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Thermoelectric Properties of PbS Doped with Bi₂S₃ and Cu₂S Prepared by Hydrothermal Synthesis and Spark Plasma Sintering

Wei Wang ¹, Cong Xian ¹, Yun Ou ², Zhijian He ¹ and Shuhong Xie ^{3,*} 

¹ Hunan Provincial Key Laboratory of Thin Film Materials and Devices, School of Materials Science and Engineering, Xiangtan University, Xiangtan 411105, China

² Hunan Provincial Key Laboratory of Health Maintenance for Mechanical Equipment, Hunan University of Science and Technology, Xiangtan 411201, China

³ Key Laboratory of Low Dimensional Materials and Application Technology of Ministry of Education, School of Materials Science and Engineering, Xiangtan University, Xiangtan 411105, China

* Correspondence: shxie@xtu.edu.cn

Abstract: Hierarchical PbS powders doped with different contents of Bi₂S₃ and Cu₂S were synthesized using the hydrothermal method. Subsequently, the powders were subjected to spark plasma sintering (SPS) for consolidation into bulk ceramics. X-ray photoelectron spectroscopy results showed that Bi₂S₃ and Cu₂S were doped into PbS successfully. The effect of doping with different Bi₂S₃ and Cu₂S contents on thermoelectric performance was investigated systematically. The results showed that pure PbS was an n-type semiconductor, and Bi₂S₃ doping or Bi₂S₃-Cu₂S co-doping could decrease the thermal conductivity of PbS effectively. PbS doped with 1% Bi₂S₃ exhibited a moderate Seebeck coefficient, high electric conductivity, and low thermal conductivity simultaneously, thus attaining a maximum figure of merit ZT of 0.55 at 773 K. PbS doped with 1% Bi₂S₃-1% Cu₂S exhibited an enhanced power factor and reduced thermal conductivity at an elevated temperature; the maximum ZT value obtained at 773 K was 0.83, which is more than twice that of pure PbS at 758 K (0.29), as a result.

Keywords: lead sulfide; hydrothermal method; doping; hierarchical powders; thermoelectric; spark plasma sintering



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1. Introduction

The rapid development of society increasing demand for energy results in energy crises and environmental pollution problems. Therefore, it is very important to find environmentally friendly sources of clean energy and improve energy efficiency. Thermoelectric materials are receiving increasing attention due to their ability to directly convert waste heat into electricity [1–9]. Thermoelectric devices, during use, have the advantages of no noise, no wear, no vibration, small size, light weight, simple structure, high reliability, long life, non-toxicity, no pollution to the environment, etc. They have broad application prospects for the utilization of waste heat and solar photothermal composite power generation. At the same time, the application of thermoelectric devices can also achieve efficient cooling and heating without any pollution. The thermoelectric device's efficiency (η_{TE}) is determined by the dimensionless figure of merit (ZT), which serves as a crucial indicator evaluating its performance. In $\eta_{TE} = (\sqrt{1 + ZT} - 1) \cdot (T_H - T_C) / [T_H \cdot (\sqrt{1 + ZT} + T_C/T_H)]$, ZT is figure of merit of corresponding material; T_C and T_H are the temperatures at the cold end and hot end of the thermoelectric devices; and ZT is defined as $ZT = (S^2\sigma T) / \kappa$, where, S , σ , κ , and T denote the Seebeck coefficient, electrical conductivity, thermal conductivity of material, and absolute temperature, respectively. Thus, for the purpose of achieving high-efficiency thermoelectric conversion, the significance of high electrical conductivity is

just as important as low thermal conductivity; however, the thermal and electric conductivities are coupled together, and when a material has high electrical conductivity, it usually also has high thermal conductivity [10–12]. These mutual influences and couplings make it difficult to substantially improve the conversion efficiency of thermoelectric devices to meet market needs, thus restricting their large-scale applications. Several techniques have been used to conquer this challenge, such as using multiphase composites [13–16], quantum dot superlattice structures [17–22], and nanowires [22–26]. Particularly, phonons' contribution to thermal conductivity can be reduced using spark plasma sintering (SPS), leading to nanocrystalline thermoelectrics with enhanced phonon scattering occurring at the boundaries and interfaces between grains [27–30]. Among the various thermoelectric materials, PbTe-based thermoelectric materials are the best for power generation applications, and are considered as one of the most promising medium-temperature thermoelectric materials [31–36]. PbTe-based thermoelectric materials have been widely used in the military and aerospace fields due to their excellent properties. However, due to their poor mechanical properties, the toxicity of lead, and the fact that tellurium is rare and expensive, their large-scale commercial application is limited. PbS is a potential alternative for PbTe, owing to its stable and simple structure, low price, abundant reserves of S, and recently reported good thermoelectric properties [37–39]. For example, reports have indicated that the figure of merit ZT can be improved to 1.1 because the second phase can be doped into PbS at a temperature of 923 K [40]. In recent years, PbS powders with different shapes (dendritic structures [41,42], hyperbranched stars [43,44], nanorods [45–47], nanotubes [48], and other shapes [49]) have also been synthesized via the self-assembly method. Encouraged by these works on PbS [50,51], we synthesized PbS hierarchical powders with different Bi_2S_3 and Cu_2S doping contents using the hydrothermal method, which is simple and inexpensive when compared to the melting method [52,53]. Then, we consolidated them into bulk ceramics via SPS and measured their thermoelectric performance. The experiment results indicate that the thermal conductivity of PbS samples with either Bi_2S_3 doping alone or Bi_2S_3 and Cu_2S co-doping is reduced significantly compared with that of pure PbS. The maximum ZT value of PbS doped with 1% Bi_2S_3 –1% Cu_2S was 0.83 at 773 K, which is a relatively high value for PbS-based materials at the specified temperature.

