Preparation and Thermoelectric Properties of Chevrel-Phase $\text{Cu}_x\text{Mo}_6\text{S}_8$ ($2.0 \leq x \leq 4.0$)

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Chevrel-phase sulfides $\text{Cu}_x\text{Mo}_6\text{S}_8$, where $2.0 \leq x \leq 4.0$, were prepared by reacting appropriate amounts of Cu, Mo, and MoS_2 powders at 1273–1523 K for 8 h in vacuum. The samples were then densified by pressure-assisted sintering at 1223–1473 K for 1 h at a pressure of 30 MPa in vacuum. The density of all the sintered samples was greater than 95% of the theoretical density. X-ray analysis showed that all the sintered samples consisted entirely of the hexagonal Chevrel phase. The value of the lattice parameters a and c increased with the Cu content. Measurement of the Seebeck coefficient, electrical resistivity, and thermal conductivity was carried out on single-phase sintered $\text{Cu}_x\text{Mo}_6\text{S}_8$ samples in the temperature range of 300–950 K. All the sintered samples had a positive Seebeck coefficient. Further, the thermoelectric properties improved when the Cu content was increased. With an increase in the Cu content, the Seebeck coefficient and electrical resistivity increased, while the thermal conductivity decreased. The highest dimensionless thermoelectric figure of merit ZT (0.4) was observed in $\text{Cu}_{4.0}\text{Mo}_6\text{S}_8$ at 950 K. [doi:10.2320/matertrans.MAW200918]

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1. Introduction

Thermoelectric devices can directly convert waste heat into electrical energy, and hence, they are expected to play an important role in establishing a sustainable society. For efficient conversion of waste heat to electrical energy, it is important to develop thermoelectric materials with high conversion efficiency. The efficiency of a thermoelectric material is determined by its thermoelectric figure of merit (ZT), which is a dimensionless parameter. ZT is given by $S^2T/\rho\kappa$, where S , T , ρ , and κ are the Seebeck coefficient, temperature, electrical resistivity, and thermal conductivity, respectively. For the metals or degenerate semiconductors, the magnitude of Seebeck coefficient is inversely proportional to the carrier concentration, and proportional to temperature, and effective mass of the carrier. The electrical resistivity is related to carrier concentration through $1/\rho = ne\mu$, where n , e , and μ are the carrier concentration, charge of an electron, and carrier mobility, respectively. The thermal conductivity is the sum of the electronic contribution κ_e and the lattice contribution κ_l , i.e., $\kappa = \kappa_e + \kappa_l$. Moreover, the electronic contribution is directly related to the electrical resistivity through the Wiedemann-Franz law, $\kappa_e = LT/\rho$, where L is the Lorenz number ($2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$).

Ternary molybdenum chalcogenides with the general formula $\text{M}_x\text{Mo}_6\text{X}_8$ ($\text{M} = \text{Li}, \text{Ti}, \text{Cr}, \text{Fe}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Cd}, \text{Sn}, \text{Pd}, \text{rare-earth metals, etc.}; \text{X} = \text{S}, \text{Se}, \text{Te}$) were first synthesized by Chevrel *et al.*,¹⁾ and therefore, they are referred to as Chevrel phases. Several reviews on the crystal structure and superconductivity of Chevrel phases have been published.^{2,3)} The host structure of a Chevrel phase consists of a stacking of Mo_6X_8 clusters. The M atoms fill the space between the Mo_6X_8 clusters. While large M atoms such as Pb result in the formation of stoichiometric compounds, small M atoms such as Cu afford nonstoichiometric com-

pounds. For example, it is well-known that the Cu content in $\text{Cu}_x\text{Mo}_6\text{S}_8$, which has a hexagonal (rhombohedral) structure (space group: $R\bar{3}$), is in the range of $1.0 \leq x \leq 4.0$.^{4–9)}

