ELSEVIER

Journal of Alloys and Compounds 388 (2005) 122–125

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Thermoelectric properties of β-$BaCu_2S_2$

Ken Kurosaki*, Hironori Uneda, Hiroaki Muta, Shinsuke Yamanaka

Department of Nuclear Engineering, Graduate School of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565-0871, Japan

Received 8 June 2004; received in revised form 5 July 2004; accepted 7 July 2004

Abstract

A polycrystalline sintered sample of β-$BaCu_2S_2$ with a natural superlattice structure was prepared by solid-state reactions. The thermal diffusivity and heat capacity were measured from room temperature to about 850 K. The thermal conductivity was evaluated from the thermal diffusivity and heat capacity. The value at room temperature is 0.86 $W\,m^{-1}\,K^{-1}$. Using the data of the electrical resistivity and the Seebeck coefficient obtained in a previous study, the dimensionless figure of merit *ZT* of β-$BaCu_2S_2$ was evaluated. The *ZT* increases with increasing temperature and reaches 0.17 at 820 K.

Keywords: β-$BaCu_2S_2$; Thermoelectric; Electrical transport; Thermal conductivity; Heat capacity

1. Introduction

The effectiveness of a material for thermoelectric applications is determined by the dimensionless figure of merit *ZT* (see for example, [1]), where T is the absolute temperature and $Z = (S^2\sigma)/\kappa$ (S is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity). The electrical properties are determined by the power factor P, defined here as $P = S^2\sigma$ or S^2/ρ, where ρ is the electrical resistivity. To be a good thermoelectric material, it is necessary to have large power factor and low thermal conductivity. In our group, thermoelectric properties of various materials such as a molybdenum telluride with Chevrel phase [2,3], thallium telluride [4,5], rare earth copper oxide [6,7] have been studied to discover high *ZT* materials.

In our previous study [8], the electrical resistivity and Seebeck coefficient of β-$BaCu_2S_2$ have been reported. The β-$BaCu_2S_2$ has a unique crystal structure, in which, Cu_2S_2 layers are sandwiched by Ba sheets [9,10] like a natural superlattice structure. We have discovered that β-$BaCu_2S_2$ has a moderate power factor ($P_{max} = 1.53 \times 10^{-4}\,W\,m^{-1}\,K^{-2}$ at around 700 K) [8]. Since the β-$BaCu_2S_2$ compound has layered structure, it is supposed that the thermal conductivity is relatively low. However, there is no data about the thermal transport properties of β-$BaCu_2S_2$.

In the present study, the β-$BaCu_2S_2$ compound is prepared by solid-state reactions. The heat capacity and thermal diffusivity are measured and the thermal conductivity is evaluated. Using the data of the power factor reported in our previous study, the dimensionless figure of merit *ZT* of β-$BaCu_2S_2$ is evaluated. The possibility of the compound as the thermoelectric materials is studied.

2. Experimental

The polycrystalline sintered sample of β-$BaCu_2S_2$ was prepared by a solid-state reaction. The appropriate ratios of BaS and Cu_2S as the starting materials were mixed and sealed in a quartz ampoule, and then the mixture was gradually heated to 1173 K and annealed for 48 h. After that, the product was cooled slowly to 973 K and the β phase was obtained by quenching from 973 K to room temperature. The obtained sample was pressed into pellets for the measurement. The density of the samples was calculated from the measured weight and dimension. The crystal structure was analyzed by a powder X-ray diffraction method at room temperature

---

[*] Corresponding author. Tel.: +81-6-6879-7905; fax: +81-6-6879-7889.
E-mail address: kurosaki@nucl.eng.osaka-u.ac.jp (K. Kurosaki).

0925-8388/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2004.06.086

using Cu Kα radiation. The chemical composition was determined by an EDX analysis. The heat capacity of β-$BaCu_2S_2$ was measured in a differential scanning calorimeter (DSC, ULVAC), in the temperature range from room temperature to about 850 K. The apparatus has a “triple-cell” system and an adiabatic temperature control system, which was originally developed by Takahashi et al. [11]. The principle of the apparatus is briefly summarized in the literature [12]. The measurement was carried out in high purity argon (99.999%) atmosphere with a flow rate of 100 ml/min. In order to check the accuracy of the apparatus, the heat capacity of α-Al_2O_3 was measured. The thermal diffusivity of β-$BaCu_2S_2$ was measured by a laser flash method from room temperature to about 850 K in vacuum (10^{-4} Pa) by using TC-7000 (ULVAC). The thermal diffusivity at the temperatures considered during the heating process was checked during the cooling cycle. The thermal conductivity was calculated from the thermal diffusivity α, heat capacity C_P, and density ρ, using the following standard expression:

$$\kappa = \alpha C_P \rho$$

3. Results and discussion

From the X-ray diffraction pattern of the sample, it is confirmed that a single phase sample of β-$BaCu_2S_2$ with the space group *I*4/*mmm* is obtained [8]. The lattice parameters of β-$BaCu_2S_2$ evaluated from the X-ray diffraction pattern are shown in Table 1; they agree well with literature data [13]. The bulk density of the sample is about 93% of the theoretical density.

Fig. 1 shows the relationship between the electrical conductivity σ and the Seebeck coefficient S, together determining the power factor $S^2\sigma$. In Fig. 1, the values for state-of-the-art thermoelectric materials such as $(GeTe)_{1-x}(AgSbTe_2)_x$ “TAGS” and sintered Bi_2Te_3 are also shown for comparison [1,14]. It is known that the power factor is required to have an order of magnitude ($W\,m^{-1}\,K^{-2}$) of about 10^{-3} for materials used in current devices. The values of the power factor of β-$BaCu_2S_2$ reach an order of magnitude of 10^{-4}. The maximum value of the power factor is $1.53 \times 10^{-4}\,W\,m^{-1}\,K^{-2}$ at around 700 K. This low value of the power factor is due to the high electrical resistivity.

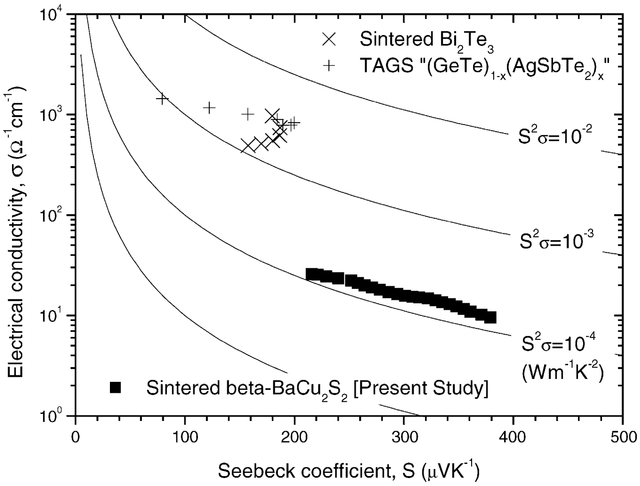

Fig. 1. Relationship between the electrical conductivity σ and Seebeck coefficient S of β-$BaCu_2S_2$ and other materials [1,14].

Table 1
Sample characteristics and physical properties of β-$BaCu_2S_2$

Lattice parameters at room temperature (nm)	
a	0.391
c	1.265
Theoretical density ($g\,cm^{-3}$)	5.63
Sample bulk density	
$g\,cm^{-3}$	5.24
T.D. (%)	93
Heat capacity, $C_P = a + bT + c/T^2$ ($J\,K^{-1}\,mol^{-1}$)	
a	132
b	2.95×10^{-2}
c	-3.92×10^{5}
Thermal conductivity at room temperature, κ ($W\,m^{-1}\,K^{-1}$)	0.86
Maximum ZT, ZT_{max}	0.17 (at 820 K)

Fig. 2 shows the temperature dependence of the heat capacity of β-$BaCu_2S_2$ measured in the DSC. In the temperature range between 300 and 900 K, the empirical equation for the C_P of β-$BaCu_2S_2$ is determined from the experimental data as follows:

$$C_P\,(J\,K^{-1}\,mol^{-1}) = 132 + 2.95 \times 10^{-2}T - \frac{3.92 \times 10^5}{T^2}$$

The thermal diffusivity of β-$BaCu_2S_2$ was measured by the laser flash method, and the thermal conductivity was evaluated. Fig. 3 shows the temperature dependence of thermal conductivity of β-$BaCu_2S_2$, together with the data of other

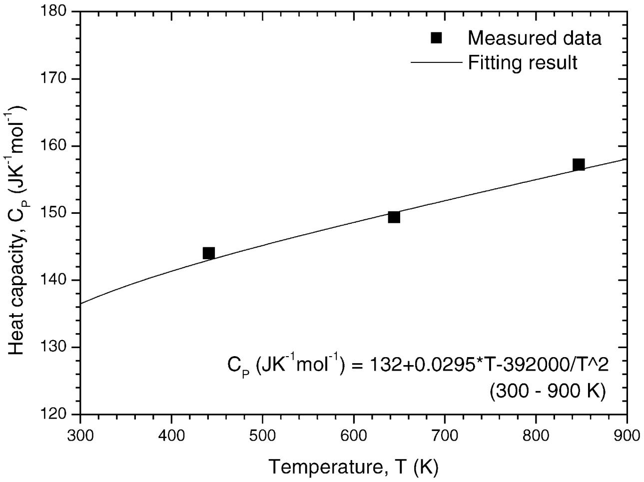

Fig. 2. Temperature dependence of the heat capacity of β-$BaCu_2S_2$.

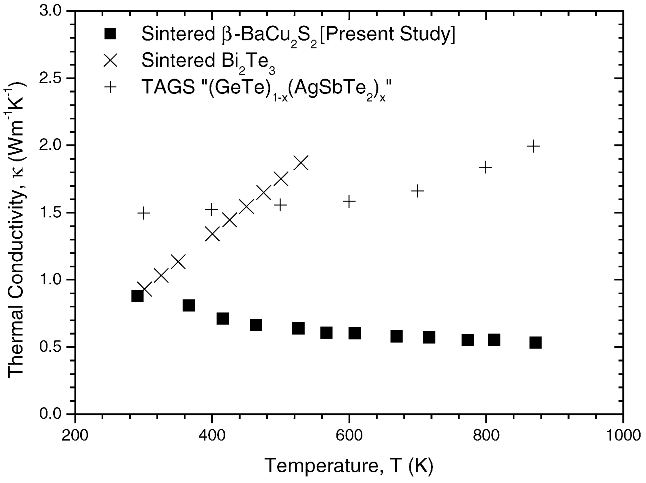

Fig. 3. Temperature dependence of the thermal conductivity of β-BaCu$_2$S$_2$ and other substances [1,14].

substances [1,14]. To be a good thermoelectric material, it is necessary to have a low thermal conductivity. The thermal conductivity of β-BaCu$_2$S$_2$ is lower than those of state-of-the-art thermoelectric materials. The value at room temperature is 0.86 W m^{-1} K^{-1}. This low thermal conductivity is due to the naturally layered structure of β-BaCu$_2$S$_2$. The thermal conductivity decreases with increasing temperature, showing typical phonon conduction characteristics.

It is well known that the total thermal conductivity κ_{total} of solids can be written as follows:

$$\kappa_{\text{total}} = \kappa_{\text{lat}} + \kappa_{\text{el}} + \cdots$$

where κ_{lat} is the lattice contribution and κ_{el} is the electronic contribution. κ_{el} can be calculated using the Wiedemann–Franz–Lorenz relation:

$$\kappa_{\text{el}} = L\sigma T$$

where L is the Lorenz number, σ is the electrical conductivity, and T is the absolute temperature. κ_{lat} is obtained by subtracting κ_{el} from κ_{total}. The variations of κ_{total} and κ_{el} of β-BaCu$_2$S$_2$ with temperature are shown in Fig. 4. The κ_{el} is extremely low compared with κ_{total}. It is found that the majority of thermal conductivity of β-BaCu$_2$S$_2$ consists of lattice contribution.

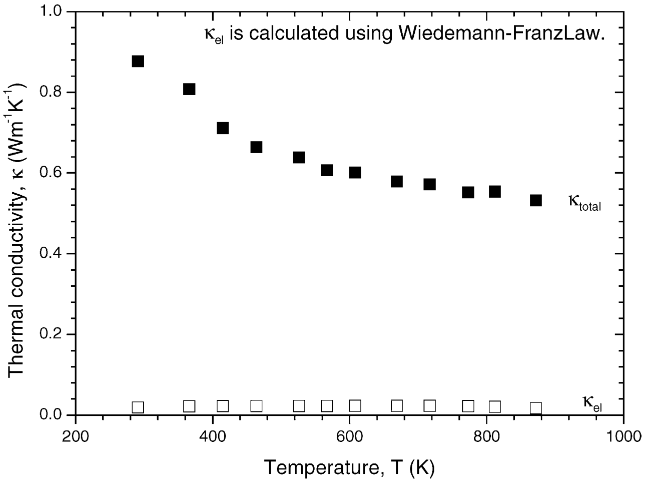

Fig. 4. Temperature dependence of κ_{total} and κ_{el} of β-BaCu$_2$S$_2$.