2. Materials and Methods

The synthesis process for obtaining Bi_2S_3 - and Cu_2S -doped PbS is as follows: 4.3 g $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ (99%, Alfa Aesar, Haverhill, MA, USA) and appropriate amounts of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (98%, Alfa Aesar) and $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (99.9%, Alfa Aesar) were dissolved into the mixed solvent of deionized water and glycol (98%, Alfa Aesar) at a 3:1 volume ratio. Then, an appropriate amount of thiourea (99%, Alfa Aesar) was added into the above solutions under stirring; then, the *mixed* solutions were moved to a 50 mL Teflon-lined stainless steel autoclave where the mixed solutions were held at a temperature of 180 °C for 24 h. After cooling to room temperature, the precipitates were collected via centrifugation, then washed several times using deionized water and ethanol (99.8%, Alfa Aesar) sequentially. Finally, the synthesized powders were dried in a vacuum oven at 60 °C for 6 h, then consolidated into bulk ceramics via spark plasma sintering (SPS-211Lx).

For the SPS process, the powders were first loaded into a graphite die with a diameter of 13 mm and maintained at a pressure of 45 MPa. Then, they were heated to 450 °C for 10 min by passing a large amount of DC current (100–500 A) through the die, and the heating rate was controlled at approximately 100 °C/min by adjusting the current. Then, the pressure was instantaneously released before turning off the heating current to prevent the sample from cracking. The entire process was executed within a vacuum chamber ($\sim 10^{-6}$ Torr) to prevent the oxidization of the graphite. The SPS specimens were disk-shaped, with dimensions of Φ 13 mm $\times$ 4 mm.

X-ray diffraction (XRD) (Rigaku D/max-rA, Rigaku, Tokyo, Japan), transmission electron microscopy (TEM) (JEM-2100, Rigaku, Tokyo, Japan) with selected area electron diffraction (SAED), and scanning electron microscopy (SEM) (LEO 1525, Carl Zeiss,

Oberkochen, Germany) were used to identify the crystal structure and the morphology of sample. X-ray photoelectron spectroscopy (XPS; K-Alpha 1063, Thermo Fisher Scientific, Waltham, MA, USA) was employed for the purpose of analyzing the atomic composition and element valence. The thermoelectric properties were evaluated along the specimen surface perpendicular to the pressing direction during the SPS process. The Seebeck coefficient and electrical resistivity were measured using a Seebeck coefficient/electric resistance measuring system (ZEM-2, ULVAC-RIKO, Yokohama, Japan). The thermal conductivity was calculated by the product of thermal diffusivity, specific heat, and density. The thermal diffusivity was assessed using a laser flash apparatus (LFA427, NETZSCH, Bavaria, Germany). Before measurement, the sample was coated with a thin layer of graphite-by-graphite spray (Graphite33) to improve its thermal homogeneity. The volumetric specific heat capacity was determined through the utilization of a differential scanning calorimeter (DSC 404 F3, NETZSCH, Bavaria, Germany). The density of the sample was measured using the Archimedes method. The thermal conductivity was calculated via the equation $\kappa = \rho DC_p$ (κ is the thermal conductivity, ρ is the density, D is the thermal diffusivity coefficient, and C_p is the specific heat capacity).

3. Results and Discussion

3.1. Thermoelectric Properties of PbS Doped with Bi₂S₃

The crystal structure of the PbS powders doped with varying amounts of Bi₂S₃ was measured by XRD, as shown in Figure 1a. All XRD peaks exhibited a cubic PbS crystal structure, and no obvious peaks of Bi₂S₃ were shown owing to its low content. The sharp diffraction peaks of the four samples indicated the superior crystallinity of the synthetic PbS-based powders, with preferential orientation along the (111), (200), and (220) planes in the four specimens. As shown in Figure 1b, the XPS results demonstrate that Bi₂S₃ was doped into PbS. When compared to the pure PbS, PbS doped with 5% Bi₂S₃ showed an extra peak of Bi 4f at a binding energy value of 164 eV, which confirms that the Bi₂S₃ was successfully doped into PbS; the peaks of O (1s) and C (1s) corresponded to the oxidation reaction in the air. The fine XPS spectra of Bi 4f peaks are presented in Figure 1c. The spectrum of the Bi 4f state consisted of two peaks at 159.2 and 164.5 eV, respectively, which also illustrates the presence of Bi³⁺ cations [54–56] and demonstrates that during the synthesis, the valence of the component did not change due to a lack of even surface oxidation by the air.

Figure 2 shows the SEM and TEM results of pure PbS and PbS doped with 1% Bi₂S₃. It can be observed that the primary morphology of the powders synthesized at 180 °C was dendritic, with hyperbranching and a small amount of star-shaped structures. Figure 2a,b show that the average grain size of Bi₂S₃-doped PbS was smaller compared to pure PbS, which was due to the addition of surfactant ethylene glycol, which reduced the surface tension of the solution and promoted nucleation, resulting in a decreased grain size. Moreover, after doping with Bi₂S₃, there was agglomeration of some fine particles on the surface of the dendritic structure. This was mainly due to the addition of ethylene glycol, which caused fractures in the dendritic and star shapes, forming many fine particles and small dendritic particles. The new generated Bi₂S₃ particles were adsorbed on the surfaces of the PbS crystals to reduce the surface energy. With the increase in the Bi₂S₃ doping amount, more and more Bi₂S₃ particles were formed, and the agglomeration of Bi₂S₃ particles occurred. Smaller grain sizes increased the interface between the grains, which was beneficial for decreasing the thermal conductivity of the materials. This led to an improvement in the thermoelectric performance of the material.

