

Demonstration of Amorphous Bulk Semiconductor for Nano-Structured Thermoelectric Materials

Masahiro ADACHI*, Makoto KIYAMA, Yoshiyuki YAMAMOTO, and Tsunehiro TAKEUCHI

Thermoelectric generators, with which one can directly convert waste heat to useful electric power, have attracted considerable attention as one of the most efficient techniques leading to a low carbon and sustainable society. The figure of merit (ZT) of constituent thermoelectric materials is generally used as a measure for the efficiency of energy conversion in thermoelectric generators. The value has never reached a large magnitude exceeding 2, despite that $ZT \geq 4$ is strongly required for automobile exhaust heat utilization systems. This large gap between the required values and obtained values let us believe that thermoelectric generators are not usable in practical applications. We need new, innovative techniques leading to a breakthrough for developing high-performance thermoelectric materials. In this study, we have developed an amorphous bulk material as a precursor of nano-structured thermoelectric semiconductors.

Keywords: thermoelectric material, amorphous, bulk

1. Introduction

Reducing the consumption of fossil fuel and the emission of carbon dioxide (CO₂) is essential for realizing a sustainable society. Generation of electricity using thermoelectric generators that can convert waste heat (thermal energy) into electric power (electrical energy) has attracted considerable attention as one of the key technologies that can enhance the efficiency of energy use.

Since the thermoelectric conversion efficiency of a thermoelectric generator depends on its dimensionless figure of merit (ZT),*¹ a large magnitude of ZT is highly required for effective electricity generation. While $ZT \geq 4$ is required to enhance the fuel efficiency of automobiles by recovering exhaust heat in the form of electric power, the ZT of practically used thermoelectric materials is reported to be limited to 1-2.⁽¹⁾ A small magnitude of ZT prevents the practical use of presently available thermoelectric materials. Expensive and/or toxic constituent elements, such as Pb, Te, Sb, and Se,⁽²⁾⁻⁽⁴⁾ are another obstacle for their use in consumer products. Therefore, it is necessary to develop an environment-friendly, low-cost thermoelectric material having a high ZT.

It is well known that ZT is defined by the following equation as a function of the Seebeck coefficient S ,*² electrical conductivity σ , and thermal conductivity k .

$$ZT = S\sigma T/k \dots\dots\dots (1)$$

Generally, k is determined by electrons and lattice vibrations and, therefore, divided into two contributions as in $k = k_{ele} + k_{lat}$, where k_{ele} and k_{lat} represent the electron thermal conductivity and lattice thermal conductivity, respectively.⁽⁵⁾

Among the physical properties to be controlled, it has already been found that the Seebeck coefficient, electrical conductivity, and electron thermal conductivity depend on the energy- and momentum-distribution of electrons (hereafter abbreviated as electronic structure) near the Fermi level.^{(6),(7)} This means that the development of techniques

for arranging the electronic structure near the Fermi level leads to an effective improvement in the performance of thermoelectric materials.

The use of quantum wells, quantum wires, quantum dots (nanoparticles), or other nanostructures*³ has been suggested as a method for controlling electronic structure.⁽⁸⁾⁻⁽¹¹⁾ Notably, however, no paper has reported a significant increase in ZT due to a quantum effect.*^{4 (11)-(17)} A possible reason is that, due to its large particle size, a nanostructure cannot create the suitable electronic states. The size of conventional nanoparticles is 5 nm or more,^{(13),(18),(19)} while the target particle size necessary for creating a quantum effect is 3 nm or less.^{(8)-(10),(14)} We emphasize here that the most important issue is how to make a nanostructure.

Recently, Makino et al. and Okamoto et al. developed techniques for precipitating nanoparticles in amorphous materials.⁽¹⁸⁾⁻⁽²⁰⁾ Notably, Makino et al. succeeded in developing a soft magnetic amorphous bulk material containing nanocrystalline particles called NANOMET.⁽²⁰⁾ They obtained an amorphous ribbon using a liquid quenching technique that is shown schematically in Fig. 1. In this technique, molten alloy is injected into a copper wheel rotating to be rapidly quenched.

