Effects of sintering temperature on thermoelectric properties of \( \text{Cu}_{1.8} \text{S} \) bulk materials

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Abstract

Due to the excellent electrical transmission and potentially excellent thermoelectric (TE) performance, digenite (\( \text{Cu}_{1.8} \text{S} \)) has attracted more attention. The combination of mechanical alloying (MA) and spark plasma sintering (SPS) was widely used in preparing \( \text{Cu}_{1.8} \text{S} \) bulk material, while the TE properties for pure sample were still low. Therefore, it’s worth to search a suitable synthesis method to enhance the thermoelectric performance for pristine \( \text{Cu}_{1.8} \text{S} \). In this study, high-density bulk samples of copper sulfide (CS) were fabricated by solid states reaction method combined with SPS at different temperatures. When the SPS temperature was over 873 K, large amounts of sulfur volatilization lead to the appearance of \( \text{Cu}_{1.97} \text{S} \) and it was considered to have great influence on the thermoelectric performances. The result reveals that the increased sintering temperature could affect the density and grain size of the bulk samples. The highest \( ZT \) value of 0.54 was obtained at 773 K for the sample sintered at 773 K, which is also the highest \( ZT \) value for the pristine \( \text{Cu}_{1.8} \text{S} \) in the literature.

1. Introduction

Due to the consumption of fossil fuel continuously and the deterioration of the environment triggered by human using energy, exploring clean and renewable energy becomes the most significant problem human faced in the 21st century. With the exploitation of new types of utilize repeatedly energy, high performance thermoelectric (TE) materials, which depend on the ability to convert waste heat to electricity, are gradually appearing in the field of research. Nowadays, part of TE materials has been employed in industrial application with many wonderful features, for example low cost, environmentally benign and nontoxic [1–5].

The efficiency of energy conversion for TE devices is mainly dominant in the dimensionless figure of merit \( ZT = 3 \alpha^2 \sigma T/\kappa L \), where \( T \) is the absolute temperature, \( \alpha \) is Seebeck coefficient, \( \sigma \) is electrical conductivity and \( \kappa \) is thermal conductivity (including electrical thermal conductivity \( \kappa_{\text{e}} \) and lattice thermal conductivity \( \kappa_{\text{l}} \)), respectively [6]. Equation shows the desired TE materials need to equip a high absolute \( \alpha \), \( \sigma \) and low \( \kappa \).

Nevertheless, it is strenuous to get command of these parameters individually on account of the forceful coupling of each other [7]. At present, the effective and straightforward methods include two aspects: one is raising the powders factor of materials by enhancing Seebeck [8]. At present, multiple efforts have achieved this effect by building nonstructural [9, 10] or adjusting states-density [11, 12]. However, the disadvantage is the case that these measures would deteriorate carrier mobility. On the other hand, we can attempt to reduce \( \kappa_{\text{e}} \) by fabricating scattering source such as point defects (Vacancies, interstitial atoms, impurity atoms, etc), [13, 14] and boundaries from impurities [18, 19], etc, to increase the number of phonon scattering. Fortunately, both of two aspects share a common characteristic that is affected by carrier concentration, we can adjust carrier concentration appropriately to improve conversation efficiency. Over the years, TE materials for various temperature ranges have been extensively explored, there are Bi\(_2\)Te\(_3\)-based alloys at the room temperature, Pb\(_b\)Q (Q = Te, Se or S) alloys, [22, 23] Skutterudite compounds at the middle temperature.
conditions have retained an increasing appeal. The x-ray diffraction patterns of the bulk samples is shown in 3.1. Phase and microstructure 3. Results and discussion Cu1.8S powders were synthesized by solid state phase method using 99.99% Cu and 99.99% S powders as elemental materials. These powders were poured in quartz tubes according to stoichiometric ratios. These tubes were then heated to 773 K, 773 K, 873 K, and 973 K for 5 min in a graphite mold and then sintered at 673 K, 773 K, 873 K, and 973 K for 5 min in a helium atmosphere from 323 to 773 K. The thermal diffusivity (D) and specific heat capacity (C_p) were obtained by using laser flash method (NETZSCH, LFA457, Germany) and thermal analysis-based (STA449, Netzsch, Germany) from a temperature of 323 K-773 K. The thermal conductivity (κ) was summarized by the formula: κ = D C_p d, in which the density d was measured by the Archimedes method.