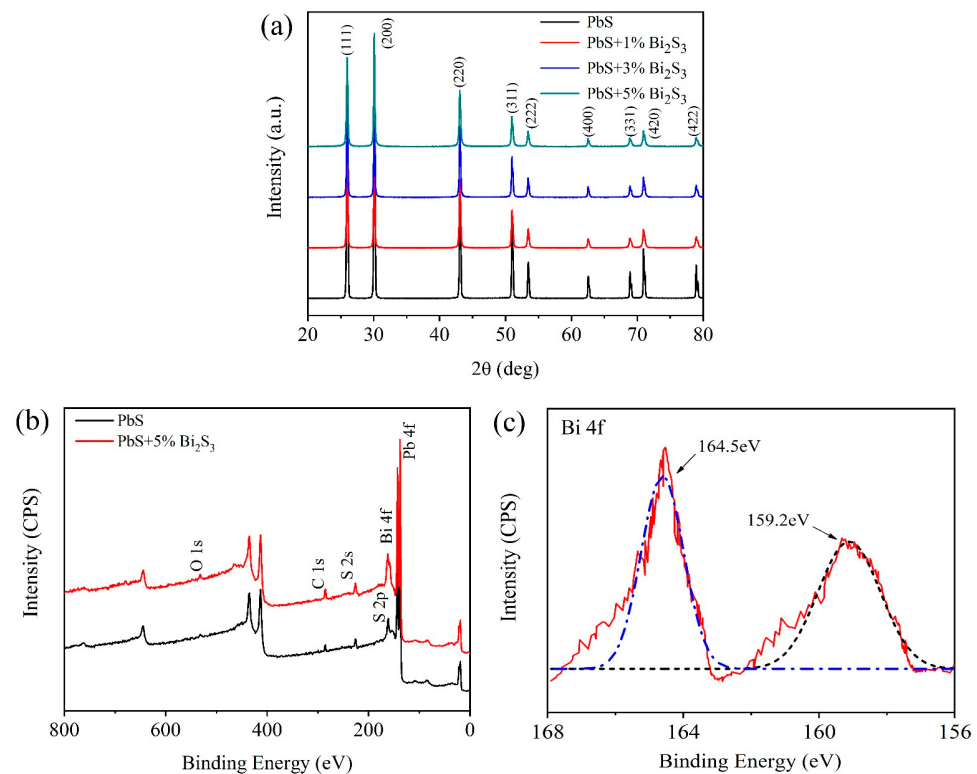


Figure 1. (a) X-ray diffraction (XRD) patterns of PbS powders doped with $x\%$ Bi_2S_3 ($x = 0, 1, 3, 5$); (b) X-ray photoelectron spectroscopy (XPS) images of pure and 5% Bi_2S_3 -doped PbS powders; (c) XPS peak of Bi 4f.

Figure 2c,d show the dendritic and star-shaped morphologies of the synthetic powders, which are composed of hierarchical grains. High-resolution TEM (HRTEM) confirmed the cubic structure of PbS doped with 1% Bi_2S_3 , where the lattice spaces were measured to be 0.346 nm along the $(1\bar{1}1)$ plane and 0.347 nm along the $(11\bar{1})$ plane, as shown in Figure 2e. However, when comparing Figure 2e with Figure 2f, we observed minor difference in the lattice space at different micro-areas of the sample in the same plane, which indicates that the lattice distortion induced by doping Bi_2S_3 was inhomogeneous.

The effect of temperature on the thermoelectric performances of PbS doped with $x\%$ ($x = 0, 1, 3, 5$) Bi_2S_3 is shown in Figure 3. Figure 3a shows that the Seebeck coefficients of all samples were negative, which indicates that the Bi_2S_3 -doped PbS was an n-type semiconductor and electrons were the major carriers. The absolute values of the Seebeck coefficients (S) increased with the increasing temperature, but obviously decreased with the increase in the doping amount of Bi_2S_3 . The absolute values of the Seebeck coefficients corresponding to PbS doped with 1, 3, and 5% Bi_2S_3 were 264.5, 187.9, and 178.8 $\mu\text{V K}^{-1}$ at 773 K, respectively, which are obviously lower than that of 360 $\mu\text{V K}^{-1}$ for pure PbS at 758 K. These results are consistent with previously reported results [40].

Figure 3b shows that the electrical conductivity (σ) decreased with the increasing temperature for samples doped with $x\%$ ($x = 0, 3, 5$) Bi_2S_3 , which indicates a typical metallic transport behavior; however, the electrical conductivity increased with the increasing temperature for PbS doped with 1% Bi_2S_3 sample. Moreover, repeated tests on the same and different samples maintained the same trend. This phenomenon can likely be explained as follows: when PbS is doped with 1% Bi_2S_3 , the total carrier concentration of the material is significantly lower owing to the powerful surface adsorption effect of hydrothermal synthesized powder, which results in low electrical conductivity. On the contrary, an increase in the percentage of doped Bi_2S_3 leads to a rise in electron carrier concentration, showing a typical n-type electrical conductivity of the semiconductor as did doping with

3% and 5% of Bi_2S_3 . At 773 K, the corresponding electric conductivities of PbS doped with 1, 3, and 5% of Bi_2S_3 were 95.3, 136.6, and 139.2 S cm^{-1} , respectively. It can be observed that the electric conductivity of the samples increased gradually with the increasing content of Bi_2S_3 at high temperatures.