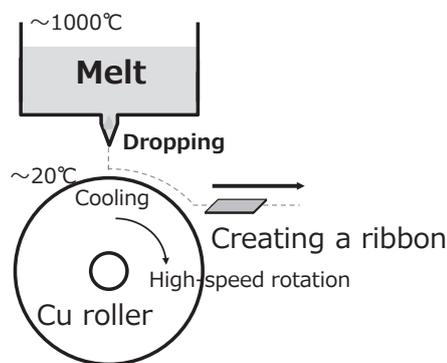


Fig. 1. Schematic illustration of the liquid quenching technique

This paper describes the results of a basic study that we completed toward the development of an amorphous bulk material containing nanocrystalline particles. As has already been described, the objective of this study was to create nanocrystalline particles precipitated in amorphous materials. The first step was developing a method for synthesizing an amorphous bulk material. In particular, we created an amorphous ribbon using a liquid quenching technique and applied high pressure to the ribbon in order to form a bulk. The key point of the liquid quenching technique was employing a composition where the material melting point becomes relatively low. This condition allows us to keep the liquid phase at low temperatures. If such a low-melting-point alloy is composed of many elements, an amorphous phase can be more easily obtained partly because the complex mixture of elements prevents atoms from diffusing toward the most stable site⁽²⁰⁾ and the enhanced entropy helps stabilize the amorphous phase. On the basis of the considerations described above, we succeeded in developing an amorphous bulk from an Al-Mn-Si alloy,⁽²¹⁾⁻⁽³⁰⁾ which is a low-cost, low-toxic multi-element thermoelectric material.^{(31),(32)}

2. Experimental Results

(1) Sample preparation method

A mother ingot was prepared by melting 99.95% pure Al, Mn, and Si in an induction heating furnace. The mother ingot was re-melted and quenched into a ribbon under an inert gas atmosphere by using the liquid quenching technique (Fig. 1). The obtained ribbon was approximately 2 mm in width, 100 mm in length, and 0.02 mm in thickness. Subsequently, the ribbon was crushed into powder and subjected to a high pressure of approximately 3 GPa at room temperature to form a bulk. The crystallinity of the specimen was evaluated by X-ray diffraction measurement and transmission electron microscopy. The Seebeck coefficient and electrical conductivity of the specimen were measured to evaluate the thermoelectric performance.

(2) Result and discussion

We first prepared samples composed solely of C40 phase ($\text{Al}_{27.5}\text{Mn}_{33.0}\text{Si}_{39.5}$), C54 phase ($\text{Al}_{33.0}\text{Mn}_{33.5}\text{Si}_{33.5}$), and HMS phase ($\text{Mn}_{36.4}\text{Si}_{63.6}$), which are typical Al-Mn-Si crystalline phases known as thermoelectric materials.⁽³⁰⁾

Powder x-ray diffraction (XRD) patterns proved that it is very difficult to stabilize the properties of an amorphous phase in these compositions of single phases. Subsequently, we prepared a specimen consisting of two or more phases to realize the low melting point, preventing the long-range diffusion of atoms in the quenching process. However, as shown in the upper panel of Fig. 2, the samples consisted of several crystalline phases in place of amorphous phases. The melting temperature of the samples was rather high at around 1100°C (determined by a radiation thermometer), and we speculated that this high melting point prevented us from obtaining amorphous phases.

We prepared, at the next step, low-melting-point samples using the ternary phase diagram.⁽³³⁾ We selected $\text{Al}_{29.0}\text{Mn}_{29.9}\text{Si}_{41.1}$ and $\text{Al}_{34.4}\text{Mn}_{21.2}\text{Si}_{44.4}$ for the sample compositions that have melting point of 1000°C and 900°C,

respectively, and prepared the ingots. The XRD patterns of samples are shown on the middle and lower panels of Fig. 2. A halo pattern was observed for the sample prepared at $\text{Al}_{29.0}\text{Mn}_{29.9}\text{Si}_{41.1}$ together with tiny sharp peaks of crystalline phases. This fact proved that the principal phases of this specimen were amorphous. In sharp contrast to the sample prepared at $\text{Al}_{29.0}\text{Mn}_{29.9}\text{Si}_{41.1}$, no XRD peak was detected for the sample at $\text{Al}_{34.4}\text{Mn}_{21.2}\text{Si}_{44.4}$, possessing lower melting temperature. We strongly emphasize here that the formation of amorphous phases in the Al-Mn-Si alloy system has not been reported yet, and this is the first success in preparing a pure amorphous phase.

