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Quick Fabrication and Thermoelectric Properties of $Cu_{12}Sb_4S_{13}$ Tetrahedrite

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Tetrahedrites, comprised mainly of earth-abundant and environment-friendly elements, copper and sulfur, may pave the way to many new and low-cost thermoelectric energy generation opportunities. However, the preparation of tetrahedrites is time- and energy-consuming. In this paper, we study the melting process and the effect of the annealing time on the microstructure and thermoelectric properties of the $Cu_{12}Sb_4S_{13}$ tetrahedrite, in an effort to shorten the synthesis (melting and annealing) time. Our results show that the $Cu_{12}Sb_4S_{13}$ tetrahedrite phase forms in the melt during cooling. Shortening the melting time does not affect the formation of $Cu_{12}Sb_4S_{13}$. The cooled ingot consists of the principal phase of $Cu_{12}Sb_4S_{13}$ and two secondary phases, Cu_3SbS_4 and $CuSbS_2$. It is found that prolonged annealing cannot eliminate the impurity phases in $Cu_{12}Sb_4S_{13}$ tetrahedrite, has a small effect on the electrical resistivity, and a negligible effect on the Seebeck coefficient and the thermal conductivity of the tetrahedrite. All our samples have a ZT above 0.47 at 600 K and the maximum ZT obtained was 0.52 when the sample was annealed for 1 day. Based on our experimental results, the time for preparing the $Cu_{12}Sb_4S_{13}$ tetrahedrite can be considerably shortened.

Key words: $Cu_{12}Sb_4S_{13}$ tetrahedrite, melting, annealing, microstructure, thermoelectric properties

INTRODUCTION

Thermoelectric (TE) materials with high performance and low cost are currently under intensive study due to their potential large-scale application in industrial waste heat recovery. The performance of TE materials depends on the dimensionless figure of merit, $ZT = \alpha^2 \sigma T/\kappa$, where α is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature and κ is the thermal conductivity. The cost depends on the raw materials and the preparation process.

Tetrahedrites are an earth-abundant natural mineral-based family with the general nominal composition of Cu_{12-x}(Zn, Fe, Ni, Mn, Hg, …)$_x Sb_4 S_{13}$, which have recently been found to display high TE performance.[1,2] The highest ZT values reported for Zn-, Ni-, Ni and Zn-, Fe-, Mn- and Te-doped tetrahedrites are 0.9,[2] 0.7,[3] 1.03,[4] 0.8,[2] 1.13[5] and 0.92,[6] respectively. They also exhibit good mechanical properties[7] and thermal stability.[8] As a result, tetrahedrites may pave the way to many new and low-cost TE energy generation opportunities. However, the preparation process of tetrahedrites is time- and energy-consuming. The melting time is about 3 days and the annealing time is 2 weeks.[2] In this work, we study the melting process and the effect of the annealing time on the microstructure and TE properties of the $Cu_{12}Sb_4S_{13}$ tetrahedrite. Our results show that the $Cu_{12}Sb_4S_{13}$ tetrahedrite with good TE performance can also be obtained by a process with considerably reduced melting and annealing times.

EXPERIMENTAL PROCEDURES

$Cu_{12}Sb_4S_{13}$ tetrahedrite ingots weighing 8 g were prepared by a direct melting method. The starting materials, Cu shots (99.999%; Alfa-Aesar), Sb shot (99.9999%; Alfa-Aesar) and S pieces (99.999%; Alfa-Aesar) were weighed out in stoichiometric ratios and loaded into silica ampoules. The ampoules were evacuated to a pressure of 0.1 Pa and then sealed in a glove box, suspended in a vertical tube furnace. To study the effect of the melting processes, the ampoules were heated to 923 K at the rate of 0.3 K min^{-1}, 5 K min^{-1} and 15 K min^{-1} and held for 12 h, 4 h and 2 h, respectively. The furnace was then switched off, and the ampoules were naturally cooled to room temperature. The resulting ingots were analyzed by scanning electron microscopy (SEM; Zeiss SUPRA 55) and electron energy dispersive spectroscopy (EDS; OXFORD Aztec X-Max80). It was found that the microstructure and phases of the ingots were almost the same, which means that the time of melting could be reduced. So, we employed the fastest melting process, heating at the rate of 15 K min^{-1} to 923 K and holding for 2 h, to prepare the ingots for the annealing experiments.

