Chalcostibite Single-Crystal CuSbS₂ as High-Performance Thermoelectric Material

Akira Nagaoka^{1,*}, Manato Takeuchi², Yusuke Shigeeda², Koki Kamimizutaru², Kenji Yoshino² and Kensuke Nishioka¹

¹Research Center for Sustainable Energy & Environmental Engineering, University of Miyazaki, Miyazaki 889-2192, Japan

²Department of Applied Physics and Electronic Engineering, University of Miyazaki, Miyazaki 889-2192, Japan

Chalcostibite CuSbS₂ has attracted attention as an environmentally friendly material in thermoelectric (TE) field. Our investigations into the TE properties of high-quality p-type CuSbS₂ single crystals revealed that they exhibit a uniquely low thermal conductivity caused by the active lone-pair electrons in Sb³⁺ ions. The electrical conductivity was improved by the high density of shallow acceptor Cu vacancies and the absence of potential barriers to carrier transport. Consequently, the figure of merit for the Cu-poor CuSbS₂ single crystal reached 0.5 at 700 K, which is 25 times higher than that of the reported polycrystalline sample. [doi:10.2320/matertrans.E-M2020850]

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1. Introduction

Thermoelectric (TE) devices allow for direct conversion between heat energy and electricity, which augurs well for sustainable energy technologies development. The adoption of such technology provides an opportunity for the easing of rising worldwide energy demands amidst the depletion of traditional fossil fuel sources. Considering the large-scale deployment of TE devices in various areas, ranging from the automobile industry to household heating and cooling, movements on behalf of environmental preservation are required, such as Pb- and Te-free materials.

The performance of TE materials can be evaluated by their dimensionless figure of merit $ZT = \sigma S^2 T / \kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the temperature, and κ is the thermal conductivity.¹⁾ In addition, it is important to note that a high power factor ($PF = \sigma S^2$) is also required for a given TE material to maximize its output power. Therefore, simultaneous optimization of the electrical and thermal transport properties of TE materials is necessary to maximize the conversion efficiency and output power for practical device applications.

The Cu–Sb–S based compounds are expected to be suitable TE materials for cost-effective applications because they are considered earth-abundant and less toxic. The tetrahedrite of Cu_{12–x}M_xSb₄S₁₃ (M = Mn, Fe, Co, Ni, and Zn) compounds exhibits a reasonable ZT value of 0.56–1.13 at 575–723 K.^{2–8)} Similarly, studies on famatinite Cu₃SbS₄ based compounds reported a ZT value of 0.72 at 623 K for Cu₃Sb_{1–x}Sn_xS₄,⁹⁾ 0.67 at 673 K for Cu₃Sb_{1–x–y}Ge_xPyS₄,¹⁰⁾ and 0.63 at 623 K for Cu₃Sb_{1–x}Ge_xS₄.¹¹⁾ Chalcostibite CuSbS₂ is not only a promising material for photovoltaics but also a potential thermoelectric material as shown in Fig. 1(a). The best performing CuSbS₂ based photovoltaic reported an efficiency of 3.2%, which is still below the theoretical limit,¹²⁾ and was fabricated by chemical synthesis using the precursor ink followed by sulfurization. However, the evaluation of TE material properties indicates a low ZT value of 0.02 around 550 K¹³⁾ for polycrystalline CuSbS₂ grown by the hot press method. Despite the current ZT value

Fig. 1 (a) Chalcostibite structure of CuSbS₂ and (b) Sb–S trigonal pyramidal arrangement coordination where lone-pair forms from Sb 5s electrons.

of Cu–Sb–S based compounds being lower than that of 2 and above recorded for state-of-the-art TE materials,¹⁴⁾ the attraction toward tetrahedrite and chalcostibite^{2–11,13)} materials is due to their intrinsically low thermal conductivity. The Sb atoms in famatinite are tetrahedrally coordinated with four S atoms by sp³ hybridisation.^{9–11)} No non-bonded Sb 5s² orbital lone-pair electrons exist in famatinite, which results in a relatively higher lattice thermal conductivity than other Cu–Sb–S based compounds having spare Sb 5s² electrons, as shown in Fig. 1(b).