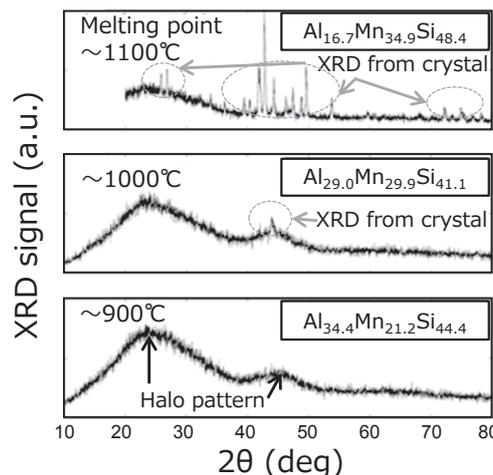


Fig. 2. X-ray diffraction signals of Al-Mn-Si alloy specimens created by liquid quenching technique (ribbon)

Before making an amorphous bulk, we clarified its crystallization temperature with a differential thermal analyzer. The result is shown in Fig. 3. An exothermic reaction was observed at a temperature near 450°C for the amorphous $\text{Al}_{34.4}\text{Mn}_{21.2}\text{Si}_{44.4}$ alloy. This fact indicates that, as long as it is kept at a temperature below 400°C, the amorphous phase would remain in the sample even in the

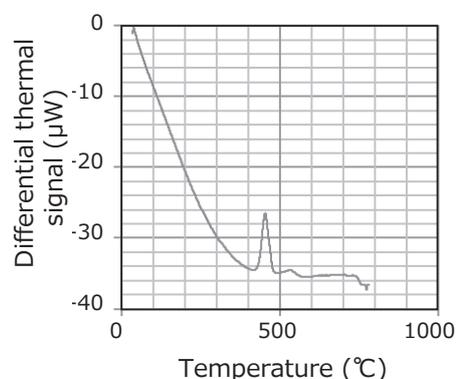


Fig. 3. Result of crystallization temperature measured by differential thermal analysis

bulk shape. We should also stress here that high crystalline temperature allows us to control the precipitation of crystal phases using heat treatment to make an appropriate structure for the quantum effects on electron transport properties.

After grinding the ribbon sample into powder, we sintered the powder into bulk by applying a high pressure of approximately 3 GPa at room temperature, which was much lower than its crystallization temperature of 400°C. A photo of the sintered sample is shown in Fig. 4 as an inset. The obtained specimen was a bulk with a cylindrical shape of 7.9 mm in diameter and 0.5 mm in thickness. The XRD patterns of the sample before and after the high-pressure process are shown in Fig. 4. No sharp peak, which indicates the precipitation of crystal phases, was detected in the XRD pattern even after the high-pressure process, verifying that the amorphous phase persisted in the sample without any precipitation of crystalline phases. We emphasize here that a bulk Al-Mn-Si amorphous material was successfully prepared to be used for thermoelectric applications.

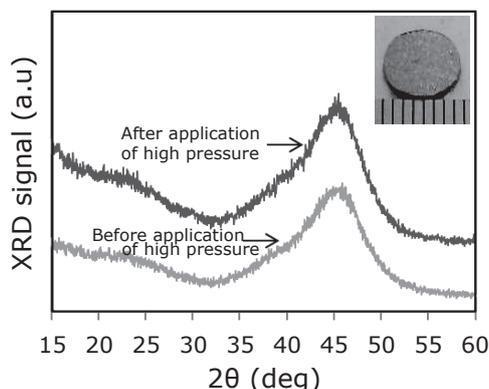


Fig. 4. XRD signals of amorphous Al-Mn-Si material before and after application of high pressure. Inset: External appearance of specimen after application of high pressure

The Seebeck coefficient and electrical conductivity of the bulk amorphous Al-Mn-Si were measured at room temperature shown in Fig. 5. The bulk amorphous Al-Mn-Si were characterized by the possession of a small Seebeck coefficient of 20 $\mu\text{V/K}$ and a large electrical conductivity of 5×10^4 S/m. It is noteworthy that the Seebeck coefficient was kept small at one-fifth of the value observed for crystalline Al-Mn-Si thermoelectric materials.^{(21),(34),(35)} The small magnitude of the Seebeck coefficient coupled with the large electrical conductivity would be attributed to a rather large density of states at the Fermi level. We expect that, in the future, the properties of amorphous Al-Mn-Si alloys can be improved by controlling the electronic structure using the nanocrystalline particles.

Although the thermoelectric performance of the prepared samples was insufficient in quality, achieving an amorphous bulk free from crystalline phases is of great importance because it has the potential to be a precursor of a nanostructured thermoelectric material. We will continue

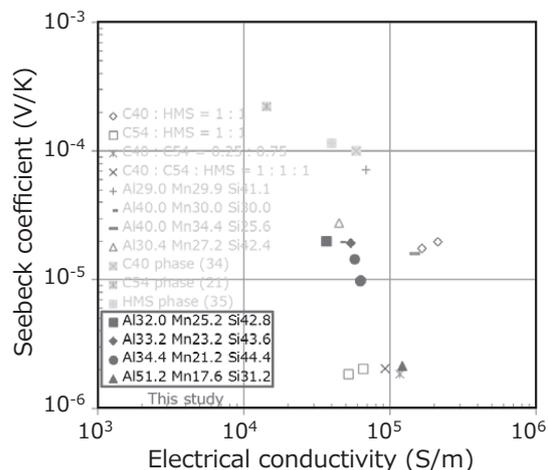


Fig. 5. Thermoelectric properties of amorphous Al-Mn-Si alloy

to investigate the best process for making nanostructured thermoelectric materials under various heat treatment conditions in order to develop a high-performance nanostructured thermoelectric material.

