Fabrication of Metal Sulfide Ag$_2$S via Zone Melting Method and Evaluation of Its Thermoelectric Property

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Abstract: Metal sulfide Ag$_2$S is an attractive semiconductor due to its excellent physical and chemical property that enable it with wide applications in fields of catalysis, sensing, optoelectronics in past years. In present work, Ø18 mm x 50 mm Ag$_2$S ingot was successfully prepared using zone melting method and its potential thermoelectric (TE) behavior was investigated. Ag$_2$S has standard monoclinic $P2_1/c$ space group ($\alpha$-Ag$_2$S phase) below 450 K and will transfer to cubic structure ($\beta$-Ag$_2$S phase) over this temperature. Ag$_2$S is a n-type semiconductor as the Seebeck coefficient $S$ is always negative due to the Ag interstitial ions in the material that can provide additional electrons. The $S$ value is about $-1200$ $\mu$V·K$^{-1}$ near room temperature and will decline to $-680$ $\mu$V·K$^{-1}$ at 440 K and finally decreases to $-100$ $\mu$V·K$^{-1}$ at $\beta$-Ag$_2$S state. The electrical conductivity $\sigma$ of $\alpha$-Ag$_2$S is almost zero. However, the value sharply jumps to $40000.5$ S·m$^{-1}$ as the material just changes to $\beta$-Ag$_2$S and then gradually deceases to 33256.2 S·m$^{-1}$ at 650 K. Hall measurement demonstrates the carrier concentration $n_s$ of Ag$_2$S is suddenly increased from the level of $10^{17}$ cm$^{-3}$ to $10^{18}$ cm$^{-3}$ during phase transition. The total thermal conductivity $\kappa$ of $\alpha$-Ag$_2$S is $0.20$ W·m$^{-1}$·K$^{-1}$ and the value is $0.45$ W·m$^{-1}$·K$^{-1}$ to $\beta$-Ag$_2$S. Ultimately, a maximum $ZT$ = 0.57 is achieved around 580 K that means Ag$_2$S might be a promising middle-temperature TE material.

Keywords: Ag$_2$S; zone melting; thermoelectric; phase transition

During the past years, metal sulfide Ag$_2$S has attracted much attention due to its excellent physical and chemical properties that enable it with various applications in fields of catalysis, sensing, optoelectronics and so on$^{[1-6]}$. For example, Dong, et al$^{[7]}$ reports Ag$_2$S-nanowire is an ideal candidate for making nano temperature and photoelectric sensors as its photoconductivity is always positive under 532 nm or 1064 nm laser radiation. Du, et al$^{[8]}$ declares Ag$_2$S Quantum Dots may act as nontoxic carrier for potential in vivo bioimaging. Zhang, et al$^{[9]}$ confirms the Ag$_2$S Quantum Dots indeed open up the possibility of in vivo anatomical imaging and early stage tumor diagnosis owing to their high emission efficiency in NIR-II imaging window. Besides, Ag$_2$S is found also suitable for solar cell and infrared sensitivity device fabrication attribute to its semiconductor character which has a $\sim 1.0$ eV band gap$^{[10]}$. Recently, it is announced Ag$_2$S exhibits a fantastic room-temperature ductile behavior. Its compression deformation can reach 50%, the bending variable surpassing 20%, and the stretching variable up to 4.2%. These shape variables are far more than known ceramic and semiconductor materials, and are equivalent to the mechanical properties of some metals. Consequently, Ag$_2$S provides a possibility of searching for producible inorganic semiconductors/ceramics for flexible electronic devices$^{[11]}$.

In order to develop more interesting functions of Ag$_2$S, the authors focus on its potential thermoelectric (TE) behavior according to the concept of Seebeck-Peltier effect$^{[12]}$. The TE device can supply green and reliable energy by direct conversion of heat into electricity. Thus, it will have wide applications in power generation. The efficiency of a thermoelectric material is usually evaluated by the dimensionless figure of merit $ZT$, $ZT = (S^2T\sigma)/\kappa$. Where $S$ is Seebeck coefficient, $T$ is absolute temperature, $\sigma$ is electrical conductivity and $\kappa$ is thermal conductivity$^{[13]}$. From the view of this formula, it is obvious the TE material with ultra-low thermal conductivity is one of a significant factor for obtaining high $ZT$. Based on this recognition, the TE behavior of

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Ag\textsubscript{2}S is worthy to be studied as it has very small thermal conductivity. Wang, et al\textsuperscript{[14]} have fabricated Ag\textsubscript{2}S ceramic using a solution method and the thermal transport analysis indicates that its total thermal conductivity is only 0.4–0.6 W·m\textsuperscript{-1}·K\textsuperscript{-1} in range of 300-600 K, which is lower than most solid TE materials. Ultimately, a maximum \(ZT = 0.55\) (580 K) is obtained that implies Ag\textsubscript{2}S is a promising middle-temperature TE material. In present work, a zone melting method which has the advantage of purifying materials is introduced for Ag\textsubscript{2}S compound fabrication. Its electrical/thermal transport properties are systematically investigated and the final figure of merit \(ZT\) is demonstrated.