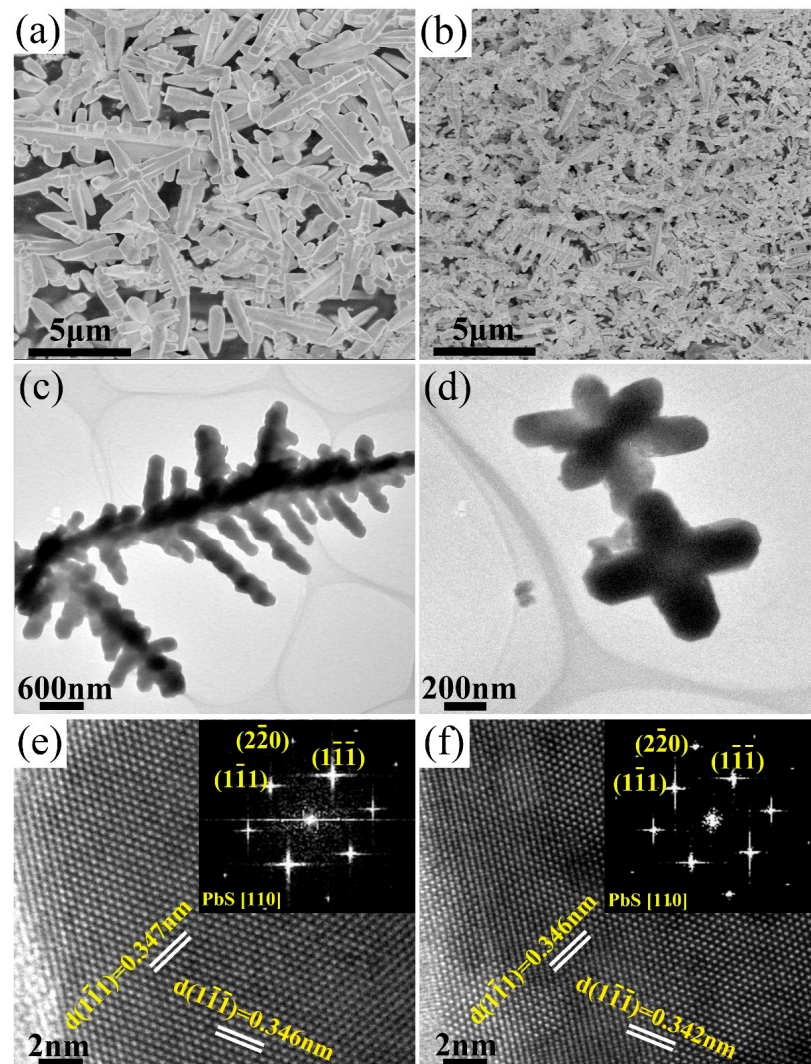


Figure 2. Scanning electron microscopy (SEM) images of (a) pure PbS and (b) PbS doped with 1% Bi_2S_3 ; transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of PbS doped with 1% Bi_2S_3 : (c) dendritic and (d) star-shaped morphologies; (e,f) HRTEM images of different micro-areas.

Based on the above values of electrical conductivity and Seebeck coefficients, Figure 3 shows the power factor PF values of the four samples, which were calculated using the formula. The power factors of the PbS samples doped with x% ($x = 1, 3, 5$) Bi_2S_3 increased sharply as the temperature increased, up to 573 K, and tended to stabilize at higher temperatures of approximately 773 K. The corresponding power factors of PbS doped with 1, 3, and 5% Bi_2S_3 at 773 K were 6.67, 4.82, and 4.45 $\mu\text{W cm}^{-1} \text{K}^{-2}$, respectively. The pure PbS showed good electrical properties at low temperatures, while the PbS doped with 1% Bi_2S_3 had better electrical properties at high temperatures. Obviously, the power factor of PbS with 1% Bi_2S_3 doping had the maximum value, owing to its higher Seebeck coefficient.

Figure 3d shows that the total thermal conductivity decreased with the increasing temperature and doping content of Bi_2S_3 simultaneously. The thermal conductivities for 1, 3, and 5% Bi_2S_3 doping were 0.93, 0.79, and 0.87 $\text{W m}^{-1} \text{K}^{-1}$ at 773 K, respectively. The

thermal conductivity of PbS doped with Bi_2S_3 was demonstrated to be lower than that of pure PbS. Figure 3e illustrates the lattice thermal conductivity ($\kappa_L = \kappa - \kappa_e$) of the samples, where the electronic thermal conductivity was calculated based on the Wiedemann–Franz law as $\kappa_e = L\sigma T$ and the Lorenz number L was set as $2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$ [57]. It was found by calculation that the electronic thermal conductivity value (κ_e) was one order of magnitude smaller than the total thermal conductivity (κ), so the lattice thermal conductivity accounted for the main portion of the total thermal conductivity. The ratio of lattice thermal conductivity (κ_L) to κ indicated that the total thermal conductivity (κ) was dominated by phonon transport. The κ_e values increased with the increasing temperature; then, the decrease in thermal conductivity was primarily attributed to the rapid decrease in the lattice thermal conductivity due to the formation of point defects and fine grain sizes by doping [58–60].

