Effect of Ball-Milling Conditions on Thermoelectric Properties of Polycrystalline CuGaTe₂

Masaya Kumagai^{1,*1,*2}, Ken Kurosaki^{1,*2}, Yuji Ohishi¹,
Hiroaki Muta¹ and Shinsuke Yamanaka^{1,2}

¹Graduate School of Engineering, Osaka University, Suita 565-0871, Japan

²Research Institute of Nuclear Engineering, University of Fukui, Tsuruga 914-0055, Japan

CuGaTe₂ has a large thermoelectric (TE) figure of merit (ZT) at high temperatures, i.e., $ZT = 1.4$ at 950 K. However, at lower temperatures, the ZT values are smaller. One reason for this is that CuGaTe₂ has a high lattice thermal conductivity (κ_{lat}) at lower temperatures. One known method for reducing κ_{lat} is manipulating the microstructure of the bulk material. Therefore, herein, the grain-size effect on the TE properties of CuGaTe₂ bulk samples produced by ball milling and hot pressing was investigated. Although κ_{lat} decreased with grain size, a simultaneous decrease in the Seebeck coefficient occurred, leading to no overall improvement in ZT . [doi:10.2320/matertrans.E-M2014821]

(Received October 16, 2013; Accepted March 14, 2014; Published May 2, 2014)

Keywords: thermoelectric, CuGaTe₂, chalcopyrite, thermal conductivity, electrical resistivity, Seebeck coefficient

1. Introduction

Thermoelectric (TE) materials can convert waste heat into electric power; this method is an attractive method to reduce greenhouse gas emissions.^{1,2)} The effectiveness of a TE material is determined by the dimensionless figure of merit, $ZT = S^2T/\rho\kappa$, where S , ρ , T , and κ are, respectively, the Seebeck coefficient, electrical resistivity, absolute temperature, and total thermal conductivity. Also, $\kappa = \kappa_{\text{lat}} + \kappa_{\text{el}}$, where κ_{lat} and κ_{el} are the lattice and electronic thermal conductivities, respectively. Because S , ρ , and κ_{el} are interrelated in bulk materials, it is difficult to control them independently. Consequently, it is perhaps easier to reduce κ_{lat} for increasing ZT . The ZT values of the materials used in current TE devices are approximately unity.

For developing a TE power generator for the consumer market such as for the automotive industry, one constraint is that the device efficiency should be of at least 15%, corresponding to a ZT value of 1.5 or more. Although several bulk materials with ZT greater than 1.5 have been developed,^{3–9)} many are based on PbTe-type alloys such as AgPb_mSbTe_{m+2} (LAST-*m*),⁵⁾ AgTe-PbTe with La,⁶⁾ PbTe-SrTe,^{7,8)} NaPb_mSbTe_{2+m} (SALT-*m*),⁹⁾ and PbTe_{1-x}Se_x.¹⁰⁾

Herein, we focus on CuGaTe₂, which has a chalcopyrite structure and a relatively large ZT of up to 1.4 at 950 K.¹¹⁾ Although CuGaTe₂ exhibits a large ZT value at elevated temperatures, at lower temperatures the ZT value is much smaller. One reason for this is that CuGaTe₂ has a high κ_{lat} at lower temperatures. Because κ_{lat} is dependent on the microstructure of bulk material, the grain-size effect on the TE properties of CuGaTe₂ bulk samples produced by ball milling and hot pressing was investigated in the present study. Ball milling is generally used to control the grain size of a sample by taking into consideration several conditions (such as milling time, the diameter of the ball, revolutions per minute, ball to powder ratio, and the type of ball). In this

study, we attempt to control the grain size by changing the milling time only.