2. Experimental section

Cu1.8S powders were synthesized by solid state phase method using 99.99% Cu and 99.99% S powders as elemental materials. These powders were poured in quartz tubes according to stoichiometric ratios. These tubes were then heated to 773 K, 773 K, 873 K, and 973 K for 5 min in a graphite mold and then sintered at 673 K, 773 K, 873 K, and 973 K for 5 min in a helium atmosphere from 323 to 773 K. The thermal diffusivity (D) and specific heat capacity (C_p) were obtained by using laser flash method (NETZSCH, LFA457, Germany) and thermal analysis-based (STA449, Netzsch, Germany) from a temperature of 323 K-773 K. The thermal conductivity (κ) was summarized by the formula: κ = D C_p d, in which the density d was measured by the Archimedes method.

3. Results and discussion

3.1. Phase and microstructure

The x-ray diffraction patterns of the bulk samples is shown in figure 1(a), which were synthesized by MA for 1 h and solid-state phase method. All the peaks of the bulk samples are sharper than the peaks of the powder sample due to grain growth. Meanwhile, all the diffraction peaks are corresponding to the α-diginite (PDF #23-0962), which illustrates that the main phase is Cu1.8S and no obvious impurities appears within the detection limit. Other than the Cu1.8S main phase, the extra diffraction peaks belonged to the Cu1.96S phase indexed by PDF #12-0224 has been detected in the CS873 and CS973 sintering samples, and the intensity of their diffraction peaks gradually increases with increasing sintering temperature. This phenomenon attributes to the volatilization of sulfur in Cu1.8S matrix and may be a result of the SPS process. As shown in figure 1(b), it is worth noting that the 20 of the (1 1 0) peak for all bulk samples deviate from the standard card and shift to the lower angle, indicating the enlargement of the lattice with increased sintering temperature. This result agrees with the calculation of cell parameters as shown in figures 1(c) and (d), the a, b and c values gradually increased with the
increased sintering temperature, which may be caused by the interactions between atoms due to the volatilization of sulfur during the SPS process.

The SEM observation of the fractured surfaces for the Cu$_{1.8}$S bulk samples are posted on figure 2, in where shows a dense micro-structure. As shown in figure 2(a), the average size of Cu$_{1.8}$S powder is approximately $4 \sim 8 \mu m$. A dense morphology of the samples sintering at CS673 and CS773 is shown in figures 2(b) and (c), respectively. It can be observed that the sample sintering at CS773 is the densest sample of all the sample, this may be due to inadequate sintering of samples below CS773. When the sintering reached the CS773 K, the sample could be fully sintered, and the number of pores increased with increasing SPS temperature. This kind of situation reached an agreement with the volatilization of sulfur, which led to the relative density of 96%, 98%, 95%, 92% (figure 2(f)) for the samples sintering at CS673, CS773, CS873 and CS973 temperature, respectively. Additionally, it is worth noting that the CS873 and CS973 samples possess larger grain sizes and more pores than that of the samples sintering at CS673, CS773, which may be due to the agglomerated grains grow further at higher temperatures and the volatilization of sulfur. From the surface topography, a certain number of pores may facilitate to reduce the thermal conductivity.

To further analyze the microstructure of Cu$_{1.8}$S, the high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) image of the Cu$_{1.8}$S bulk sample sintering at 773 K was presented in figure 3. The HRTEM image displayed that no obvious pores exist in the matrix, agreeing with the high density of the sample, which identifies with the SEM images (figure 2(c)). A measured stripe interval of 0.2581 nm is in accord with the (1 0 13) plane of Cu$_{1.8}$S and the SAED image was indexed to a Cu$_{1.8}$S phase.