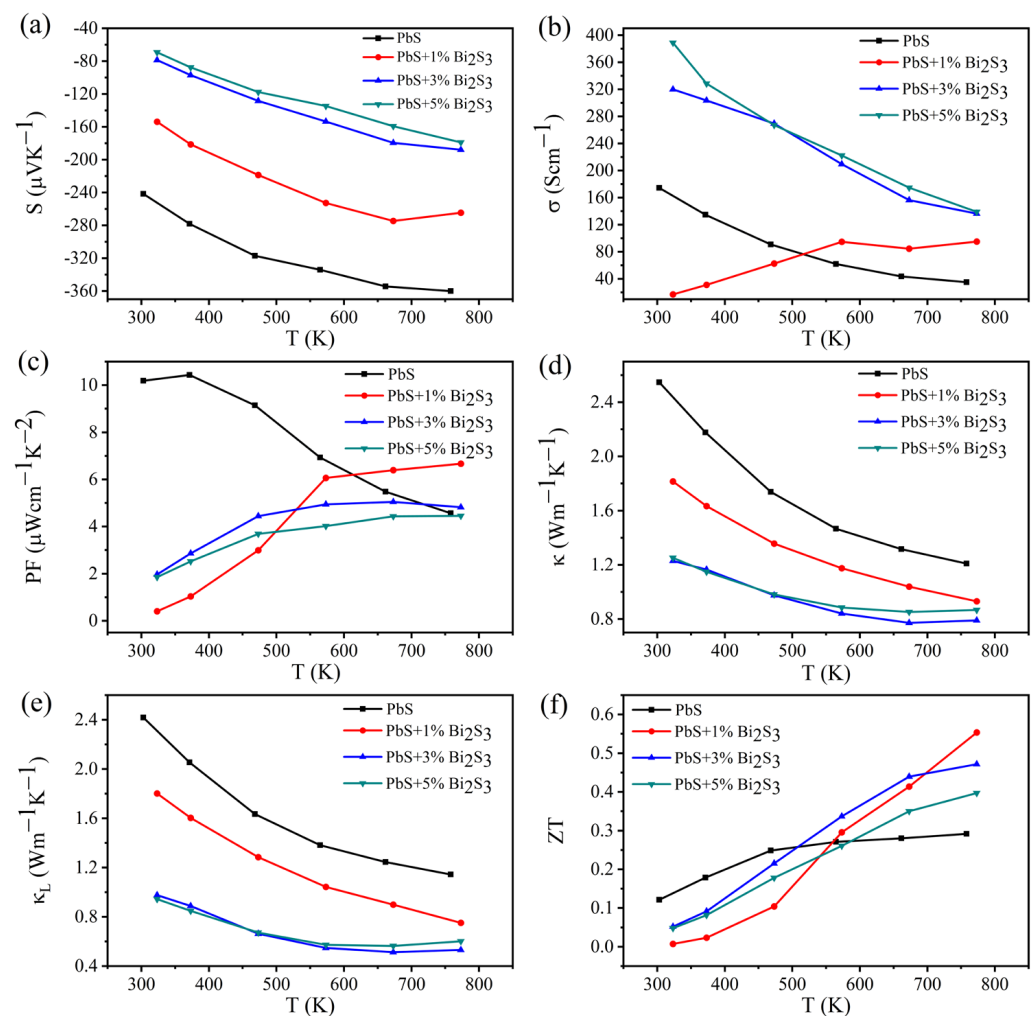


Figure 3. Effect of temperature on the thermoelectric performances of PbS doped with $x\%$ ($x = 0, 1, 3, 5$) Bi_2S_3 : (a) Seebeck coefficient, (b) electric conductivity, (c) power factor, (d) total thermal conductivity, (e) lattice thermal conductivity, and (f) figure of merit.

According to the measured electrical conductivity, Seebeck coefficient, and thermal conductivity, we calculated the ZT values as shown in Figure 3f. The ZT values of all samples increased with the increasing temperature. The ZT values corresponding to 1, 3, and 5% Bi_2S_3 doping were 0.55, 0.47, and 0.40 at 773 K, respectively, while that of the pure PbS was only 0.29 at 758 K. Among all the samples, PbS doped with 1% Bi_2S_3 showed the maximum ZT value, and its thermoelectric performance was improved by nearly 90% compared with that of the pure PbS, which can be attributed to an increase in the power

factor alongside a decrease in thermal conductivity. Table 1 lists the detailed transport properties of PbS doped with different Bi₂S₃ doping amounts.

Table 1. Thermoelectric performance of PbS with different amounts of Bi₂S₃ and Cu₂S doping.

Sample	T (K)	S ($\mu\text{V K}^{-1}$)	σ (S cm^{-1})	PF ($\mu\text{W cm}^{-1} \text{K}^{-2}$)	κ ($\text{W m}^{-1} \text{K}^{-1}$)	κ_L ($\text{W m}^{-1} \text{K}^{-1}$)	ZT _{max}
PbS	758	−360.0	35.2	4.56	1.21	1.14	0.29
PbS + 1% Bi ₂ S ₃	773	−264.5	95.3	6.67	0.93	0.75	0.55
PbS + 3% Bi ₂ S ₃	773	−187.9	136.6	4.82	0.79	0.53	0.47
PbS + 5% Bi ₂ S ₃	773	−178.8	139.2	4.45	0.87	0.60	0.40
PbS + 1% Bi ₂ S ₃ + 1% Cu ₂ S	773	−193.7	172.6	6.48	0.60	0.27	0.83
PbS + 1% Bi ₂ S ₃ + 3% Cu ₂ S	773	−207.4	97.5	4.19	0.61	0.43	0.53
PbS + 3% Bi ₂ S ₃ + 3% Cu ₂ S	773	−172.0	128.7	3.81	0.45	0.21	0.66
PbS + 3% Bi ₂ S ₃ + 5% Cu ₂ S	773	−178.1	97.0	3.08	0.36	0.18	0.65