We focused on a chalcostibite CuSbS₂ single crystal as an environmentally friendly TE material because of its stable orthorhombic structure until reaching the melting point, as well its characteristically low thermal conductivity <1.0 W/mK.¹⁵⁾ We have reported that the CuSbS₂ single crystals were grown using the zone-melting method at 600°C, and its TE properties were measured at room temperature. Without a grain-boundary barrier, single crystal samples exhibit potential for better electrical performance. The impediment to using CuSbS₂ as TE material, which was its low electrical conductivity of less than 1 S/cm near room temperature until 550 K¹³⁾ can thus be removed. However, further research is required to improve the understanding of its TE properties. Meanwhile, the physical properties extracted from a single crystal can be used as a reference

*Corresponding author, E-mail: nagaoka.akira.m0@cc.miyazaki-u.ac.jp

to quantitatively discuss TE properties. For example, the anisotropy of thermal conductivity, the effect of grain boundary or intrinsic point defects on thermal conductivity and the effects of extrinsic doping on electrical properties.

In this study, we highlight the potential of directly using chalcostibite CuSbS_2 single crystal as a high-temperature TE material. There is a possibility that CuSbS_2 single crystals could maintain both high electrical conductivity without adding a potential barrier to carrier transport, such as grain boundaries and low intrinsic thermal conductivity while remaining environmentally friendly. Our results improve the application profile of Cu–Sb–S-based TE compounds.

2. Experimental Procedure

We fabricated different compositional feed polycrystalline including a stoichiometric CuSbS_2 , and Cu-poor $\text{Cu}_{0.95}\text{SbS}_2$ from high purity starting materials ($>99.999\%$). CuSbS_2 single crystals were grown from its feed polycrystalline by the zone melting method at a growth temperature of 600°C , the temperature gradient of $40^\circ\text{C}/\text{cm}$, and growth speed of $4\text{ mm}/\text{day}$ as previously reported.¹⁵⁾ The grown crystals were cut with a diamond blade, polished mechanically with a $0.01\text{ }\mu\text{m}$ Al_2O_3 paste, and then etched with a 5% $\text{Br}_2/\text{Methanol}$ solution for 5 min. TE measurements were carried out along the c -axis because the sample size in other directions was too small for measurements.

The structural properties were measured by a combination of X-ray diffraction methods (XRD; X'Pert PRO, Panalytical) after grinding the bulk crystals and Raman spectroscopy (T64000, HORIBA). The tube voltage, tube current, and step width were 40 kV , 40 mA , and 0.01° , respectively, using a Cu- $K\alpha$ radiation source for XRD. Raman spectroscopy was performed with a 514 nm Ar^+ laser, focusing on the sample with an objective lens of 0.55 numerical aperture. The laser power directed at the sample was 100 mW . The spectra were calibrated based on the position of the Si peak at 520 cm^{-1} . The average composition of the samples was analyzed using scanning electron microscopy (SEM, S-5500 Hitachi) and energy-dispersive X-ray spectroscopy (EDS). The orientation mapping was carried out by electron backscatter diffraction (EBSD; FEI Quanta 600 SEM). The samples were polished

and imaged at 30 kV using an SEM probe and that used an off-axis backscatter detector.

The electrical conductivity σ and Seebeck coefficient S were measured simultaneously in a helium atmosphere at $300\text{--}700\text{ K}$ using a commercial system (ZEM3; ADVANCE RIKO) on the samples with approximate dimensions of $2\text{ mm} \times 2\text{ mm} \times 10\text{ mm}$. The thermal conductivity κ was calculated based on the equation $\kappa = \lambda C_p D$, where λ is the thermal diffusivity, C_p is the specific heat capacity, and D is the density. The thermal diffusivity was measured by the laser flash method (LFA457; Netzsch) on the rectangular samples with $8\text{ mm} \times 8\text{ mm} \times 1\text{ mm}$ coated with a thin layer of graphite to minimize errors from the emissivity of the material. The specific heat capacity was measured by differential scanning calorimetry (DSC; Rigaku Thermo plus EVO2 DSCvesta) on the samples with $3\text{ mm} \times 3\text{ mm} \times 3\text{ mm}$. The density value was measured using the Archimedes method at room temperature.

The hole concentration was obtained by Hall effect measurement (ResiTest8300; TOYO Corporation), operated in a 0.45 T magnetic field in the van der Pauw geometry at room temperature. For electrical measurements, Au contacts, each with a diameter of 1 mm and thickness of approximately 200 nm , were evaporated onto the corners of the sample.

3. Results and Discussions

3.1 Structural properties

The stoichiometric CuSbS_2 single-crystal ingot is shown in Fig. 2(a). Its dimensions are 10 mm in diameter and 30 mm in length. For the electrical and TE measurements, CuSbS_2 single crystals were cut perpendicular to growth direction ($=c$ -axis), which the (004) reflect plane can be observed by XRD in Fig. 2(b). To identify the orientation associated with sample, we performed SEM based EBSD imaging with optical image shown in Fig. 3. The $[001]$ crystallographic orientation can be observed in both stoichiometric and Cu-poor samples without grain-boundaries on the millimeter scale.

The powder XRD patterns for different compositional single-crystal and the stoichiometric polycrystalline samples of CuSbS_2 are shown in Fig. 4. The feed polycrystalline

Fig. 2 (a) Picture of stoichiometric CuSbS_2 single crystal ingot grown by zone melting method and (b) XRD of the cutting plane perpendicular to growth direction ($=c$ -axis). Inset pictures: how crystals were cut for directional measurements.

Fig. 3 EBSD and optical images of stoichiometric and Cu-poor CuSbS₂ single crystals on the millimeter scale. The coloring indicates the crystallographic orientation.

Fig. 4 Powder XRD patterns of different compositional CuSbS₂ single crystals and stoichiometric feed polycrystalline samples.

sample contains major peaks of the secondary phase for Sb₂S₃ at approximately 25.0° and 29.3°. After zone melting growth, the CuSbS₂ single crystals exhibit major peaks corresponding to the diffraction lines of the orthorhombic chalcostibite structure of CuSbS₂ (ICDD #01-088-0822) without any impurities or secondary phases.

Raman spectroscopy was used as a complementary tool for phase analysis because the XRD peaks of CuSbS₂ overlap with the secondary phases, most notably Sb₂S₃. The Raman spectrum from the CuSbS₂ single crystals exhibited peaks at 138, 248, and 332 cm⁻¹, corresponding to the reported values shown in Fig. 5.¹⁶ The strongest peak that was observed at 332 cm⁻¹ was attributed to A_g symmetry, which is the Raman active mode.¹⁷ The insets in Fig. 5 show the optical image in which the secondary phase can be observed in the feed polycrystal. The peak observed at 202 cm⁻¹ was attributed to the Sb₂S₃ secondary phase.¹⁸ High-purity CuSbS₂ single crystals can be obtained by zone melting growth.

3.2 Compositional properties

In this study, we fabricated samples with different

Fig. 5 Raman spectra of different compositional CuSbS₂ single crystal and stoichiometric feed polycrystalline samples. Insets are optical image.

Table 1 The composition of each single crystal sample determined by EDS.

	Cu (at%)	Sb (at%)	S (at%)
Cu-poor	24.0	25.7	50.3
Stoichiometric	25.1	24.8	50.1

compositions, including a stoichiometric composition and Cu-poor composition, as shown in Table 1. Both samples were CuSbS₂ single-phase by XRD and Raman measurements. The sign of the Seebeck coefficient S is always positive for samples, as expected for these p-type materials. From first-principle calculations, the Cu on Sb antisite defect (Cu_{Sb}) and the Cu vacancy (V_{Cu}) are the dominant acceptors with low formation energy in CuSbS₂, which leads to p-type conductivity.¹⁹ The V_{Cu} is a shallow acceptor in CuSbS₂, which is similar to the situation in other Cu-based sulfide or selenide compounds such as CuInSe₂ and Cu₂ZnSnS₄.²⁰ One impediment of stoichiometric CuSbS₂ for TE material deployment its low conductivity of <1 S/cm,¹³ and thus, the Cu-poor composition has the potential for improvement of conductivity.

3.3 Electrical and TE properties

The temperature-dependent electrical conductivity of CuSbS₂ single crystals from 300 K to 700 K is shown in Fig. 6. As expected, the electrical conductivity with a Cu-poor composition increased, which is about one order of magnitude greater than the stoichiometric value shown in Fig. 6. The conductivity data can be described quantitatively as band conduction from the valence band to the defect level $\sigma(T) = \sigma_B \exp(-\frac{E_A}{k_b T})$, where σ_B is the pre-factor, E_A is the relevant activation energy, and k_b is the Boltzmann constant. Theoretical calculations predict that the dominant shallow V_{Cu} acceptor level under Cu-poor conditions is at 30 meV above the valence band maximum.¹⁹ Cu on Sb antisite defect (Cu_{Sb}) becomes the dominant deep acceptor level at 250 meV

Fig. 6 Temperature dependence of electrical conductivity fitted by $\sigma(T) = \sigma_B \exp(-E_A/k_B T)$ for different compositional CuSbS_2 single crystals.

under near-stoichiometric and Cu-rich compositions. The E_A value of 65 meV in Cu-poor composition is lower than that of 155 meV in stoichiometric composition, which leads to higher electrical conductivity values because of the increasing concentration of V_{Cu} acceptor. In addition, the hole concentration of $8.9 \times 10^{17} \text{ cm}^{-3}$ for the Cu-poor sample is higher than that of $4.5 \times 10^{16} \text{ cm}^{-3}$ for the stoichiometric sample. High hole mobility of $53.7 \text{ cm}^2/\text{Vs}$

for Cu-poor sample is larger than that of reported thin film samples.^{16,19)}

The values of S start increasing slightly with an increase in temperature because more holes are thermally activated to high-energy states, which leads to a higher average entropy of holes in Fig. 7(a). The high S values range from 350 to 460 $\mu\text{V/K}$ throughout the measured temperature, which is in good agreement with literature¹³⁾ and can be expected from the bandgap value of 1.4 eV.^{19,21)} The temperature dependence of PF is shown in Fig. 7(b). The PF value of the Cu-poor sample at 700 K is $486 \mu\text{W/mK}^2$, which is higher than that of the selenide compound CuSbSe_2 polycrystalline sample.²²⁾

The temperature dependence of thermal conductivity, κ , is shown in Fig. 7(c), where the sample density D is 4.85–4.91 g/cm^3 at room temperature and the specific heat capacity C_p is 0.41–0.49 J/gK at the measured temperature. The values of κ decreased with increasing temperature, which indicates that phonon conductivity dominates for both samples. Even though these are single crystals that do not benefit from lattice thermal conductivity reduction due to grain boundary scattering, the value of κ is low $< 1.0 \text{ W/mK}$ at the measured temperature. Such low values are only moderately higher than the reported values of related polycrystalline CuSbS_2 , which is 0.4 W/mK around 600 K.¹³⁾ The ability to achieve such low thermal conductivity due to the stereochemically active lone-pair electrons in Sb^{3+} ions. This results in anharmonicity in

Fig. 7 Temperature dependence of (a) Seebeck coefficient, (b) power factor, (c) Thermal conductivity and (d) Figure of merit ZT for different compositional CuSbS_2 single crystals.

the lattice because of the electrostatic repulsion between the lone-pair electrons and the neighboring chalcogen ions.^{13,22,23)}

Taken together, the high electrical properties of Cu-poor CuSbS₂ single crystals with relatively low thermal conductivity demonstrated a TE figure of merit $ZT = 0.5$ at 700 K (Fig. 7(d)). From the existing literature consulted,¹³⁾ the reported ZT value of the CuSbS₂ polycrystalline sample is approximately 0.02 around 550 K. The CuSbS₂ single-crystal demonstrates a ZT value 25-times that of the reported polycrystalline sample, and 7-times that of our stoichiometric sample. Our results imply that CuSbS₂ can compete with related environmentally friendly TE compounds such as tetrahedrite and famatinite.

4. Conclusion

High-quality single crystals of chalcostibite CuSbS₂ offer the possibility of environmentally friendly p-type TE materials at medium temperature. We investigated the TE properties of CuSbS₂ single crystals and found two advantages: high electrical conductivity because of the lack of potential barriers to carrier transport and low thermal conductivity by lone-pair electrons. This study has the following highlights: (1) the Cu-poor sample was better at improving conductivity than the stoichiometric sample due to its high density of the shallow acceptor V_{Cu}; (2) intrinsic low thermal conductivity <1 W/mK by enharmonic scattering could be observed without a traditional phonon scattering strategy such as grain boundaries, and (3) we obtained a high ZT of 0.5 for the Cu-poor sample at 700 K, which increases by a factor of 7 compared to the stoichiometric sample. These results demonstrate that CuSbS₂ is competitive with related high- ZT materials such as tetrahedrite and famatinite. To improve the ZT value, we will seek to increase the conductivity by optimizing intrinsic or extrinsic doping.

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