3. Conclusion

In this study, we developed an Al-Mn-Si amorphous thermoelectric bulk as a precursor of a nanostructured thermoelectric material using liquid-quenching technique with high pressure subsequently applied at room temperature. The amorphous ribbon was obtained by controlling the composition with consideration of the melting point. The finally determined composition was $\text{Al}_{34.4}\text{Mn}_{21.2}\text{Si}_{44.4}$ and its melting point was 900°C. Then, a high pressure of approximately 3 GPa was applied to the ribbon to make it into a bulk without having any precipitation of crystalline phases. The amorphous bulk material created in this process should be used as a precursor of a nanostructured thermoelectric material that would possess high thermoelectric performance.

4. Acknowledgments

Some of the findings presented in this paper were obtained from a study commissioned by the New Energy and Industrial Technology Development Organization (NEDO). We acknowledge Research Associate Takenaka and Prof. Makino of Tohoku University; Prof. Okamoto of the National Defense Academy of Japan; Prof. Kosuga and Prof. Yamada of Osaka Prefecture University; Prof. Takarabe of Okayama University of Science; and Prof. Yoshino of Okayama University for their valuable suggestions and support in this R&D work.

• NANOMET is a trademark of TOKIN Corporation and Tohoku Magnet Institute Co., Ltd.

Technical Terms

- *1 Dimensionless figure of merit, ZT: A dimensionless quantity used to represent the thermoelectric conversion performance (efficiency) of a material. Thermoelectric conversion efficiency ζ is given by the following equation:

$$\zeta = \frac{T_h - T_l}{T_h} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_l/T_h}$$

where T_h and T_l are the higher and lower temperatures, respectively, and T is $(T_h + T_l)/2$. This equation shows that thermoelectric efficiency ζ increases monotonically as ZT increases. This means that increasing ZT is essential to the development of a thermoelectric material.

- *1 Seebeck coefficient: An intrinsic physical quantity of a material, which represents its voltage generation capability under a temperature difference. Assume that a temperature difference of ΔT generates a voltage of ΔV between the hot and cool points of the material. Then its Seebeck coefficient is calculated from $-\Delta V/\Delta T$.
- *3 Nanostructure: A structure composed of crystals of a few nanometers in size. When an electronic energy difference is given between the crystalline structure and the material surrounding the structure, electrons are confined in the structure. This phenomenon is considered to be useful for developing a quantum effect.
- *4 Quantum effect: When electrons (or positive holes) are confined in a local space (several nanometers in size) in a material, their wave property becomes tangible and causes a dramatic change in the value of energy that can accommodate electrons. As a result, the state density or the number of electrons that can exist in each unit of energy changes dramatically. Changing the state density is a promising means of improving the thermoelectric properties of materials.

References

- (1) http://www.nedo.go.jp/activities/ZZJP_100097.html
- (2) H. J. Goldsmid, A. R. Sheard, and D. A. Wright, *Br. J. Appl. Phys.* 9 (1958) 365
- (3) G. E. Smith and R. Wolfe, *J. Appl. Phys.* 33 (1962) 841–846
- (4) R. W. Fritts, in *Thermoelectric Materials and Devices*, edited by I. B. Cadoff and E. Miller (Reinhold, New York, 1960), 143–162
- (5) A. F. Ioffe, *Semiconductor Thermoelements and Thermoelectric Cooling* (Infosearch Limited, London, 1957), pp. 1–35
- (6) T. Takeuchi, *Mater. Trans.* 50 (2009) 2359
- (7) N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, 1960), pp. 308–314
- (8) L. D. Hicks, and M. S. Dresselhaus, *Phys. Rev. B* 47 (1993) 12727
- (9) L. D. Hicks, and M. S. Dresselhaus, *Phys. Rev. B* 47 (1993) 16631
- (10) L. D. Hicks, *Dr thesis* (1996)
- (11) M. S. Dresselhaus, G. Chen, M. Y. Tang, R. Yang, H. Lee, D. Wang, Z. Ren, J. P. Fleurial, and P. Gogna, *Adv. Mater.* 19 (2007) 1043
- (12) S. Yamasaka, K. Watanabe, S. Sakane, S. Takeuchi, A. Sakai, K. