

Preparation of Single-Phase Pb-Filled Chevrel-Phase Sulfide and Its Thermoelectric Properties

Hiroataka Nishiate, Michihiro Ohta*, Atsushi Yamamoto,
Haruhiko Obara, Chul-Ho Lee and Kazuo Ueno

Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST),
Tsukuba 305-8568, Japan

Pb-filled Chevrel-phase sulfides $\text{PbMo}_6\text{S}_{8-y}$ were prepared from PbS, Mo, and MoS_2 . The single phase was formed in the nominal composition $\text{PbMo}_6\text{S}_{7.8}$ ($8 - y = 7.8$). While the secondary PbS and Mo phases were formed in sulfur-poor compositions, the secondary MoS_2 phase was formed in sulfur-rich compositions. The sintered sample had a positive Seebeck coefficient. The Seebeck coefficient and electrical resistivity increased with temperature. Furthermore, the thermal conductivity was dominated by the electronic thermal conductivity, and the complex crystal structure yielded a low lattice thermal conductivity. The thermoelectric figure of merit ZT increased with temperature, reaching a value of 0.08 at 850 K. [doi:10.2320/matertrans.E-M2011808]

(Received November 20, 2010; Accepted March 31, 2011; Published May 25, 2011)

Keywords: thermoelectric materials, single phase, Chevrel-phase sulfides, lead filling, pressure-assisted sintering, thermoelectric properties

1. Introduction

Transition-metal sulfides with complex crystal structures have garnered attention for several years as high-temperature thermoelectric materials.¹⁻⁵⁾ Thermoelectric materials are evaluated by thermoelectric figure of merit $ZT = (S^2T/\rho\kappa)$, where S is Seebeck coefficient, T is temperature, ρ is electrical resistivity, and κ is thermal conductivity. The thermal conductivity can be separated into the electronic thermal conductivity κ_e and the lattice thermal conductivity κ_l , such that $\kappa = \kappa_e + \kappa_l$. Moreover, the electronic thermal conductivity can be estimated from the electrical resistivity and Lorenz number L ($2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$): $\kappa_e = LT/\rho$. The rare-earth sulfides are promising n-type thermoelectric materials for high temperature. In $\text{NdGd}_{1.02}\text{S}_3$, the highest ZT value achieved is 0.51 at 950 K.²⁾ The Chevrel-phase sulfides have interesting potential as p-type thermoelectric materials for high temperature. The ZT value of 0.4 has been found in $\text{Cu}_{4.0}\text{Mo}_6\text{S}_8$ at 950 K.¹⁾ The complex crystal structures of these thermoelectric sulfides reduce the thermal conductivity. In this study, we focus on Chevrel-phase sulfides for further investigation of p-type sulfide thermoelectric materials.

Chevrel-phase sulfides of the general formula $\text{M}_x\text{Mo}_6\text{S}_8$ (M = metal) have been known since the 1970s.⁶⁾ The host structure consists of stacked Mo_6S_8 clusters, with M atoms filling the cavities between them. The thermoelectric properties of $\text{M}_x\text{Mo}_6\text{S}_8$ (M = Cr, Mn, Fe, Cu) can be explained in terms of the cluster-valence-electron count (cluster VEC).^{1,3)} The cluster VEC is calculated by adding the valence electrons of M atom and of Mo atoms, and then subtracting the number of electrons required to fill the octets of the S atoms from the resultant valence electrons. Next, the resultant value is divided by the number of Mo atoms.⁷⁻⁹⁾ The ZT value is generally improved by increasing the cluster VEC.³⁾

Although many M atoms fill the cavities, most previous studies have focused mainly on the effect of small M atoms in terms of their thermoelectric properties. While large M atoms such as Pb fill the cavities between the Mo_6S_8 clusters within a narrow composition range ($x \approx 1$), small M atoms such as Cu fill the cavities within wide composition ranges ($0 < x \leq 4$). Since single phases form within this narrow composition range for large M atoms, it is difficult to prepare the single phase with large M atoms. Therefore, very few studies have reported the thermoelectric properties of Chevrel-phase sulfides filled with large M atoms. Tsubota *et al.*¹⁰⁾ investigated the thermoelectric properties of the Pb-filled Chevrel-phase sulfide. However, the sample showed low ZT (0.03 at 700 K) because it contained a large amount of secondary phase contamination. Therefore its potential for thermoelectric applications was not evaluated in their results.

This study investigates the thermoelectric properties of the single-phase Pb-filled Chevrel-phase sulfides. A sintered sample was prepared by reacting PbS, Mo, and MoS_2 followed by pressure-assisted sintering. The Seebeck coefficient, electrical resistivity, and thermal conductivity of the sintered sample were measured between 300 and 850 K.

2. Experimental

The Pb-filled Chevrel-phase sulfides $\text{PbMo}_6\text{S}_{8-y}$ ($6.8 \leq 8 - y \leq 8.2$) powders were prepared by reacting PbS, Mo, and MoS_2 . Commercial PbS powder (99.9%, Kojundo Chemical Laboratory Co., Ltd., Japan), Mo powder (99.9%, Kojundo Chemical Laboratory Co., Ltd., Japan), and MoS_2 powder (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, which were then inserted in an alumina tube. The mixtures were heated to 1273 K for 8 h in a vacuum ($7.0 \times 10^{-3} \text{ Pa}$). The heating and cooling rates were 5 K min^{-1} and 10 K min^{-1} , respectively.

*Corresponding author, E-mail: ohta.michihiro@aist.go.jp

The prepared powders were then consolidated by pressure-assisted sintering apparatus (SPS-515S, SPS Syntex Inc., Japan) in graphite dies. The sintering was conducted at 1223 K for 2 h under a pressure of 30 MPa in a vacuum (7.0×10^{-3} Pa). The heating and cooling rates were 10 K min^{-1} and 20 K min^{-1} , respectively.

The crystal phases of the prepared powders and sintered sample were studied by powder X-ray diffractometry (XRD) using Cu K_α radiation (Rint-Ultima+, Rigaku Co., Japan). The density of the sintered sample was measured by the Archimedes method. The microstructure of the fractured surface was examined under a scanning electron microscope (SEM; JSM-6301F, JEOL Ltd., Japan) at 20 kV accelerating voltage.

The sintered sample was cut into plates that were 10 mm long, 4 mm wide, and 2 mm thick to measure the Seebeck coefficient and electrical resistivity. The Seebeck coefficient was measured by a temperature differential method (ZEM-3, ULVAC-RIKO, Inc., Japan) in a helium atmosphere between room temperature and 873 K. In this measurement, the temperature difference was less than 10 K. The electrical resistivity was measured by a four-probe method (ZEM-3) in a helium atmosphere in the same temperature range.

To measure thermal conductivity, the sintered sample was fabricated in disks that were 10 mm in diameter and 1.6 mm thick. The thermal conductivity was measured by a laser flash method (TC-7000, ULVAC-RIKO, Inc., Japan) in a vacuum between room temperature and 873 K.

3. Results and Discussion

Figure 1 shows the XRD patterns of $\text{PbMo}_6\text{S}_{8-y}$ powders prepared from PbS, Mo, and MoS_2 . We succeeded in achieving a single-phase powder with a nominal composition $\text{PbMo}_6\text{S}_{7.8}$ ($8 - y = 7.8$), although a trace amount of PbS remained. We believe that since the degree of contamination is negligible, our study includes such powder in our definition of a single-phase powder. As the sulfur content decrease from $8 - y = 7.8$, secondary PbS and Mo phases are formed. On the other hand, the secondary MoS_2 phase is formed for powders with $8 - y > 7.8$. The formation behavior of secondary phases is almost identical to those of the findings in previous studies.^{11,12)}

The hexagonal lattice parameters, X-ray densities of the single-phase powder and sintered sample, and sintered density are shown in Table 1. The hexagonal lattice parameters of the sintered sample are in good agreement with those of the powder. Moreover, these lattice parameters are in similar agreement with those measured in previous studies.^{11–13)} The sintered density is 91% of the X-ray

density. This low sintered density appears to adversely affect the thermoelectric properties. Therefore, we will attempt to improve the sintered density.

Figure 2 shows the SEM micrograph of $\text{PbMo}_6\text{S}_{7.8}$ sintered sample's fractured surface. The examination reveals a few remaining isolated pores, which is consistent with the low sintered density. The grain size is less than $5 \mu\text{m}$.

Because the single phase is formed with the nominal composition $\text{PbMo}_6\text{S}_{7.8}$, this sintered sample is probably suitable for investigation of its thermoelectric properties. The

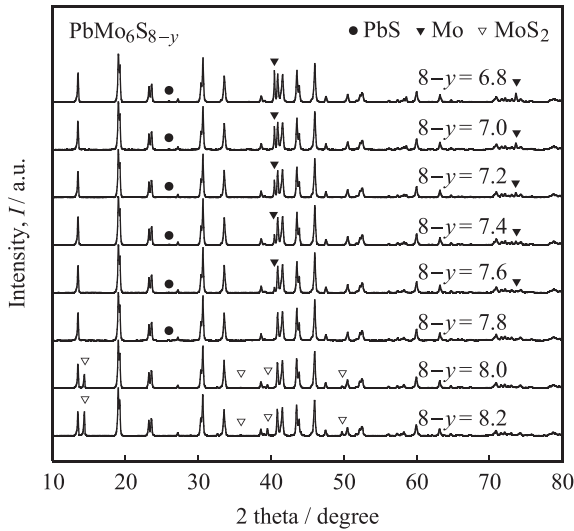


Fig. 1 XRD patterns of $\text{PbMo}_6\text{S}_{8-y}$ powders prepared from PbS, Mo, and MoS_2 .

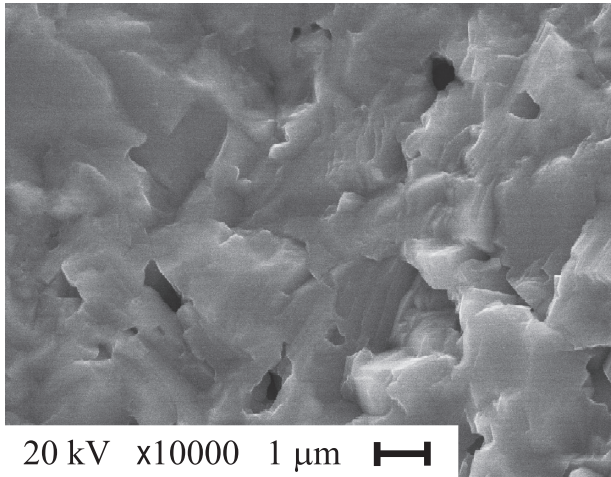


Fig. 2 SEM micrograph of $\text{PbMo}_6\text{S}_{7.8}$ sintered sample's fractured surface.

Table 1 Nominal composition, hexagonal lattice parameters, X-ray densities of single-phase powder and sintered sample, and sintered density.

	Nominal composition	Hexagonal lattice parameters		X-ray density (g cm^{-3})	Sintered density	
		<i>a</i> (nm)	<i>c</i> (nm)		(g cm^{-3})	(% of X-ray density)
Powder	$\text{PbMo}_6\text{S}_{7.8}$	0.918	1.145	6.10	—	—
Sintered sample	$\text{PbMo}_6\text{S}_{7.8}$	0.921	1.142	6.10	5.5	91

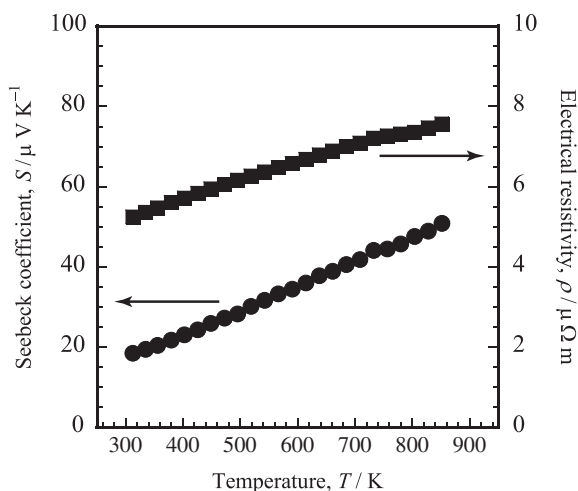


Fig. 3 Temperature dependence of Seebeck coefficient and electrical resistivity for $\text{PbMo}_6\text{S}_{7.8}$.