3.2. Thermoelectric Properties of PbS Co-Doped with Bi₂S₃ and Cu₂S

Figure 4a shows the XRD peaks corresponding to the cubic structure of PbS. The peak positions observed are consistent with those shown in Figure 1a, and no obvious peaks of Bi₂S₃ and Cu₂S can be observed due to the use of doping amounts of no more than 5%. XPS was used to demonstrate that both Bi₂S₃ and Cu₂S are doped into the PbS, as shown in Figure 4b. Extra peaks of Bi 4f and Cu 2p at the binding energies of 164 and 932.3 eV, respectively, can be observed for PbS doped with 1% Bi₂S₃-1% Cu₂S, which confirms that the Bi₂S₃ and Cu₂S were successfully co-doped into PbS. Figure 4c also illustrates that the valence of Cu ions was +1, because the corresponding binding energy of Cu 2p peak of Cu²⁺ was 933.6 eV, which indicates that no redox reaction may occur between the reduced form of the metal copper and the sulfide during the synthesis process due to the lack of uniform air surface oxidation.

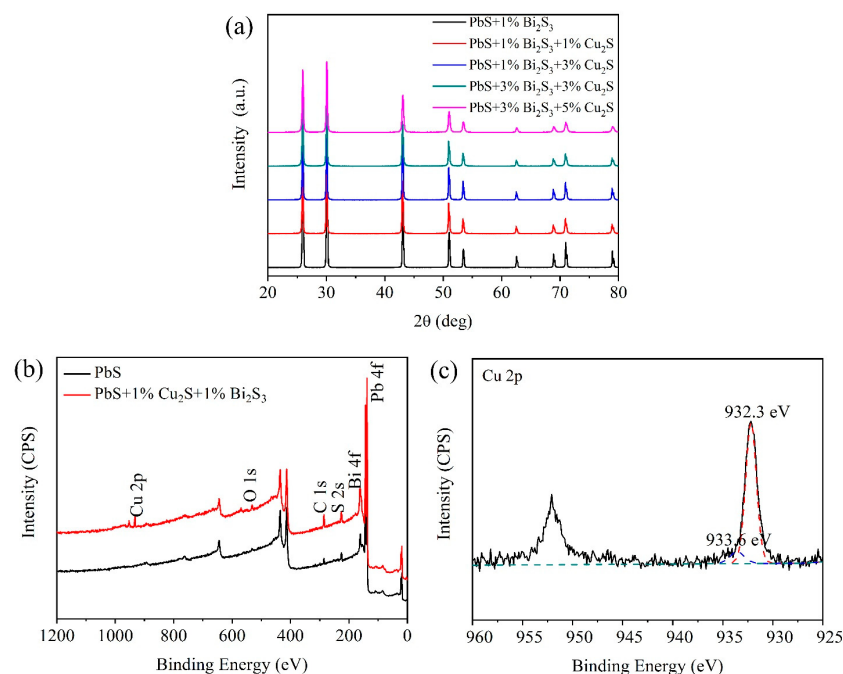


Figure 4. (a) XRD patterns for PbS powders doped with x% ($x = 1, 3$) Bi₂S₃-y% ($y = 1, 3, 5$) Cu₂S; (b) XPS images of pure and 1% Bi₂S₃-1% Cu₂S co-doped PbS powders; (c) XPS peak of Cu 2p.

Figure 5 shows the SEM and TEM images of PbS powders doped with different percentages of Bi₂S₃ and Cu₂S. Figure 5a,b show that the primary morphology of the co-doped samples was similar to that of Bi₂S₃-doped PbS, with predominantly dendritic

and star-like shapes, and small amounts of spherical particles, which were probably Bi_2S_3 , as it lacks a preferred growth direction and easily forms a spherical structure during the hydrothermal process [61]. The TEM images shown in Figure 5c,d confirm the hierarchical dendritic, star-shaped, and spherical structures of the powders, which effectively increased the interface between the grains and reduces the thermal conductivity at high temperatures. The SAED pattern shown in Figure 5e illustrates the single-crystal nature of the PbS-based powder synthesized by the hydrothermal method. Figure 5f displays the HRTEM of co-doped PbS. The lattice space was 0.346 nm along the (111) plane, which is similar to that of the Bi_2S_3 -doped PbS.