Recently, Chevrel phases have attracted considerable attention since they are potential high- ZT thermoelectric materials.^{10–26)} Most of the previous studies on Chevrel phases have focused on Chevrel-phase selenides. Band structure calculations have been carried out for several Chevrel-phase selenides for predicting their thermoelectric properties.^{11,13,14,17,24)} The results suggest that CrMo_6Se_8 , FeMo_6Se_8 , NiMo_6Se_8 , $\text{Cu}_2\text{Mo}_6\text{Se}_8$, and SnMo_6Se_8 exhibit metallic behavior, while TiMo_6Se_8 , $\text{Zn}_2\text{Mo}_6\text{Se}_8$, and $\text{Cd}_2\text{Mo}_6\text{Se}_8$ behave like semiconductors.^{11,13,14,17)} Moreover, the results imply that the Fermi level of $\text{TiMo}_6\text{Se}_{8-y}$ shifts to the valence band edge when the Se content decreases.²⁴⁾ Therefore, the thermoelectric properties of Chevrel phases would be improved by altering their chemical compositions. However, the effect of M content on the thermoelectric properties of $\text{M}_x\text{Mo}_6\text{Se}_8$ has not yet been investigated in detail.

Caillat *et al.*¹⁶⁾ measured the Seebeck coefficient, electrical resistivity, and thermal conductivity of $\text{M}_x\text{Mo}_6\text{Se}_8$ ($\text{M} = \text{Cu}, \text{Fe}, \text{Ti}$) and found that ZT of $\text{Cu}_{1.38}\text{Fe}_{0.66}\text{Mo}_6\text{Se}_8$ is 0.6 at 1150 K. Since Chevrel-phase chalcogenides have similarity in the electrical and thermal properties, the Cu-filled Chevrel-phase sulfides are also expected to have excellent high-temperature thermoelectric properties.

Tsubota *et al.*¹⁵⁾ have investigated the thermoelectric properties of Chevrel-phase sulfides $\text{M}_x\text{Mo}_6\text{S}_8$ ($\text{M} = \text{Fe}, \text{Ni}, \text{Ag}, \text{Zn}, \text{Sn}, \text{Pb}, \text{Cu}$). However, X-ray analysis shows that all the aforementioned sulfides contain a large amount of impurity MoS_2 phase. The ZT of all the aforementioned sulfides is less than 0.1. In order to confirm whether Chevrel-phase sulfides can be used as thermoelectric materials, it is necessary to investigate the thermoelectric properties of single-phase samples.

The purpose of this study was to prepare single-phase $\text{Cu}_x\text{Mo}_6\text{S}_8$ samples and study the effect of Cu content on their thermoelectric properties so as to confirm the feasibility of using Chevrel-phase sulfides as thermoelectric materials. The samples were prepared by reacting appropriate amounts of Cu, Mo, and MoS_2 powders at 1273–1523 K and subjecting the resulting product to pressure-assisted sintering. The Seebeck coefficient, electrical resistivity, and thermal conductivity of the sintered samples were measured over the temperature range of 300–950 K.

2. Experimental

The preparation method used in this study is almost the same as that developed by Kondo *et al.*²⁷⁾ Commercial Cu powder (purity: 99.99%; particle size: 1 μm ; Kojundo Chemical Laboratory Co., Ltd., Japan), Mo powder (purity: 99.9%; particle size: 1.5 μm ; Kojundo Chemical Laboratory Co., Ltd., Japan), and MoS_2 powder (purity: 99.9%; Kojundo Chemical Laboratory Co., Ltd., Japan) were used as the starting materials. Appropriate amounts of these powders were mixed well and placed in boron nitride crucibles. The crucibles were then inserted in an alumina tube, and the tube was evacuated to 7.0×10^{-3} Pa. The samples were heated to 1273–1523 K at a rate of 5 K/min and maintained at this temperature range for 8 h. The samples were then gradually cooled to room temperature.

The samples were consolidated by pressure-assisted sintering for the fabrication of dense compacts. The powders prepared as mentioned above were placed into graphite dies. The dies were set in a pulsed electric current sintering apparatus (SPS-515S, SPS Syntex Inc., Japan). The chamber of the apparatus was then evacuated to 7.0×10^{-3} Pa. Sintering was carried out at 1223–1473 K for 1 h at a pressure of 30 MPa. The heating and cooling rates were 10 K/min and 20 K/min, respectively.

The crystal phase in the sintered samples was studied by powder X-ray diffractometry (XRD) using Cu $K\alpha$ radiation (Rint-Ultima+, Rigaku Co., Japan). The density of each sintered sample was measured using the Archimedes method (AUX120-SMK401, Shimadzu Co., Japan). The microstructure of the fractured surfaces and the polished and corroded surfaces was observed under a scanning electron microscope (SEM; JSM-6301F, JEOL Ltd., Japan) at 20 kV accelerating voltage.