To study the effect of the annealing time on the microstructure and TE properties of the $Cu_{12}Sb_4S_{13}$ tetrahedrite, the ingots were crushed and ground into powders, and then cold-pressed and placed into silica ampoules which were kept in a box furnace and annealed at 723 K for 1 day, 3 days, 7 days and 14 days, respectively. The annealed pellets were ground into powders, loaded into graphite dies of 15.5 mm in diameter, and then hot-pressed at 723 K under 70 MPa for 30 min. For comparison, a disc was also hot-pressed under the same conditions with the un-annealed powders. The sintered disks were cut for characterization of their TE properties.

The samples were examined by powder x-ray diffraction (XRD; Rigaku Rint 2000, Cu K$_x$). The microstructure and phase composition were also examined by SEM and EDS. The densities were measured using the Archimedean method. The Seebeck coefficient and electrical resistivity were measured using the standard 4-probe method (LINSEIS LSR-3) in helium atmosphere. The thermal conductivity was calculated from the measured thermal diffusivity D, specific heat C_p, and density d according to the relationship $\kappa = DC_p d$. The thermal diffusivity and specific heat of the samples were measured by a laser flash method (LINSEIS LFA 1000) and differential scanning calorimetry (Netzsch DSC-404), respectively. The uncertainties in the electrical conductivity and thermal conductivity were ±5–7%. The uncertainty in the Seebeck coefficient was ±5%.

RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction patterns of the $Cu_{12}Sb_4S_{13}$ tetrahedrite powder samples. The major peaks of the un-annealed sample match the
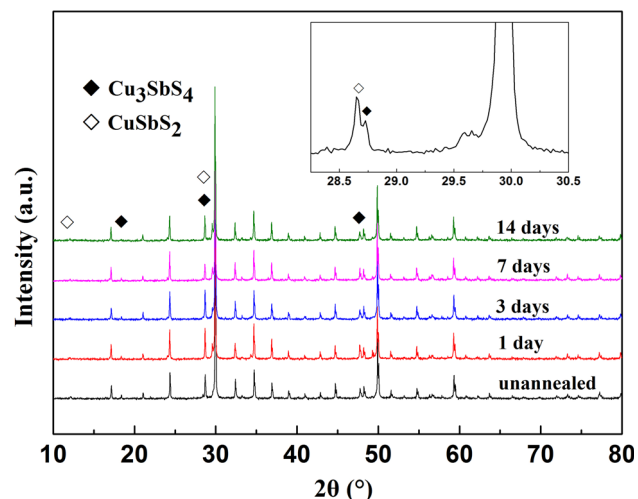

Fig. 1. X-ray diffraction patterns for the $Cu_{12}Sb_4S_{13}$ tetrahedrite powder samples.

$Cu_{12}Sb_4S_{13}$ phase, and a few peaks match the Cu_3SbS_4 and $CuSbS_2$ phases, implying that the $Cu_{12}Sb_4S_{13}$ tetrahedrite phase forms in the melt during cooling, and that the ingots consist of the principal $Cu_{12}Sb_4S_{13}$ tetrahedrite and the secondary Cu_3SbS_4 and $CuSbS_2$. XRD refinement and phase amount calculations were carried out for the samples before and after annealing for 14 days. The amounts of $Cu_{12}Sb_4S_{13}$, Cu_3SbS_4 and $CuSbS_2$ were 86.3%, 7.7% and 6.0% for the un-annealed sample, and 86.8%, 7.7% and 5.5% for the sample annealed for 14 days, respectively. It seems that annealing has a negligible effect on eliminating Cu_3SbS_4 and $CuSbS_2$ impurity phases in the $Cu_{12}Sb_4S_{13}$ tetrahedrite. Suekuni[1] and Chetty[9] observed Cu_3SbS_4 in the synthesized $Cu_{12}Sb_4S_{13}$. Barbier[8] also observed the secondary phases of $Cu_{1.5}Sb_{0.5}S_2$ (about 13%) and Cu_3SbS_4 (about 2%) in the as-synthesized $Cu_{12}Sb_4S_{13}$ tetrahedrite powder, besides the principal phase of $Cu_{12}Sb_4S_{13}$ (about 85%). Lu[2,4,6] obtained single phase tetrahedrite. We compared his preparation process with those of the others, and found that ball milling may play an nonnegligible role in avoiding the secondary phase. In other words, pure $Cu_{12}Sb_4S_{13}$ was difficult to obtain by the melting and annealing method alone.