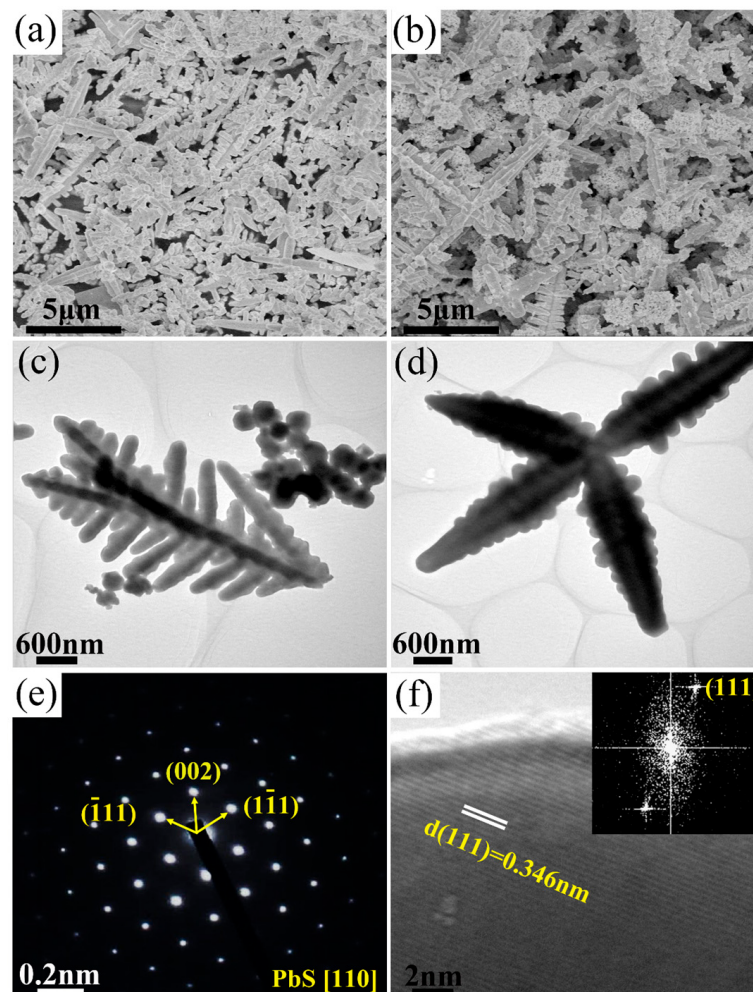


Figure 5. SEM images of PbS doped with (a) 1% Bi_2S_3 -1% Cu_2S and (b) 3% Bi_2S_3 -5% Cu_2S ; TEM results of PbS doped with 1% Bi_2S_3 -1% Cu_2S : (c) dendritic and spherical particles, (d) hyperbranched star-shaped particle; (e) selected area electron diffraction pattern; (f) HRTEM image.

Figure 6 shows the thermoelectric performances of PbS with different amounts of co-doped Bi_2S_3 and Cu_2S as a function of temperature. The Seebeck coefficients were negative, which indicates that the PbS doped with Bi_2S_3 and Cu_2S was still an n-type semiconductor, as shown in Figure 6a. The absolute value of the Seebeck coefficients increased with the increasing temperature and decreased with the increasing percentage of Cu_2S doping, which is due to the higher carrier concentration. At 773 K, the absolute values of the Seebeck coefficients for the five samples were 264.5, 193.7, 207.4, 172.0, and 178.1 $\mu\text{V K}^{-1}$, respectively. Figure 6b shows that the PbS-based samples doped with Cu_2S exhibited significantly low electrical conductivity at 323 K, with values less than 1 S cm^{-1} . The electrical conductivity of the co-doped PbS sample increased with the

increasing temperature; at a temperature of 773 K, the maximum electrical conductivity value was 172.6 S cm^{-1} for the PbS doped with 1% Bi_2S_3 -1% Cu_2S sample. The electrical conductivities of samples doped with 1% Bi_2S_3 , 3% Bi_2S_3 -3% Cu_2S , and 3% Bi_2S_3 -5% Cu_2S showed a turning point at 573 K due to the continuously increasing carrier concentration and high temperature range [62–64], and the corresponding values were 95.3, 128.7, and 97.0 S cm^{-1} at 773 K, respectively. However, the sample doped with 1% Bi_2S_3 -3% Cu_2S showed a turning point at 673 K, with electrical conductivity of 97.5 S cm^{-1} at 773 K. The electric conductivities of the PbS-based samples decreased with the increasing Cu_2S content at high temperatures. The power factor values are shown in Figure 6c. The power factor of all the samples increased with the increasing temperature, and tended to stabilize at higher temperatures. The corresponding PF values of the five samples were 6.67, 6.48, 4.19, 3.81, and $3.08 \mu\text{W cm}^{-1} \text{ K}^{-2}$ at 773 K. When doped with 1% Bi_2S_3 and different amounts of Cu_2S (0%, 1%, 3%), the corresponding power factors were 6.67, 6.48, and $4.19 \mu\text{W cm}^{-1} \text{ K}^{-2}$ at 773 K, respectively. Additionally, when doped with 3% Bi_2S_3 and different amounts of Cu_2S (3%, 5%), the power factors of the two samples were 3.81 and $3.08 \mu\text{W cm}^{-1} \text{ K}^{-2}$ at 773 K, respectively. When the doping amount of Cu_2S was increased, the electrical transport performance of PbS decreased. It can be observed that the power factor of PbS-based samples declined when the Bi_2S_3 and Cu_2S contents were increased.