The Seebeck voltage and electrical resistivity of the sintered samples were measured simultaneously (ZEM-3, ULVAC-RIKO, Inc., Japan). The measurements were carried out under a helium atmosphere to prevent the oxidation. Moreover, the high-accuracy measurements are feasible in high temperature since helium gas has a high thermal conductivity. The samples were cut into plates of 12 mm length, 4 mm width, and 2 mm thickness by using a diamond cutter (IsoMet Low Speed Saw, Buehler Ltd., USA) for the Seebeck voltage and electrical resistivity measurements. The Seebeck coefficient is given by $V/\Delta T$, where V and ΔT are the Seebeck voltage and temperature difference, respectively. Therefore, the Seebeck coefficient was determined from the slope of the plot of Seebeck voltage versus temperature difference. In this study, the temperature difference between

the ends of each plate was varied from 0 to 10 K. A four-probe technique was used to measure the electrical resistivity. Further, the sample disks of 10 mm diameter and 2 mm thickness were fabricated for the thermal conductivity measurements. The thermal conductivity was measured in vacuum using a laser-flash method (TC-7000, ULVAC-RIKO, Inc., Japan); in this method, the thermal conductivity was calculated from the density, heat capacity, and thermal diffusivity.

3. Results and Discussion

Figure 1 shows the XRD patterns of the sintered $\text{Cu}_x\text{Mo}_6\text{S}_8$ samples. These XRD patterns are in good agreement with those previously published,⁹⁾ thereby showing that all the prepared samples consist entirely of single-phase $\text{Cu}_x\text{Mo}_6\text{S}_8$. No impurity phases are formed in any of the samples. The change in the Cu content results in the changes in the atomic positional parameters, and hence the changes in the XRD peak intensities and positions. As shown in Fig. 2, the value of the hexagonal lattice parameters a and c increases with the Cu content. The values of a and c also agree well with those reported.^{4–9)}

The density of all the sintered samples is found to be greater than 95% of the theoretical density. As shown in Fig. 3, SEM examination of the fractured surfaces reveals

Fig. 1 XRD patterns of the sintered $\text{Cu}_x\text{Mo}_6\text{S}_8$ samples.

Fig. 2 Plot of lattice parameters a and c versus Cu content for $\text{Cu}_x\text{Mo}_6\text{S}_8$.

Fig. 3 SEM micrographs of the fractured surface of (a) $\text{Cu}_{2.0}\text{Mo}_6\text{S}_8$ and (b) $\text{Cu}_{4.0}\text{Mo}_6\text{S}_8$. Fig. 4 Temperature dependence of the Seebeck coefficient for $\text{Cu}_x\text{Mo}_6\text{S}_8$. Fig. 5 Temperature dependence of the electrical resistivity for $\text{Cu}_x\text{Mo}_6\text{S}_8$.

that the samples have a dense structure, which is consistent with the results of density measurements. The fracture surface of Chevrel-phase sulfides has been conventionally used for the grain size measurement.^{28,29)} From Fig. 3, the grain size of the sintered samples is estimated to be of the order of micrometers. Similarly, in polished and corroded surfaces, the grain size is estimated to be of the order of micrometers. Since the grain size is much larger than the mean free path of electron and phonon, the grain boundaries have no effect on the thermoelectric properties.

Since the sintered samples consist of single-phase $\text{Cu}_x\text{Mo}_6\text{S}_8$ and have nearly full density, they can be used for investigating the thermoelectric properties of Chevrel-phase sulfides. The temperature dependence of the Seebeck coefficient and electrical resistivity are shown in Figs. 4 and 5, respectively. All the samples have a positive Seebeck coefficient, indicating that the dominant carriers are holes. Moreover, the Seebeck coefficient and electrical resistivity show metallic temperature dependence, i.e., they increase linearly with temperature. It is worth mentioning that the chemical composition of the samples has a remarkable effect on the Seebeck coefficient and electrical resistivity—an increase in the Cu content results in increases in both the Seebeck coefficient and electrical resistivity. These increases in the Seebeck coefficient and electrical resistivity are mainly

due to a decrease in the carrier concentration. The electrical properties of the Chevrel phase can be explained in terms of the cluster-valence-electron count (cluster-VEC).^{2,12)} The cluster-VEC of $\text{M}_x\text{Mo}_6\text{S}_8$ is calculated as follows: the number of electrons required to fill the octets of the S atoms is subtracted from the sum of the number of valence electrons of the M and Mo atoms; the resulting value is then divided by the number of Mo atoms.²⁾ In the case of $\text{Cu}_x\text{Mo}_6\text{S}_8$, the increase in the Cu content results in an increase in the cluster-VEC and a resultant decrease in the carrier concentration.

As shown in Fig. 6, the thermal conductivity of $\text{Cu}_x\text{Mo}_6\text{S}_8$ is relatively low, ranging from 1.3 to $3.9 \text{ W K}^{-1}\text{m}^{-1}$, and increases with temperature. Since the electrical resistivity increases with the Cu content, the electronic contribution decreases with an increase in the Cu content. On the other hand, the lattice contribution remains essentially unchanged when the Cu content is increased and ranges from 0.9 to $1.1 \text{ W K}^{-1}\text{m}^{-1}$ at 950 K.

Figure 7 shows the temperature dependence of the thermal conductivity, electronic contribution, and lattice contribution for $\text{Cu}_{4.0}\text{Mo}_6\text{S}_8$. The electronic contribution is higher than the lattice contribution over the entire temperature range considered in this study. The lattice contribution of $\text{Cu}_{4.0}\text{Mo}_6\text{S}_8$ is very low and increases with temperature. This low value of the lattice contribution is most probably

Fig. 6 Temperature dependence of the thermal conductivity for $\text{Cu}_x\text{Mo}_6\text{S}_8$.

Fig. 7 Temperature dependence of the thermal conductivity, electronic contribution, and lattice contribution for $\text{Cu}_{4.0}\text{Mo}_6\text{S}_8$.

due to phonon scattering by the Cu vacancies. There are twelve Cu sites in each Mo_6S_8 cluster in $\text{Cu}_x\text{Mo}_6\text{S}_8$.³⁰⁾ However, the upper occupancy limit has been experimentally found to correspond $x = 4.0$.⁴⁻⁹⁾ Therefore, there are numerous vacancies at the Cu sites. These vacancies are most likely to cause disorder at the Cu sites and thus reduce the lattice contribution.

The ZT values calculated from the measured values of the Seebeck coefficient, electrical resistivity, and thermal conductivity are shown in Fig. 8. From the figure, it is evident that the ZT value of all the samples increases with temperature. It is also to be noted that the ZT value shows a significant increase with the Cu content. The highest value of ZT (0.4) is observed for $\text{Cu}_{4.0}\text{Mo}_6\text{S}_8$ at 950 K. This observation indicates that similar to Chevrel-phase selenides, Chevrel-phase sulfides too are potential candidates for high-temperature thermoelectric devices.

The ZT value of $\text{Cu}_x\text{Mo}_6\text{S}_8$ is expected to improve further if the Cu content is increased. However, since the non-stoichiometric range of Cu is $1.0 \leq x \leq 4.0$,⁴⁻⁹⁾ it is necessary to increase the cluster-VEC with substituting Cu by other metals in our future research so as to improve the ZT value.

Fig. 8 Temperature dependence of the figure of merit ZT for $\text{Cu}_x\text{Mo}_6\text{S}_8$.

4. Summary

Single-phase $\text{Cu}_x\text{Mo}_6\text{S}_8$ sintered samples with $2.0 \leq x \leq 4.0$ have been prepared by reacting appropriate amounts of Cu, Mo, and MoS_2 powders and by subjecting the resultant product to pressure-assisted sintering. The sintered samples have nearly full density. Over the temperature range of 300–950 K, the sintered samples have a positive value of the Seebeck coefficient and exhibit metallic behavior. With an increase in the Cu content, the Seebeck coefficient and electrical resistivity increase, while the thermal conductivity decreases. As a result, the ZT value increases with the Cu content. The highest ZT (0.4) is observed for $\text{Cu}_{4.0}\text{Mo}_6\text{S}_8$ at 950 K. On the basis of these observations, it is concluded that Chevrel-phase sulfides are suitable candidate materials for high-temperature thermoelectric devices.

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