Figure 2 shows the back-scattering images of the samples sintered with powders before and after annealing for 14 days. It can be seen that the sintered samples consist of a ight gray matrix, while the secondary phases are in dark gray and white. EDS results show that they are $Cu_{12}Sb_4S_{13}$, Cu_3SbS_4 and $CuSbS_2$, respectively, which is consistent with the results of the XRD observations.

Figure 3 gives the temperature dependence of the electrical resistivity for the $Cu_{12}Sb_4S_{13}$ samples sintered with powders before and after annealing. The electrical resistivity of the $Cu_{12}Sb_4S_{13}$ tetrahedrite samples rises with increasing temperature.
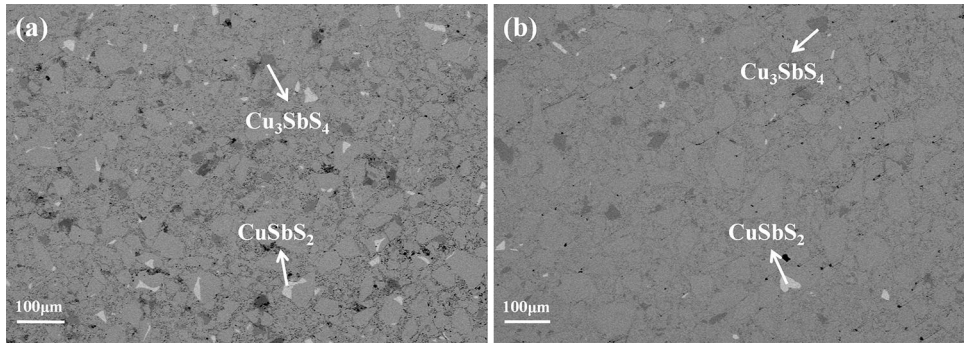
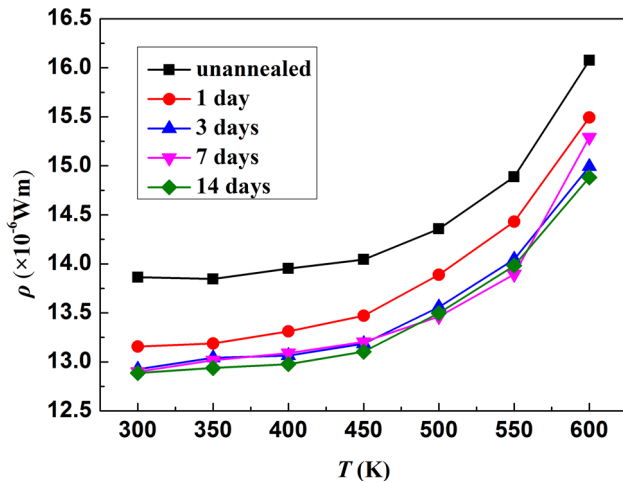Fig. 2. Back-scattering images of the $Cu_{12}Sb_4S_{13}$ tetrahedrite samples sintered with powders before (a) and after (b) annealing for 14 days.