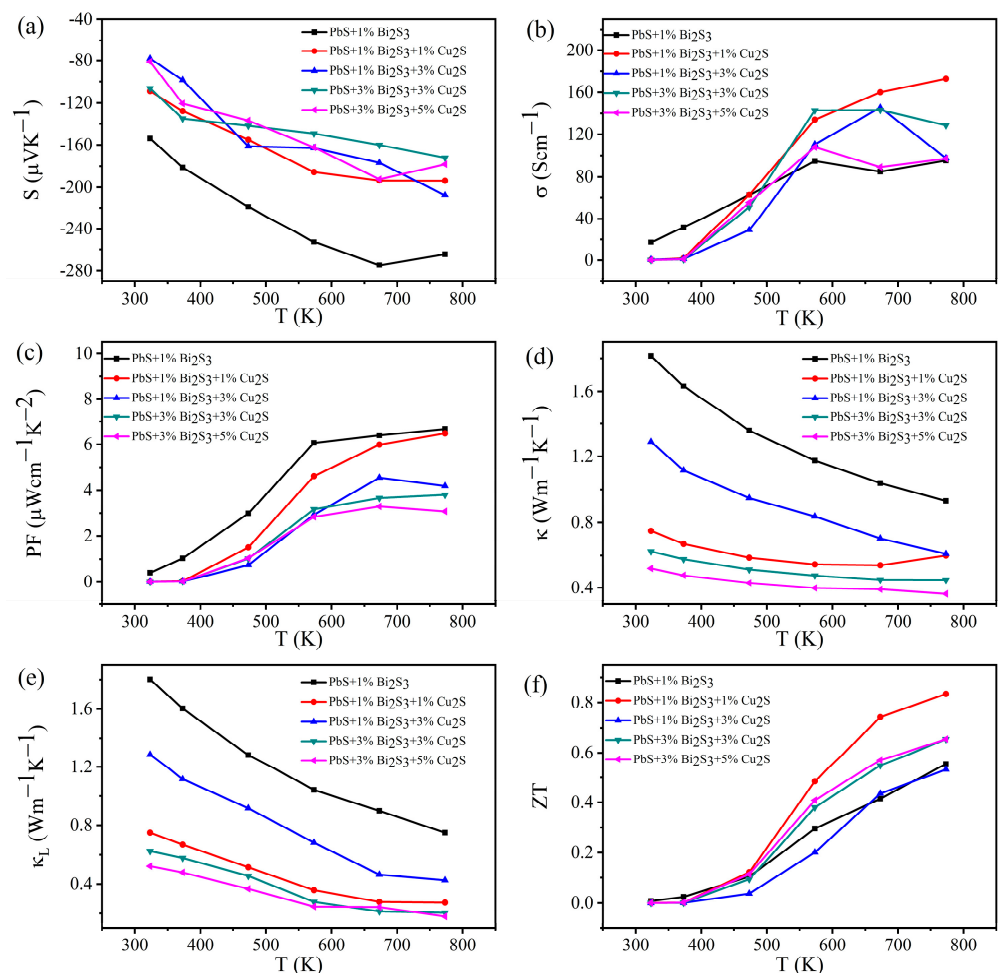


Figure 6. Effect of temperature on the thermoelectric performance of PbS with different amounts of co-doped Bi_2S_3 and Cu_2S : (a) Seebeck coefficient, (b) electric conductivity, (c) power factor, (d) total thermal conductivity, (e) lattice thermal conductivity, and (f) figure of merit.

The thermal conductivity of the samples exhibited a decline as the temperature increased, as illustrated in Figure 6d, except for the PbS doped with 1% Bi_2S_3 -1% Cu_2S at

a high temperature. The corresponding thermal conductivity values of the five samples were 0.93, 0.60, 0.61, 0.45, and 0.36 W m⁻¹ K⁻¹ at 773 K. The PbS sample doped with 3% Bi₂S₃-5% Cu₂S exhibited the lowest thermal conductivity, which suggests that the thermal conductivity of PbS-based samples reduced with the increasing doping content. Through calculation, it was found that the value of electronic thermal conductivity (κ_e) was one order of magnitude smaller than the total thermal conductivity (κ), indicating that lattice thermal conductivity dominates the total thermal conductivity. The ratio of lattice thermal conductivity (κ_L) to total thermal conductivity (κ) suggests that the total thermal conductivity is mainly determined by phonon transport. The lattice thermal conductivity (κ_L) of the specimens is displayed in Figure 6e. The κ_L values clearly reduced with the increasing temperature; the corresponding values were 0.75, 0.27, 0.43, 0.21, and 0.18 W m⁻¹ K⁻¹ at 773 K for the five samples. The decreased thermal conductivity can be primarily attributed to the rapid decrease in the lattice thermal conductivity. The corresponding ZT values of the five samples were 0.55, 0.83, 0.53, 0.66 and 0.65 at 773 K, as shown in Figure 6f. The detailed transport properties of PbS doped with different Bi₂S₃-Cu₂S are listed in Table 1. The ZT values of all samples increased with the increasing temperature. It was found that, when doping with 1% Bi₂S₃ and different amounts of Cu₂S (1%, 3%), the ZT values of the samples were 0.83 and 0.53 at 773 K, respectively. This indicates that as the Cu₂S doping ratio increased while the Bi₂S₃ doping ratio remained at 1%, and the thermoelectric properties of the samples decreased, mainly due to the decrease in power factor (PF) with the increasing Cu₂S doping ratio. When doping with 3% Bi₂S₃ and varying amounts of Cu₂S (3%, 5%), the corresponding ZT values of the samples were 0.66 and 0.65 at 773 K, respectively. It is evident that as the Cu₂S doping ratio increased while the Bi₂S₃ doping ratio was kept at 3%, the thermoelectric properties of the samples also decreased, which can be mainly attributed to the decrease in thermal conductivity and power factor with the increasing Cu₂S doping ratio. PbS doped with 1% Bi₂S₃-1% Cu₂S exhibited the maximum ZT value of 0.83 at 773 K, which was 51% higher than 0.55 for PbS with doping of 1% Bi₂S₃, owing to the lower thermal conductivity, and 186% higher than 0.29 for pure PbS, owing to the higher power factor and lower thermal conductivity.

4. Conclusions

In summary, dendritic and star-shaped PbS powders with varying Bi₂S₃ contents and Cu₂S doping were successfully synthesized using the hydrothermal method and sintered into bulk ceramics via SPS. Appropriate amounts of Bi₂S₃ doping into PbS were shown to improve the electric conductivity and decrease the thermal conductivity simultaneously; moreover, the maximum ZT value reached 0.55 at 773 K for PbS doped with 1% Bi₂S₃. Furthermore, doping 1% Cu₂S into Bi₂S₃-doped PbS increased the electric conductivity sharply and Seebeck coefficient gradually, and decreasing the corresponding thermal conductivity resulted in a high ZT value of 0.83 at 773 K in PbS doped with 1% Bi₂S₃-1% Cu₂S. This work presents a highly effective approach to enhance the performance of thermoelectric materials, with the potential to promote the application of thermoelectric devices with high conversion efficiency.

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