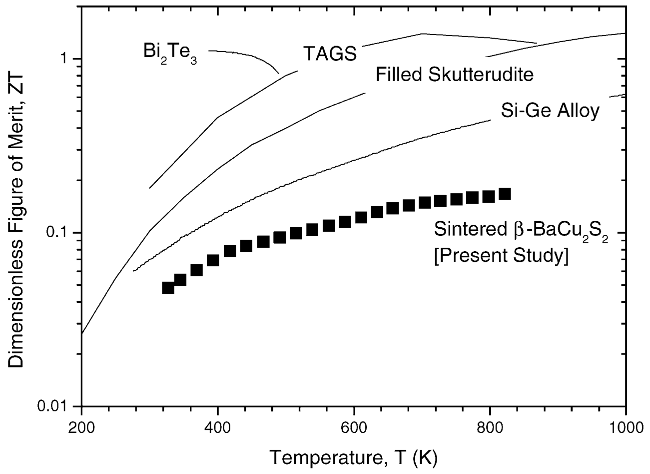

Fig. 5. Temperature dependence of the dimensionless figure of merit, ZT of β-BaCu$_2$S$_2$ and other substances [1,14,15].

The dimensionless figure of merit ZT of β-BaCu$_2$S$_2$ was evaluated by using the data of the electrical resistivity, Seebeck coefficient, and thermal conductivity. The temperature dependence of ZT of β-BaCu$_2$S$_2$ is shown in Fig. 5, together with the data of state-of-the-art thermoelectric materials [1,14,15]. The ZT of β-BaCu$_2$S$_2$ increases with increasing temperature, and reaches a maximum value of 0.17 at 820 K. It is confirmed that β-BaCu$_2$S$_2$ has a potential for thermoelectric application. In order to enhance the thermoelectric performance of the material, it is necessary to optimize the carrier density. Now, we are trying to increase the electrical conductivity by doping with other elements. The result will be reported in the near future.

4. Conclusion

Polycrystalline sintered β-BaCu$_2$S$_2$ was prepared and the thermal properties were measured from room temperature to 850 K. The thermoelectric properties of β-BaCu$_2$S$_2$ were evaluated. A dense sample with 93% of the theoretical density was obtained in this study. The empirical equation for the C_P of β-BaCu$_2$S$_2$ is determined from the experimental data as follows:

$$C_P\,(\text{J K}^{-1}\,\text{mol}^{-1}) = 132 + 2.95 \times 10^{-2}T - \frac{3.92 \times 10^5}{T^2}$$

The thermal conductivity of β-BaCu$_2$S$_2$ is relatively low and the value at room temperature is 0.86 W m^{-1} K^{-1}. The ZT of β-BaCu$_2$S$_2$ increases with increasing temperature. The maximum value of the ZT is obtained as 0.17 at 820 K.

References

[1] D.M. Rowe, CRC Handbook of Thermoelectrics, CRC Press, New York, 1995.

[2] K. Kurosaki, A. Kosuga, M. Uno, S. Yamanaka, J. Alloys Compd. 334 (2002) 317.

[3] K. Kurosaki, A. Kosuga, S. Yamanaka, J. Alloys Compd. 351 (2002) 208.

[4] K. Kurosaki, A. Kosuga, S. Yamanaka, J. Alloys Compd. 351 (2002) 279.

[5] S. Yamanaka, A. Kosuga, K. Kurosaki, J. Alloys Compd. 352 (2002) 275.

[6] S. Yamanaka, H. Kobayashi, K. Kurosaki, J. Alloys Compd. 349 (2002) 321.

[7] K. Kurosaki, H. Kobayashi, S. Yamanaka, J. Alloys Compd. 350 (2002) 340.

[8] K. Kurosaki, H. Uneda, H. Muta, S. Yamanaka, J. Alloys Compd. 385 (2004) 312–315.

[9] M. Saeki, M. Onoda, H. Nozaki, Mater. Res. Bull. 23 (1988) 603.

[10] M. Onoda, M. Saeki, Mater. Res. Bull. 24 (1989) 1337.

[11] Y. Takahashi, M. Asou, T. Terai, T. Yoneoka, M. Kamimoto, A. Maesono, in: Proceedings of the 12th Japan Symposium on Thermophysical Properties, Kyoto, 1991, p. 339.

[12] Y. Takahashi, M. Asou, Thermochim. Acta 223 (1993) 7.

[13] D.C. Palmer, Output generated by CrystalDiffract, 1995–99, http://www.crystalmaker.co.uk (CrystalDiffract is a companion program to CrystalMaker—interactive crystallography for MacOS).

[14] R.S. Caputo, V.C. Truscello, in: Proceedings of the IECEC, 1974, p. 637.

[15] B.C. Sales, D. Mandrus, R.K. Williams, Science 272 (1996) 1325–1328.