Fig. 3. Temperature dependence of the electrical resistivity for the $Cu_{12}Sb_4S_{13}$ tetrahedrite samples sintered with powders before and after annealing.
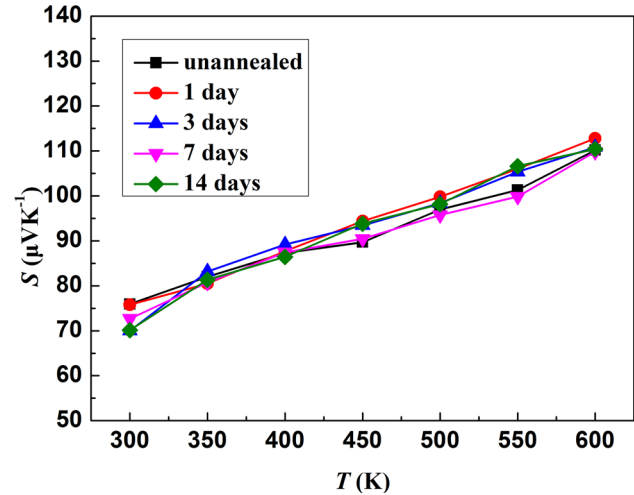

Fig. 4. Temperature dependence of the Seebeck coefficients for the $Cu_{12}Sb_4S_{13}$ tetrahedrite samples sintered with powders before and after annealing.

The trend of the electrical resistivity is in agreement with that of Suekuni[3] and Heo,[5] but inconsistent with that of Lu.[6] The electrical resistivity of the samples decreases with the increase of annealing time. When the annealing time exceeds 3 days, the electrical resistivity remains almost unchanged. Although the electrical resistivity of the samples is different, the difference is small. For the samples annealed for more than 3 days, the electrical resistivity is $12.9–15.3 \times 10^{-6}$ Ohm m in the whole temperature range. For the un-annealed sample and that annealed for 1 day, the electrical resistivity is within $13.9–16.1 \times 10^{-6}$ Ohm m and $13.2–15.5 \times 10^{-6}$ Ohm m, respectively. Our result is between those reported by Suekuni[3] and Lu.[6]

The Seebeck coefficient as a function of temperature for all samples is shown in Fig. 4. The Seebeck coefficient of the $Cu_{12}Sb_4S_{13}$ samples is positive and increases with increasing temperature, indicating that holes are the dominant charge carriers. Although the Seebeck coefficient of the samples is different, the difference is very small and within the measurement error, implying that the annealing time has a negligible influence on the Seebeck

coefficient of the $Cu_{12}Sb_4S_{13}$ tetrahedrite. In the temperature range of 300–600 K, the Seebeck coefficient goes from about 70 to 110 μVK^{-1}, which is in agreement with that reported by Suekuni[3] and Heo.[5]

Figure 5 shows the temperature dependence of the thermal conductivity for the $Cu_{12}Sb_4S_{13}$ samples sintered with powders before and after annealing. The thermal conductivity of the $Cu_{12}Sb_4S_{13}$ samples rises with increasing temperature, and then drops slightly over the temperature range of 450–600 K, a trend agreeing with previous reports.[2–6] This was attributed to a low lattice thermal conductivity resulting from the complex crystal structure and strong lattice anharmonicity and dominant electronic thermal conductivity which increases with temperature according to the Wiedemann–Franz law.[6] For all the samples, the thermal conductivity of the one annealed for 14 days is the highest, 0.88–1.00 $Wm^{-1} K^{-1}$, over the temperature range of 300–600 K, while those of the un-annealed and 1 day-annealed samples are among the lowest, 0.86–0.97 $Wm^{-1} K^{-1}$. The difference in the thermal conductivity is within the
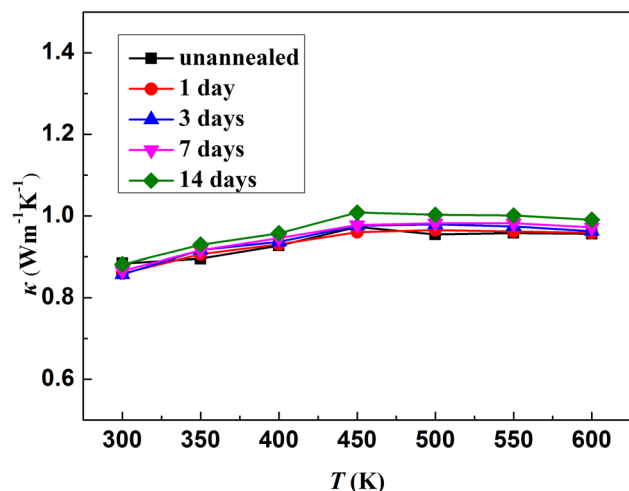
Fig. 5. Temperature dependence of the thermal conductivity for the $Cu_{12}Sb_4S_{13}$ tetrahedrite samples sintered with powders before and after annealing.