1 Experimental

1.1 Ag\textsubscript{2}S preparation

99.999\% high purity Ag and S elements were used as start materials for Ag\textsubscript{2}S synthesis, they were weighed in accordance with the standard stoichiometric ratio and the total weight was about 60.5 g. The start materials were loaded into a Ø18 mm quartz ampoule and then sealed with a vacuum less than \(10^{-2}\) Pa, after that, the quartz ampoule was placed into a 1000 °C rocking furnace. After Ag and S were totally melted, the rocking system was worked at a rate of 20 r/min for 30 min to enhance Ag\textsubscript{2}S synthesis homogeneity. Ultimately, Ag\textsubscript{2}S compound was obtained as the furnace was cooled to room temperature naturally. Subsequently, the synthesized Ag\textsubscript{2}S raw material with the same ampoule was put into a homemade zone melting furnace. The ampoule was supported by a Al\textsubscript{2}O\textsubscript{3} pedestal and a pair of thermal-couples was installed near the bottom for temperature indication. Fig. 1(a) shows the schematic diagram of the zone melting furnace, it was heated by a couple of Si-Mo heaters to form a narrow high temperature zone. Fig. 1(b) is the temperature profile along vertical direction, the temperature gradient for Ag\textsubscript{2}S solidification was about 30–35 °C/cm. The furnace temperature was controlled at 920 °C. After Ag\textsubscript{2}S raw material was melted, the quartz ampoule was lowered down in the speed of 3.0 mm/h until all the solution was exhausted. The parameters for Ag\textsubscript{2}S solidification were summarized in Table 1.

| Parameters | Zone melting |
|------------|-------------|
| Weight of raw material/g | 60.5 |
| Quartz ampoule size/mm | Ø18 |
| Vacuum of quartz ampoule/Pa | \(<10^{-2}\) |
| Furnace temperature/°C | 920 |
| Temperature gradient/(°C·cm\textsuperscript{-1}) | 30–35 |
| Lowering speed/(mm·h\textsuperscript{-1}) | 3.0 |

Fig. 1 Schematic diagram of the zone melting furnace (a) and temperature profile along vertical direction (b)

1.2 Characterization

The density \(\rho\) was measured by Archimedes principle. Phase structure of the material was analyzed by X-ray diffraction (Bruker D8, Germany) using Cu K\(\alpha\) radiation (\(\lambda = 0.15406\) nm) at room temperature. The morphological and chemical composition were investigated using SEM (JSM-6610, JEOL Ltd.) and EDS (JED-2300T) equipment. The Seebeck coefficient and electrical conductivity were measured simultaneously (ULVAC-RIKO ZEM-3) from 300 K to 650 K. The thermal diffusivity \(D\) was tested by laser flash method (Netzsch, LFA-457, Germany). The total thermal conductivity \(\kappa\) was obtained using \(\kappa = D\cdot\rho\cdot C_p\), where \(C_p\) is specific heat capacity.
2 Results and discussion

The as-grown Ag$_2$S ingot ($\varnothing$18 mm $\times$ 50 mm) is easily separated from quartz ampoule and displays bright metallic luster, as Fig. 2 shows. Such phenomenon indicates Ag$_2$S has none reaction with quartz ampoule during the whole process. Its density is measured to be 7.20 g/cm$^3$ that is nearly 100% close to the theoretical value 7.23 g/cm$^3$. Fig. 3(a) is the XRD pattern of Ag$_2$S powder, it is observed all the diffraction peaks are matched well to that of standard $\alpha$-Ag$_2$S monoclinic P2$_1$/c space group (PDF#14-0072) at room temperature. The lattice parameters $a$, $b$ and $c$ are calculated via a general structure analysis system, and the values are 0.4251, 0.6962 and 0.7873 nm, respectively. EDS measurement implies the atom percent of Ag is 67.2% and S is 32.8% in matrix that agrees well with the standard stoichiometric composition of Ag$_2$S, as Fig. 3(b) shows.

During SEM testing, it is interesting some micro size particles are oozed from the material. Fig. 4(a) shows the original Ag$_2$S surface under 25 kV voltage. However, in a very short time, numerous white particles come up and then gradually grow up for about 30 s, as Fig. 4(b) and Fig. 4(c) demonstrate. Thereafter, the particle sizes are kept stable. EDS analysis reveals the particle composition is 100% Ag. This result is concluded mainly attribute to the special liquid-like character of Ag$_2$S. As previous literature reported, Ag ions are weakly bonded to the neighbour atoms in silver chalcopyrites Ag$_2$M (M= S, Se, Te) semiconductors, and apt to migrate from one site to another if there is sufficient energy force on them. For example, the external heat or voltage are both able to drive Ag ions movement$^{[15]}$. Therefore, it is easy to understand the high energy electron beam in SEM system plays a significant role causing the deposition of Ag. In fact, similar metal element deposition is also noticed in other type of liquid-like materials, such as Cu$_2$Se, Cu$_2$S, Ag$_8$SnSe$_6$ and so on$^{[16-18]}$.

As for thermoelectric property evaluation, sample 1# for electrical transport measurement is cut parallel to Ag$_2$S solidification direction, and sample 2# for thermal transport testing is processed along perpendicular
orientation, as the insert in Fig. 5(a) shows. Here, we should note such sample processing modes are widely adopted in other zone melting thermoelectric materials, such as Bi₂Te₃, SnSe, etc[19-20]. In Fig. 5(a), the relationship of temperature with Seebeck coefficient S is displayed. It is found S is always negative that means Ag₂S is a n-type semiconductor. This conductive behavior might be due to the Ag interstitial ions in crystal structure that act as donor impurities providing additional electrons[14]. Near room temperature, the S value is about ~1200 µV·K⁻¹. As temperature is increased to 440 K, S is linearly deceased to ~680 µV·K⁻¹. However, when temperature is continuously increased to 450 K, S undergoes a sharp decline and the value is around ~100 µV·K⁻¹. This dramatic change is mainly attributed to the phase transition of Ag₂S. Below 450 K, the material has an α-Ag₂S monoclinic structure. Nevertheless, it would transfer to β-Ag₂S body centered cubic structure as temperature surpasses 450 K. After that, S maintains a relative stable state regardless the increasing of temperature to 650 K. Fig. 5(b) shows the dependence of conductivity σ on temperature. It is amazing that the σ of α-Ag₂S is almost zero before 450 K. However, the σ value sharply jumps to ~40000.5 S·m⁻¹ as the material just finishes phase transition. Then, σ is gradually decreased to 33256.2 S·m⁻¹ near 650 K. Fig. 5(c) exhibits power factor PF vs temperature that calculated from PF= S²σ. It is observed that the PF of α-Ag₂S is much poorer because of its weak conductive property. As for β-Ag₂S, PF is practically a constant ~6 µW·cm⁻¹·K⁻² in range of 450–650 K temperature.

Fig. 5 The relationship of Seebeck (a), electrical conductivity σ (b) and power factor PF (c) with temperature

In order to better understand the electrical transport behavior of Ag₂S, the Hall properties are also characterized. Fig. 6(a) shows the temperature dependence of carrier concentration n_H. Near room temperature, the n_H value is on level of ~10¹⁷ cm⁻³. Then, as temperature is increased to the threshold of phase transition, n_H is climbed to ~10¹⁸ cm⁻³. This phenomenon is formed mainly due to the increase of carrier concentration from valence band to conduction band when temperature is added. As expected, when Ag₂S is transformed from monoclinic to body centered cubic structure, n_H is increased suddenly to ~10¹⁹ cm⁻³ near 450 K. Later, a growing number of carriers are generated in β-Ag₂S and n_H is risen to a highest ~10²⁰ cm⁻³ level at 650 K. Fig. 6(b) is the carrier mobility μ_H diagram with temperature. Similar to carrier concentration, μ_H has a dramatic jump during phase transition. Besides, it is noticed μ_H is always declined when it is in α-Ag₂S and β-Ag₂S states, respectively. The maximum μ_H= 161.6 cm²·V⁻¹·s⁻¹ happens at the moment as Ag₂S finishes phase transition.

Fig. 6 Carrier concentration n_H (a) and mobility μ_H (b) vs temperature
As for thermal transport property, the relationship of total thermal conductivity $\kappa$ with temperature is given in Fig. 7. When Ag$_2$S is in monoclinic structure, the $\kappa$ value is 0.20 W·m$^{-1}$·K$^{-1}$ at room temperature and is 0.21 W·m$^{-1}$·K$^{-1}$ near 400 K. Here it is necessary to mention that the thermal conductivity is deduced from the measured thermal diffusion coefficient and then approximately calculated through Dulong-Petit law. Thus, there may be certain errors to the accurate $\kappa$ of the material. However, the result indicates the thermal conductivity of $\alpha$-Ag$_2$S is indeed ultralow and very stable. In $\alpha$-Ag$_2$S, two S atoms and six Ag atoms form weak chemical bonds along (100) plane. Thus, $\alpha$-Ag$_2$S would show low phonon vibration frequency because of the weak binding force of S to Ag$^{[11]}$. As a result, the low-frequency optical branch dominated by Ag atoms can strongly scatter lattice phonons which have similar frequency. This is the key reason why $\alpha$-Ag$_2$S has ultralow thermal conductivity. When $\alpha$-Ag$_2$S turns to $\beta$-Ag$_2$S, $\kappa$ is quickly increased and keeps steady between 450–600 K and the value is $\approx$0.45 W·m$^{-1}$·K$^{-1}$. It should be noted that the sulfur element might has slight volatilization during experiment. However, the effect of possible sulfur loss on thermoelectric properties is negligible, as the Ag$_2$S hardly allows stoichiometric deviation of 2:1 according to the Ag-S phase diagram. Even though there is any sulfur loss is taken place, the excessive Ag would precipitate on the sample surface to maintain Ag$_2$S composition stability.