2. Experiment

CuGaTe₂ was prepared by a direct reaction of pieces of Cu (99.99%), Ga (99.99%), and Te (99.999%) in a sealed silica tube. The ingots obtained after melting were crushed into powder by hand, followed by ball milling. A planetary ball mill (Fritsch Japan Co., Ltd., PULVERISETTE7) with a WC vial volume of $45 \times 10^3 \text{ mm}^3$ and WC balls with a diameter of 1.6 mm was used. The ball to powder ratio was set to 2.6 : 1. Milling was performed at 300 rpm under Ar atmosphere. To control the grain size, the ball-milling time was set to 0, 1, or 3 h. Following ball milling, each powder was hotpressed in a graphite die using hotpress systems (Motoyama Co., Ltd.) at 823 K for 3 h in a flowing Ar atmosphere. The resulting bulk samples were characterized using powder X-ray diffraction (XRD) with CuK α radiation (Rigaku Corp., UltimaIV) at room temperature. The microstructure of the samples was examined using field emission-scanning electron microscopy (FE-SEM). JSM-6500F (JEOL Ltd.) microscope was used to obtain SEM images. The values of ρ and S were measured in the temperature range 300–973 K in a He atmosphere using a commercial measurement system (ULVAC, ZEM-1). The Hall coefficient (R_H) was measured at room temperature by the van der Pauw method under an applied magnetic field of 0.5 T using the Hall effect/resistivity measurement system (TOYO Corp., ResiTest-8300). The values of Hall carrier concentration (n_H) and Hall mobility (μ_H) were calculated from R_H based on the assumptions of a single-band model and a Hall factor of 1, i.e., $n_H = 1/(eR_H)$ and $\mu_H = R_H/\rho$, where e is the elementary electric charge. The parameter κ was evaluated from thermal diffusivity (α), heat capacity (C_p), and density (d) using the relationship $\kappa = \alpha C_p d$. The value of α was measured in vacuum from room temperature to 973 K using a laser flash thermal constant analyzer (ULVAC, TC-7000). In this study, C_p was estimated from $C_p = 3nR + 9B_TTV_m\alpha_c^2$, where n is the number of atoms per formula unit and R is the gas

*1Graduate Student, Osaka University

*2Corresponding author, E-mail: kumagai-m@ms.see.eng.osaka-u.ac.jp, kurosaki@see.eng.osaka-u.ac.jp

Table 1 Ball-milling conditions, estimated grain size, sample bulk density, Hall carrier concentration (n_H), and Hall mobility (μ_H) for CuGaTe₂ samples. Density, n_H , and μ_H were evaluated at room temperature.

Ball-milling condition	Grain size estimated from FE-SEM images/ μm	Density/%T.D.	$n_H/10^{24}\text{ m}^{-3}$	$\mu_H/10^{-4}\text{ m}^2\text{ V}^{-1}\text{ s}^{-1}$	$R_H/10^{-6}\text{ m}^3\text{ C}^{-1}$
Not ball milled	~ 50	99.7	3.35	67.8	1.86
300 rpm, 1 h	~ 5	99.9	13.2	34.9	0.47
300 rpm, 3 h	~ 0.5	95.7	45.6	13.7	0.13

constant, B_T is the isothermal bulk modulus, V_m is the specific volume, and α_e is the average coefficient of linear thermal expansion. B_T was estimated from $B_T = B_s/(1 + \alpha_e \gamma T)$, B_s being the adiabatic bulk modulus and γ the Grüneisen parameter.¹²⁾ In this study, the values of B_s and γ of CuGaTe₂ were 51.5 GPa and 1, respectively.¹¹⁾ The density of the hot-pressed samples was calculated from the measured weight and dimensions.

3. Results and Discussion

The grain size in the CuGaTe₂ powder was controlled by changing the ball-milling time. The FE-SEM images of the fractured surface of bulk samples produced by hot pressing are shown in Figs. 1(a), 1(b), and 1(c) for ball-milling times of 0, 1, and 3 h, respectively. The estimated grain size of the samples using the ball-milling times of 0, 1 and 3 h from the FE-SEM images were ~ 50 , 5, and 0.5 μm respectively. These results are listed in Table 1.

Figure 2 shows the powder XRD patterns for the hot-pressed samples, together with the peak positions for CuGaTe₂ reported in Ref. 13). All the peaks in the XRD patterns can be indexed in terms of the chalcopyrite structure with the space group $I\bar{4}2d$. The purities of the source materials were 99.99, 99.99, and 99.999% for Cu, Ga, and Te, respectively. Furthermore, all the peaks in the XRD patterns of the samples agreed well with the data presented in the literature, as shown in Fig. 2. Therefore, the total amount of impurities is less than 1%, which leads to no significant influence on the TE properties of the samples. Moreover, it can be concluded that single-phase samples of CuGaTe₂ were obtained in the present study. The lattice parameters calculated from the XRD patterns are shown in Fig. 2, and are slightly different from the reported values.¹³⁾

The ball-milling conditions, estimated grain size, sample bulk density, Hall coefficient (R_H), Hall carrier concentration (n_H), and Hall mobility (μ_H) for the CuGaTe₂ samples are summarized in Table 1. The values of density, R_H , n_H , and μ_H were evaluated at room temperature. The relative densities of the two samples with ball-milling times of 0 and 1 h were $\sim 100\%$ of the theoretical density, while that of the sample with ball milling time of 3 h was $\sim 96\%$. The R_H values for all the samples were positive, signifying that most of the charge carriers were holes. The n_H value increased with ball-milling time. It is considered that the mechanical energy associated with ball milling causes the Cu atoms to move to interstitial sites, leaving Cu vacancies that act as acceptors.^{14,15)} In

Fig. 1 FE-SEM images of CuGaTe₂ samples after hot pressing; (a) without ball milling, (b) ball milled (300 rpm, 1 h), and (c) ball milled (300 rpm, 3 h).

addition, because the most common intrinsic defects in CuGaTe₂ are Te vacancies, Cu atoms vacating the Cu sites tend to occupy the Te sites. Therefore, it is likely that the hole concentration increases with ball-milling time. However, those defects could not be confirmed from the variation of lattice parameters, as shown in Fig. 2. Additionally, a favorable result was not achieved from Rietveld analysis based on the XRD patterns. On the other hand, the hole mobility μ_H was found to decrease with increasing ball-

milling time; this is thought to be due to an increase in the number of grain boundaries and point defects (e.g., Cu vacancies), which are responsible for carrier scattering.

The temperature dependence of the TE properties of the samples is shown in Fig. 3. All S values are positive, indicating that the majority of the charge carriers are holes.

Fig. 2 Powder XRD patterns for CuGaTe₂ samples after hot pressing, together with literature data.

This is consistent with the results of the Hall effect measurements. For all the samples, S first increased slightly up to ~ 500 K, and then decreased with increasing temperature. Because the three samples indicated different density values, the κ and ρ values of the samples were compensated to those for fully dense CuGaTe₂ by Maxwell-Eucken's equation.¹⁶⁾

$$\kappa_p = \kappa(1 - p)/(1 + \beta p), \quad (1)$$

where p is the porosity, β is the constant determined by the conditions of the pores (in the present case, $\beta = 0.5$), κ_p is the thermal conductivity with porosity p , and κ is the thermal conductivity of a fully dense sample. The electrical resistivity was also compensated by the same method, wherein κ was replaced by $1/\rho$. The compensated results are plotted in Figs. 3(a) and 3(c). The ρ values for all the samples were almost independent of temperature up to ~ 500 K, and then decreased with increasing temperature. These results imply that below 500 K, electron excitation arises from impurity levels; however, at high temperature, the influence of the impurities becomes negligible. The decrease in both the ρ and absolute values of S above 500 K is believed to be due to the thermal excitation of holes. In addition, both the ρ and absolute values of S decrease with increasing ball-milling time because of the increase in the hole concentration (Figs. 3(a) and (b)).

The decrease in κ with increasing temperature roughly follows the T^{-1} relationship (Fig. 3(c)). This means that thermal conduction in CuGaTe₂ is mainly determined by the typical lattice contribution dominated by Umklapp scattering.

Fig. 3 Temperature dependence of thermoelectric properties of CuGaTe₂ samples; (a) Seebeck coefficient S , (b) electrical resistivity ρ , (c) thermal conductivity κ , and (d) dimensionless figure of merit ZT . Filled symbols in Fig. 3(b) represent results obtained from Hall measurements.

To evaluate κ_{lat} , the electronic contribution ($\kappa_{\text{el}} = LT\rho^{-1}$, where $L = 1.5 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$ for nondegenerate materials) was subtracted from the measured κ , i.e., $\kappa_{\text{lat}} = \kappa - LT\rho^{-1}$. At room temperature, κ_{el} can be considered to be negligible. It was also found that κ decreased with increasing ball-milling time at room temperature. This can be attributed to an increase both in grain boundary scattering due to the decreased grain size and point defect scattering due to the Cu vacancies.