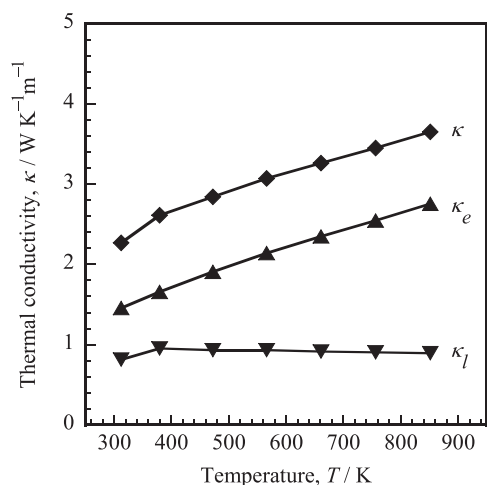


Fig. 4 Temperature dependence of thermal conductivity, electronic thermal conductivity, and lattice thermal conductivity for $\text{PbMo}_6\text{S}_{7.8}$.

temperature dependence of the Seebeck coefficient and electrical resistivity for $\text{PbMo}_6\text{S}_{7.8}$ are shown in Fig. 3. The sintered sample exhibits a positive Seebeck coefficient, and metal-like conduction. Because the Seebeck coefficient and electrical resistivity linearly increase with temperature, the power factor (S^2/ρ) also increases with temperature.

Figure 4 shows the temperature dependence of the thermal conductivity, electronic thermal conductivity, and lattice thermal conductivity for $\text{PbMo}_6\text{S}_{7.8}$. The electronic thermal conductivity is higher than the lattice thermal conductivity. Because of the complex crystal structure, the lattice thermal conductivity is low ($0.8 \leq \kappa_l \leq 1.0 \text{ W K}^{-1} \text{ m}^{-1}$). The sample of PbMo_6S_8 has been found to have the relatively low Debye temperature (245 K).¹⁴ This fact fits our result that the sintered sample of $\text{PbMo}_6\text{S}_{7.8}$ has a low lattice thermal conductivity.

Our previous studies^{1,3}) showed that the Seebeck coefficient, electrical resistivity, and electronic thermal conductivity of $\text{M}_x\text{Mo}_6\text{S}_8$ ($\text{M} = \text{Cr, Mn, Fe, Cu}$) increase with the cluster VEC. The electrical properties of $\text{PbMo}_6\text{S}_{7.8}$ also

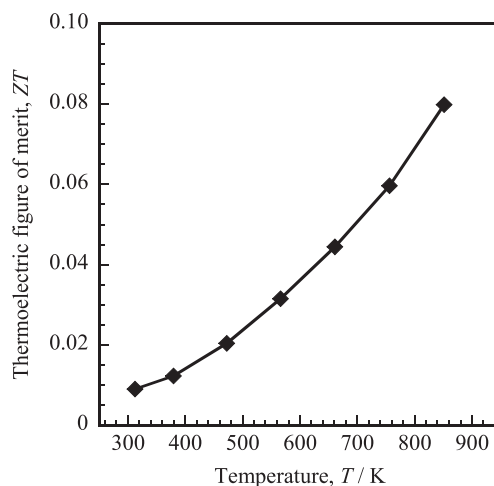


Fig. 5 Temperature dependence of thermoelectric figure of merit ZT for $\text{PbMo}_6\text{S}_{7.8}$.

follow the same trend; the Seebeck coefficient, electrical resistivity, and electronic thermal conductivity of $\text{PbMo}_6\text{S}_{7.8}$ with cluster VEC of 3.73 are between those of $\text{Cu}_{2.0}\text{Mo}_6\text{S}_8$ with cluster VEC of 3.67 and $\text{Cu}_{2.5}\text{Mo}_6\text{S}_8$ with cluster VEC of 3.75.

The ZT value of $\text{PbMo}_6\text{S}_{7.8}$ is calculated from the measured values of Seebeck coefficient, electrical resistivity, and thermal conductivity. As shown in Fig. 5, the ZT increases with temperature, reaching a value of 0.08 at 850 K. The important point here is that the ZT of the sintered sample ($ZT = 0.05$ at 700 K) is higher than that of the sample contaminated with secondary MoS_2 phase ($ZT = 0.03$ at 700 K).¹⁰ In other words, the ZT value is improved by the formation of the single phase. Nevertheless, the ZT of $\text{PbMo}_6\text{S}_{7.8}$ with cluster VEC of 3.73 is lower than that of $\text{Cu}_{4.0}\text{Mo}_6\text{S}_8$ with cluster VEC of 4.00 ($ZT = 0.34$ at 850 K). The cluster VEC can be tuned generally by changing the filling content so as to improve the ZT . However, the tuning of cluster VEC is difficult for $\text{PbMo}_6\text{S}_{8-y}$ since the single phase is formed within the narrow composition range.

4. Conclusion

Pb-filled Chevrel-phase sulfides were prepared by reacting PbS, Mo, and MoS_2 at 1273 K for 8 h in a vacuum. We successfully prepared the single-phase powder with the nominal composition $\text{PbMo}_6\text{S}_{7.8}$. While the secondary PbS and Mo phases are formed in sulfur-poor compositions, the secondary MoS_2 phase is formed in sulfur-rich compositions. The sintered sample with 91% of the X-ray density was fabricated by pressure-assisted sintering of the single-phase powder at 1223 K for 2 h under a pressure of 30 MPa in a vacuum. The sintered sample exhibits p-type metal-like conduction between 300 and 850 K. Moreover, the thermal conductivity is dominated by the electronic thermal conductivity, and the complex crystal structure yields a low lattice thermal conductivity. The ZT value is improved by the formation of the single phase, and it increases with temperature, reaching a value of 0.08 at 850 K.

Acknowledgments

This study was partially supported by a grant from the Iketani Science and Technology Foundation.

REFERENCES

- 1) M. Ohta, H. Obara and A. Yamamoto: *Mater. Trans.* **50** (2009) 2129–2133.
- 2) M. Ohta and S. Hirai: *J. Electron. Mater.* **38** (2009) 1287–1292.
- 3) M. Ohta, A. Yamamoto and H. Obara: *J. Electron. Mater.* **39** (2010) 2117–2121.
- 4) M. Ohta: *J. Thermoelectrics Soc. Jpn.* **6** (2010) 7–10.
- 5) M. Ohta: *Materia Japan* **49** (2010) 477–481.
- 6) R. Chevrel, M. Sergent and J. Prigent: *J. Solid State Chem.* **3** (1971) 515–519.
- 7) K. Yvon and A. Paoli: *Solid State Commun.* **24** (1977) 41–45.
- 8) K. Yvon: *Current topics in materials science*, Vol. 3, ed. by E. Kaldos, (North-Holland, Amsterdam, 1979) pp. 53–129.
- 9) R. Chevrel and M. Sergent: *Superconductivity in Ternary Compounds I (Topics in Current Physics)*, Vol. 32, ed. by Ø. Fischer and M. B. Maple, (Springer, Berlin, 1982) pp. 25–86.
- 10) T. Tsubota, M. Ohtaki and K. Eguchi: *J. Ceram. Soc. Jpn.* **107** (1999) 697–701.
- 11) S. Yamamoto, M. Wakihara and M. Taniguchi: *Mater. Res. Bull.* **20** (1985) 1493–1500.
- 12) H. Yamasaki and Y. Kimura: *Mater. Res. Bull.* **21** (1986) 125–135.
- 13) W. M. Miller and D. M. Ginsberg: *Phys. Rev. B* **28** (1983) 3765–3769.
- 14) B. Wolf, J. Molter, G. Bruls, B. Lüthi and L. Jansen: *Phys. Rev. B* **54** (1996) 348–352.