Ultimately, the temperature dependence of ZT is displayed in Fig. 8. Due to the extremely weak electrical transport property, $\alpha$-Ag$_2$S has very small ZT although its thermal transport is quite low. Nevertheless, the ZT of $\beta$-Ag$_2$S is about 0.35 at 450 K and reaches 0.57 near 600 K. The present maximum ZT is comparable to that of Ag$_2$S fabricated by melting method ($\text{ZT}=0.55, 580 \text{ K})^{[14]}$, and is on the same level compared with other Ag-based materials, such as Ag$_2$Se, Ag$_2$Te, CuAgSe and so on$^{[21–23]}$. This result verifies such metal sulfide Ag$_2$S is a potential low-temperature thermoelectric material. In the future work, Ag$_2$S with element doping is suggested that would do help for thermoelectric property improvement.

3 Conclusions

A Ø18 mm×50 mm Ag$_2$S ingot was fabricated using zone melting method. It undergoes a phase transition from $\alpha$-Ag$_2$S monoclinic P2$_1$/c space group to $\beta$-Ag$_2$S body centered cubic structure near 450 K, which has remark influence on its electrical and thermal properties. Ag$_2$S is a n-type semiconductor as the Seebeck constant $S$ is always negative. The PF of $\alpha$-Ag$_2$S is much poor because of the weak conductive behavior, but the value would suddenly jump to $\approx$6 $\mu$W·cm$^{-1}$·K$^{-2}$ when phase transition is happened. The $\kappa$ of $\alpha$-Ag$_2$S and $\beta$-Ag$_2$S are $\approx$0.20 W·m$^{-1}$·K$^{-1}$ and $\approx$0.45 W·m$^{-1}$·K$^{-1}$, respectively. Finally, Ag$_2$S displays a largest ZT= 0.57 near 580 K that means it might be a potential middle-temperature TE material.

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区熔法制备金属硫化物 Ag₂S 及其热电性能研究

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摘 要: 金属硫化物 Ag₂S 因具有优异的物理化学性能，在催化、传感及光电子等领域具有广阔的应用空间。本工作利用一种区熔技术制备了尺寸为 \( \varnothing 18 \text{ mm} \times 50 \text{ mm} \) 的 Ag₂S，并对其潜在热电性能进行了研究。Ag₂S 在 450 K 温度以下具有标准的 \( \alpha\text{-Ag₂S} \) 单斜 P2_1/c 结构，450 K 以上发生相变成为立方 \( \beta\text{-Ag₂S} \) 相。Ag₂S 在 300-650 K 范围始终具有负的 Seebeck 系数而呈现 \( n \) 型半导体特征，这主要是因为材料中存在 Ag 间隙离子而提供了多余电子。Ag₂S 的 Seebeck 系数在室温下约为 \(-1200 \mu\text{V-K}^{-1} \)，440 K 时降为 \(-680 \mu\text{V-K}^{-1} \)，当转变为 \( \beta\text{-Ag₂S} \) 后则大幅降至 \(-100 \mu\text{V-K}^{-1} \)。\( \alpha\text{-Ag₂S} \) 的电导率几乎为零，然而在发生 \( \beta\text{-Ag₂S} \) 相变时，电导率突然增加至 \( \sim 40000 \text{ S·m}^{-1} \)，而后随着温度持续升高，其值在 650 K 降低为 33256.2 S·m⁻¹。霍尔测试表明 Ag₂S 的载流子浓度 \( n_H \) 在相变时可从 \( \sim 10^{17} \text{ cm}^{-3} \) 剧烈增加到 \( \sim 10^{18} \text{ cm}^{-3} \) 量级。\( \alpha\text{-Ag₂S} \) 和 \( \beta\text{-Ag₂S} \) 的总热导率 \( k \) 几乎是常数，分别为 \(-0.20 \text{ W·m}^{-1}·\text{K}^{-1} \) 和 \(-0.45 \text{ W·m}^{-1}·\text{K}^{-1} \)。最终 Ag₂S 在 580 K 获得最大 ZT 值 0.57，说明它是一种很有发展潜力的材料。
力的中温热电材料。

关键词：Ag$_2$S；区熔；热电；相转变

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