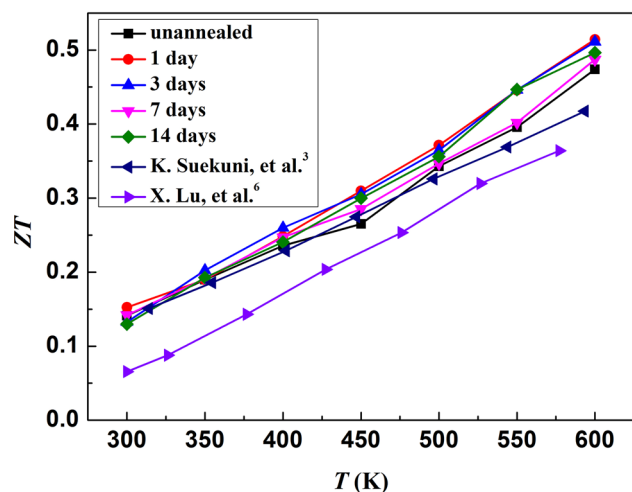Fig. 6. Temperature dependence of the figure of merit for the $Cu_{12}Sb_4S_{13}$ tetrahedrite samples and some representative $Cu_{12}Sb_4S_{13}$ tetrahedrites from the literature.

measurement errors, indicating that the prolonged annealing time has a negligible effect on the thermal conductivity of the $Cu_{12}Sb_4S_{13}$ tetrahedrite. The thermal conductivity of the samples is much lower than that reported by Suekuni[3] and Lu.[6] By calculation, the relative density of the sintered samples is about 91%, which is lower than those reported (over 96%) and the small density may lead to the lowering of the thermal conductivity.

The dimensionless TE figure of merit ZT of our samples is calculated based on the above data and is presented in Fig. 6, together with other representative values of ZT for the $Cu_{12}Sb_4S_{13}$ tetrahedrites. It is clear that all our samples have a ZT above 0.47 at 600 K and that the maximum ZT value is 0.52 for the sample annealed for 1 day, which is higher than those reported by Suekuni[3] and Lu.[6] This means that it is unnecessary to prolong the annealing time (7 days, 14 days) to obtain the $Cu_{12}Sb_4S_{13}$ tetrahedrite with high TE performance. So the time for preparing the $Cu_{12}Sb_4S_{13}$ tetrahedrite can be considerably reduced.

In summary, tetrahedrite was fabricated by a fast melting and annealing method. The $Cu_{12}Sb_4S_{13}$ tetrahedrite phase forms in the melt during cooling. Reducing the melting time does not affect the formation of $Cu_{12}Sb_4S_{13}$. The ingots consist of the principal phase of $Cu_{12}Sb_4S_{13}$ and two secondary phases, Cu_3SbS_4 and $CuSbS_2$. Annealing has a negligible effect on eliminating the Cu_3SbS_4 and $CuSbS_2$ phases in the $Cu_{12}Sb_4S_{13}$ tetrahedrite. Prolonged annealing has a slight effect on the electrical resistivity, and a negligible effect on the Seebeck coefficient and the thermal conductivity of the $Cu_{12}Sb_4S_{13}$ tetrahedrite. All our samples have a ZT above 0.47 at 600 K and the maximum ZT value we obtained in this study is 0.52 for the sample annealed for 1 day. Based on our experimental results, the time for preparing the $Cu_{12}Sb_4S_{13}$ tetrahedrite can be considerably shortened.

ACKNOWLEDGEMENT

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