### 3.2. Thermoelectric properties

Figure 4(a) exhibits the temperature dependence of electrical conductivity ($\sigma$) for the Cu$_{1.8}$S bulk materials. The electrical conductivity for all samples primatively increased and then decreased with a peak value. The peak can be explained by the phase transition around 361 K, which is also attributed to the dominating phase for Cu$_{1.8}$S from ordered hexagonal phase to disordered cubic phase with the increasing sintering temperature. Meanwhile, with the SPS temperature raising to 973 K, the peak shifted to the higher temperature from $\sim$361 K to $\sim$383 K, manifesting an advance in phase transition temperature. The reasons for the increased phase transition temperature is probably because a great deal of Cu$_{1.96}$S phase was detected at CS873 and CS973 sintering samples, which resulted in their $\sigma$ turn point aren’t consistent with those of all the other samples. This result is due to the volatilization of sulfur in the Cu$_{1.8}$S matrix, corresponding to the XRD. The sample sintering at CS673 acquired the largest $\sigma$ (up to 3451 Scm$^{-1}$) at 361 K, which decreased to 1225 S cm$^{-1}$ with increasing measuring temperature due to the second phase and pores. Due to the emergence of the second phase, the $\sigma$ values of the samples sintering at CS873 and CS973 are much lower than that of other samples. The $\sigma$ values decreased with increasing sintering temperature due to the decrease in both the carrier concentration and mobility caused by the second phase and pores. Electrical conductivity ($\sigma$) consists of the carrier concentration ($n$), charge ($\varepsilon$) and carrier mobility ($\mu$): $\sigma = ne\varepsilon\mu$. The previous studies have proved that increasing Cu$_{1.8}$S sintered temperature normally will lead to the production of Cu$_{1.96}$S. Cu$_{1.8}$S and Cu$_{1.96}$S is both p-type semiconductor with holes as the majority carriers, merely Cu$_{1.96}$S has a lower electrical conductivity compared to Cu$_{1.8}$S due to the fewer Cu vacancies. With the decrease of S content, more electrons were introduced to keep
the matrix charge balance, reducing the carrier concentration of Cu$_{1.8}$S matrix. In terms of pristine Cu$_{1.8}$S, the electrical conductivity of sample synthesized by solid phase method is higher than that of MA, one of the advantages of the solid phase method is to reduce the S volatilization compared to the mechanical energy.
synthesis process, mainly reflecting in the elimination of sulfur volatilization during ball milling. Therefore, the volatilization of sulfur is reason for reducing electrical conductivity.

The temperature dependence of the Seebeck coefficients curves for all the samples is demonstrated in figure 4(b). The positive $\alpha$ values confirm that all the samples are p-type semiconductors. The $\alpha$ value increased from 20 to 98 $\mu$V/K of the bulk sample sintering at CS673. The highest $\alpha$ value (108 $\mu$VK$^{-1}$) was obtained for the Cu$_{1.8}$S bulk sample sintering at CS973. According to the expression: $\alpha \approx \gamma^{-1}n\mu$, in which $\gamma$ is the scattering factor, $n$ the carrier concentration, respectively. The second phase and pores significantly affect the $\alpha$ value by reducing the carrier concentration and enhancing the phonon scattering, which was attributed to the volatilization of sulfur. This is consistent to the upper $\alpha$ obtained by increasing the sintering temperature. It is worth noting that the best performing set of process is twice as high as the mechanical alloy method between

Figure 4. (a) the temperature dependence of the electrical conductivity, (b) the Seebeck coefficient and (c) the power factor for each bulk sample.
300 K and 700 K. One possible reason is that more electrons generated due to the volatilization of sulfur. Another possibility is the second phase in the matrix. This special structure is devoted to contributing to increase the complexity and disorder of system, all these factors would assist to enhance the Seebeck coefficient. This is noteworthy for Cu$_{1.8}$S, because Cu-S composites possess higher electric conductivity and lower Seebeck than most of other thermoelectric materials. The enhancement of Seebeck is significant to improve the power factor, which would provide prospect to improve the thermoelectric properties of Cu-S composites.

According to the aforementioned $\alpha$ and $\sigma$, the power factor ($PF$) can be calculated by using the equation, $PF = \alpha^2 \sigma$, which describes the electrical transport properties of the sample. The temperature dependence of $PF$ is illustrated in figure 4(c). The $PF$ value has an increased trend with increasing measurement temperature since that the Seebeck coefficient dramatically increased. The $PF$ value by solid state method has a slight decrease with increasing sintering temperature from CS673 to CS973 mostly due to the significant reduction in electrical concentration and carrier mobility. Nonetheless, the ideal $PF$ value of TE materials usually demand the balance of $\sigma$ and $\alpha$. Thus a optimal $PF$ value of 1310 $\mu$Wm$^{-1}$K$^{-2}$ for the sample sintering at CS773 was obtained at 773 K, which was 1.16 times higher than that of MA. If the sample sintering at CS773 temperature is also equipped with appropriate thermal conductivity, it is expected to be the ideal process for optimizing the pristine Cu$_{1.8}$S.

The thermal diffusivity values ($D$) at 323 K–773 K test temperature for all bulk samples were presented in figure 5(a). The $D$ values of Cu$_{1.8}$S bulk sample decreased with increasing sintering temperature, which also verifies the hypothesis in scanning electron microscopy. All the curves show that the $D$ primitively increased and then decreased with increasing test temperature. This change accords with the phase transition of Cu$_{1.8}$S from an ordered hexagonal phase to a disordered cubic phase at 361 K. The mean free path of phonons decreases by enhanced complicated microstructure by introducing the second phase, therefore resulting in a decreased $D$ with the increasing sintered temperature.

