grain boundaries decrease significantly. Energy dispersive X-ray spectrometer (EDX) elemental mapping results demonstrate that, for doped Cu$_2$S samples, the Cu, In and S elements are not uniformly distributed at the microstructural level (Fig. S2 – Fig. S5). As shown in the TEM image of Cu$_2$S-2%In$_2$S$_3$ (Fig. 3), some nanoparticles, ranging from several nanometers to 100 nm, can be clearly observed in the Cu$_2$S matrix. The composition of these nanoparticles can be further identified to CuInS$_2$ phase by EDX analysis (Fig. 3 and Fig. S6). This result is also confirmed by HR-TEM, and the lattice spacing of 3.2 Å corresponds to the (112) planes of CuInS$_2$ (Fig. 3 Inset), consistent with the XRD results (Fig. 1).

Fig. 2 SEM images of Cu$_2$S and Cu$_2$S-2%In$_2$S$_3$. a. Cu$_2$S. b. Cu$_2$S-2%In$_2$S$_3$. 
Inset shows HR-TEM image. Further reaches 6.47×10⁻³ for Cu₂S, and then increases to 2.91×10⁻³ at 325 K. This evident increase in electrical conductivity is attributed to the pronounced increase in Hall carrier concentration by In₂S₃ doping. Combining the electrical and thermal transport properties, the calculated ZT values of undoped and doped Cu₂S are shown in Fig. 5a. Upon In₂S₃ doping, ZT is enhanced considerably. The maximum ZT value of 1.23 at 850 K is achieved for the Cu₂S-2%In₂S₃, which is more than 3.5 times higher than that of undoped Cu₂S (ZT=0.34). More importantly, the power factor of 1361 μW m⁻¹ K⁻² at 850 K is achieved for the Cu₂S-2%In₂S₃, which is more than 13 times higher than undoped Cu₂S. Fig. 5b compares the power factor and ZT of Cu₂S-2%In₂S₃ in this work with those of Cu₂S-based materials reported in previous reports. The Cu₂S-2%In₂S₃ exhibits much higher power factor than other Cu₂S-based materials reported in previous work. Moreover, Cu₂S-2%In₂S₃ also shows comparable ZT with the highest reported ZT values for Cu₂S-based materials.

3.3 Electrical transport properties

Figure 6a shows the temperature-dependent electrical conductivities of undoped and doped Cu₂S. The electrical conductivity of Cu₂S exhibits a dramatic enhancement upon In₂S₃ doping. For example, the electrical conductivity of Cu₂S decreases by more than 4 orders of magnitude at room temperature compared with undoped Cu₂S. This evident increase in electrical conductivity is attributed to the pronounced increase in Hall carrier concentrations. The electrical conductivities of doped Cu₂S (Cu₂S-xIn₂S₃; x=2%, 5% and 10%) first increase at low temperatures, and then decrease with increasing temperature, exhibiting the behavior typical of semiconductors at low temperatures and metals at high temperatures. Such a temperature dependent behavior of electrical conductivity for doped Cu₂S is totally different from that of pristine Cu₂S, which might be intimately related to the suppression of phase transition with increasing temperature, as evidenced by the temperature-dependent specific heat capacity (Fig. 8). The doped Cu₂S (Cu₂S-xIn₂S₃; x=2%, 5% and 10%) shows peak values in electrical conductivity in the temperature range of 510 – 570 K. Notably, the electrical conductivity of Cu₂S-xIn₂S₃ reaches the maximum value of 8.54×10⁻⁵ S m⁻¹ at about 570 K, which is much higher than previously reported value by introducing copper deficiency in Cu₂S (Cu₁.97S, about 1.00×10⁻⁵ S m⁻¹).²⁹

The temperature-dependent Seebeck coefficients of undoped and doped Cu₂S, as shown in Fig. 6b, reveal that the Seebeck coefficients are positive, suggesting a p-type electrical transport behavior with holes as charge carriers, which might be caused by its intrinsic properties of copper deficiency.²⁶ The Seebeck coefficient
Electronic thermal conductivity. Seebeck coefficient. Power factor. InCuS decreases in the temperature range of 325 – 700 K, then increase above 700 K. Notably, the Seebeck coefficients drop drastically in the temperature range of 650 – 700 K. Such a temperature dependent behavior of CuS is expected to be related to the phase transition, which is also evidenced by the temperature dependence of specific heat capacity. With increasing InS3 doping content, the Seebeck coefficient values decrease significantly, which is consistent with the increase in carrier concentrations. The Seebeck coefficients of doped CuS increase monotonically with temperature in the investigated temperature range. Unlike undoped CuS, the suddenly dramatic decrease in the Seebeck coefficients in the temperature range of 650 – 700 K disappears gradually with InS3 doping (Fig. 6b), which is due to the phase transition suppression.

The power factor is enhanced significantly by InS3 doping (Fig. 6c), especially for 2 mol% InS3 doping, which is improved more than 13 times compared with undoped CuS. Such an evident enhancement in the power factor is attributed to the strongly enhanced electrical conductivity and less affected Seebeck coefficient. Among doped samples, CuS-2%InS3 exhibits strikingly high power factor value of 1361 μW m⁻¹ K⁻² at 850 K, which is higher than those previously reported values for CuS-based thermoelectric materials by different groups. Such a high power factor value is comparable with the state-of-the-art hole-doped single-crystal SnSe. Therefore, such a high power factor value is definitely beneficial for practical applications from the viewpoint of power generation.

3.4 Thermal transport properties

Figure 7 compares the temperature-dependent thermal conductivities of undoped and doped CuS. The undoped CuS exhibits ultralow intrinsic thermal conductivity, which is comparable to previously reported values. The total thermal conductivity (κtot) shows an increasing trend with increasing InS3 doping content. According to Wiedemann–Franz relation, the electronic thermal conductivity (Fig. 7b) can be calculated by the equation of κe=LσT (where L is the Lorenz number, which was determined based on the Seebeck coefficient measurements (L=1.5×exp[-|s|/116]), as proposed by Kim and Snyder et al). The contribution of electronic thermal conductivity to total thermal conductivity increases significantly due to a dramatic increase in electrical conductivity after InS3 doping. Therefore, the rise in the total thermal conductivity after InS3 doping is attributed to the significant increase in the electronic thermal conductivity (κe).

3.5 Suppression of phase transition and copper segregation

Upon InS3 doping, the temperature-dependent specific heat capacity of CuS changes significantly and the phase transitions of CuS at about 400 K and 700 – 740 K are evidently suppressed (Fig. 8). The suppression of phase transition is consistent with the suppression of copper segregation (Fig. 57), which can be easily observed at the surface of the pressed CuS columns after the synthesis process by SPS.

The phase transition and copper segregation of CuS are related to the facile Cu-ion migration, which can be characterized by the change of relative electrical resistance (R/R0, R0 and R are the initial electrical resistance and the electrical resistance, respectively) in the current stress test as proposed by Chen's
group because Cu-ion migration leads to a decrease in electrical resistance.\textsuperscript{15, 31} Herein, we use the maximum standard current density (12 A cm\textsuperscript{-2}) in thermoelectric property measurement system (ZEM 3) to evaluate the Cu-ion migration at 573 K, and these conditions are the same to the previous reports.\textsuperscript{24, 31} As shown in Fig. 9, the $R/R_0$ of Cu$_2$S drops abruptly to about 30\% after 4000 s. Such a significant variation of $R/R_0$ may be caused by the significant copper segregation.\textsuperscript{31, 32} In the case of Cu$_2$S-2\%In$_2$S$_3$, there is no obvious decrease in $R/R_0$ even after 90000 s. Furthermore, the sample of Cu$_2$S shows an obvious copper segregation and distortion after current stress test (Fig. 9 inset). After In$_2$S$_3$ doping, the sample shows no obvious difference before and after current stress test. Therefore, the less variation of $R/R_0$ and sample status after the current stress test suggests that Cu$_2$S becomes more stable after In$_2$S$_3$ doping. This stability enhancement is consistent with the phase suppression by In$_2$S$_3$ doping, as evidenced in the temperature-dependent $C_p$ results (Fig. 8).

It is widely acknowledged that doping can suppress the phase transition.\textsuperscript{33-40} The well-known anatase-to-rutile phase transition can be significantly inhibited by doping either metals\textsuperscript{35, 36} or metal oxides\textsuperscript{38-40} due to the reduction of oxygen vacancies or formation of interstitial atoms, which prevent the nucleating process for anatase-to-rutile phase transition (Ti and O atoms rearrangement). In addition, the thermoelectric material Zn$_3$Sb$_2$ shows evident $\beta$ to $\alpha/\alpha'$ phase transition, which can be fully inhibited by In or Ag doping.\textsuperscript{33, 34} Because the replacement of dopant atoms for interstitial Zn atoms can impede the motion and diffusion of Zn atoms (ions). Therefore, after doping, the substitution of original atom sites in the host lattice by foreign atoms triggers the compositional and structural changes in the host matrix, which suppress the phase transition of the host matrix by impeding the motion or diffusion of the host atoms.

For Cu$_2$S, the phase transition occurs once the positions of the Cu atom move from ordered states to disordered states by Cu-ion migration or diffusion.\textsuperscript{20, 41} After Cu$_2$S doped by In$_2$S$_3$, the Cu ions incorporate into the In$_2$S$_3$ lattice to form nanoscale CunIn$_2$S$_3$ particles with chalcopyrite structure,\textsuperscript{42, 43} as suggested by XRD and HR-TEM (Fig. 1 and Fig. 3). These nanoscale CunIn$_2$S$_3$ particles can possibly serve as “obstacles” to block the Cu-ion migration channels to suppress phase transition by impeding the Cu-ion migration or diffusion, as confirmed by the current stress test (Fig. 9). This is similar to the case of the pinning effect in Cu$_2$FeS$_4$ reported by Chen’s group, in which the atomic-scale Fe ions serve as blockers for Cu-ion migration. Thus, In$_2$S$_3$ doping can suppress the phase transition and copper segregation of Cu$_2$S, which is greatly beneficial for practical applications.

4. Conclusions

In summary, In$_2$S$_3$ doping has been shown to be a facile and effective route to simultaneously enhance the power factor and thermoelectric performance of Cu$_2$S. The dramatic increase in carrier concentrations leads to the highly enhanced power factor and thermoelectric performance. In particular, for 2\% In$_2$S$_3$ doped Cu$_2$S (Cu$_2$S-2\%In$_2$S$_3$), the power factor reaches as high as 1361 $\mu$W m$^{-1}$ K$^{-2}$ at 850 K, coupling with the moderate thermal conductivity of 0.95 W m$^{-1}$ K$^{-1}$ at 850 K, and the $ZT$ value of 1.23 can be achieved at 850 K, which is more than 3.5 times higher than that of undoped Cu$_2$S at the same temperature. The high power factor of Cu$_2$S-2\%In$_2$S$_3$ and decent $ZT$, along with suppression of phase transition and copper segregation, promises its practical applications in power generation.

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Graphitic Abstract

Simultaneously enhancing the power factor and thermoelectric performance of copper sulfide is realized by introducing In$_2$S$_3$, which will be beneficial to the practical application of Cu$_2$S.