The maximum ZT for the samples used in the present study was ~ 1.2 at 973 K (Fig. 3(d)). This value is slightly lower than the maximum value reported.¹¹⁾ It was also found that ZT decreased with increasing ball-milling time, and this can be primarily attributed to the decrease in the absolute value of S .

The reproducibility of the experimental results is very important. In the present case, we measured the TE properties a few times for each sample and confirmed that the results were consistent with each other within the experimental errors for each measurement, i.e., approximately $\pm 7\%$ for ρ , $\pm 7\%$ for S , and $\pm 5\%$ for α . On the basis of the errors for each measurement, the errors of ZT for the three samples with ball-milling times of 0, 1, and 2 h were estimated to be 26, 37, and 31%, respectively.

4. Summary

We attempted to control the microstructure of CuGaTe_2 bulk samples produced by ball milling of CuGaTe_2 powders followed by hot pressing. The grain size was found to decrease from ~ 50 to $0.5 \mu\text{m}$ with increasing ball-milling time. In the final hot-pressed samples, it was considered that increasing the ball-milling time increased the number of grain boundaries and Cu vacancies. This led to a greater hole concentration and a decrease in mobility and lattice thermal conductivity κ_{lat} . Consequently, ZT decreased with increasing ball-milling time. In the present study, the maximum ZT value was ~ 1.2 at 973 K, and was obtained for the sample

milled for 1 h. However, because a reduction in κ_{lat} also occurred simultaneously, it is possible that ZT can be improved by adjusting the carrier concentration through doping.

Acknowledgements

This work was supported in part by a Grant-in-Aid for Scientific Research (No. 23686091) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

REFERENCES

- 1) T. M. Tritt and M. A. Subramanian: *MRS Bull.* **31** (2006) 188–198.
- 2) G. Homm and P. J. Klar: *Phys. Status Solidi RRL* **5** (2011) 324–331.
- 3) X. Shi, J. Yang, J. R. Salvador, M. Chi, J. Y. Cho, H. Wng, S. Bai, J. Yang, W. Zhang and L. Chen: *J. Am. Chem. Soc.* **133** (2011) 7837–7846.
- 4) S. H. Yang, T. J. Zhu, T. Sun, J. He, S. N. Zhang and X. B. Zhao: *Nanotechnology* **19** (2008) 245707.
- 5) K. F. Hsu, S. Loo, F. Guo, W. Chen, J. S. Dyck, C. Uher, T. Hogan, E. K. Polychroniadis and M. G. Kanatzidis: *Science* **303** (2004) 818–821.
- 6) Y. Pei, J. Lensch-Falk, E. S. Toberer, D. L. Medli and G. J. Snyder: *Adv. Funct. Mater.* **21** (2011) 241–249.
- 7) K. Biswas, J. He, Q. Zhang, G. Wang, C. Uher, V. P. Dravid and G. Kanatzidis: *Nat. Chem.* **3** (2011) 160–166.
- 8) K. Biswas, J. He, I. D. Blum, C. I. Wu, T. P. Hogan, D. N. Seidman, V. P. Dravid and M. G. Kanatzidis: *Nature* **489** (2012) 414–418.
- 9) P. F. P. Poudeu, J. D. Angelo, A. D. Downey, J. L. Short, T. P. Hogan and M. G. Kanatzidis: *Angew. Chem. Int. Ed.* **45** (2006) 3835–3839.
- 10) Y. Pei, X. Shi, A. Lalonde, H. Wang, L. Chen and G. J. Snyder: *Nature* **473** (2011) 66–69.
- 11) T. Plirdpring, K. Kurosaki, A. Kosuga, T. Day, A. Firdosy, V. Ravi, G. J. Snyder, A. Harnwungmong, T. Sugaharam, Y. Ohishi, H. Muta and S. Yamanaka: *Adv. Mater.* **24** (2012) 3622–3626.
- 12) G. A. Slack and V. G. Tsoukala: *J. Appl. Phys.* **76** (1994) 1665–1671.
- 13) I. V. Bodnar and N. S. Orlova: *Cryst. Res. Technol.* **21** (1986) 1091–1096.
- 14) G. Masse and E. Redjai: *J. Phys. Chem. Solids* **47** (1986) 99–104.
- 15) H. Neumann: *Cryst. Res. Technol.* **18** (1983) 901–906.
- 16) A. Eucken: *Forschung* **11** (1940) 6–20.