The dependence of thermal conductivity ($\kappa$) for Cu$_{1.8}$S with different sintering temperature was revealed in figure 5(b). The thermal conductivity can be expressed as: $\kappa = DCpd$, where $D$, $C_p$, $d$ is thermal diffusivity, the heat capacity and the mass density, respectively. Apparently, the $\kappa$ values for the samples undergoes convex type curve with increasing sintering temperature. The $\kappa$ value is 1.93 Wm$^{-1}$K$^{-1}$ at 773 K of a sample sintering at CS673 temperature, which has a higher relative density of 96%. Because of the appearance of both Cu$_{1.8}$, Cu$_{1.96}$S (figure 1) and pores (figure 2), the $\kappa$ of the bulk sample sintering at CS773, CS873 and CS973 gradually decreased. The sample sintering at CS973 presents the lowest thermal conductivity of 1.69 Wm$^{-1}$K$^{-1}$ in four
temperature curves and has a relative density of 91.3%. The low $\kappa$ of Cu$_{1.8}$S may be due to its low electrical conductivity, which leads to low electronic thermal conductivity. The $\kappa$ value generally is the sum of the electronic thermal conductivity ($\kappa_{\text{ele}}$) and the part lattice thermal conductivity ($\kappa_{\text{latt}}$) by the expression: $\kappa = \kappa_{\text{ele}} + \kappa_{\text{latt}}$. Among the rest, the electronic thermal conductivity may be the main reason of the high thermal conductivity for Cu$_{1.8}$S due to its high electrical conductivity, which can be expressed the following equation by the Wiedemann–Franz relation: $\kappa_{\text{ele}} = L \sigma T$ (where $L$ is the Lorenz number), which is proportional to electrical conductivity ($\sigma$). However, this equation may be unsatisfied for Cu$_{1.8}$S supersonic conductors owing to different thermal transport properties between electron/hole carriers and ion carriers.

According to the measured electrical transport ($\sigma$, $\alpha$) and thermal conductivity, the temperature dependence of the calculated ZT values is shown in figure 5(c). Because of the optimized PF and decreased $\kappa$, the ZT values of the Cu$_{1.8}$S samples improved significantly with increasing measurement temperature. Obviously, the sample sintered at CS773 temperature received the maximum power factor among all samples, and benefited from an advisable thermal conductivity, a ZT value of 0.54 was obtained at 773 K, which is much higher than the reported ZT value of 0.45 for the Cu$_{1.8}$S bulk sample in the previous database. The maximum ZT value obtained by exploring different sintering temperatures is conducive to optimizing the thermoelectric properties of Cu$_{1.8}$S materials. In terms of Cu$_{1.8}$S TE performance, despite a high thermal conductivity, it can need to be further enhanced through other heavy atoms doping or tuning the carrier concentration.

The sintering temperature dependence of the average ZT for the Cu$_{1.8}$S bulk samples is observed in figure 5(d). The average ZT of Cu$_{1.8}$S prepared by solid phase method is 0.173, 1.189, 0.192, 0.198 for the samples sintering at CS673, CS773, CS873, CS973, respectively. The solid-state method yields a significantly improved ZT$_{\text{ave}}$ compared to mechanical alloying (0.125). This indicates that the TE properties of Cu$_{1.8}$S composites synthesized by the solid phase method have a better potential for application which makes it a low cost, earth abundant elements and environmentally friendly, is expected to high efficiently convert waste heat in electricity.

4. Conclusion

A p-type superionic conductor Cu$_{1.8}$S materials were fabricated by using solid phase method and SPS technique under different sintering temperatures. The results indicated that the thermoelectric performances of Cu$_{1.8}$S bulk sample were distinctly affected by the sintering temperature due to the volatilization of sulfur. The electrical conductivity decreased with increasing sintering temperature due to the increased Cu$_{1.96}$S second phase. Meanwhile, the Seebeck coefficient increased with increasing sintering temperature by the reduced carrier concentration and the enhanced phonon scattering. A combination of the above two aspects, the highest power factor of 1300 $\mu$W m$^{-1}$K$^{-2}$ at 773 K for the sample sintering at CS773 was obtained. A peak ZT of 0.54 at 773 K was achieved for the Cu$_{1.8}$S bulk sample sintering at 773, which is 20% higher than that of the sample prepared by SPS but using MA-derived powders (0.45 at 773 K).

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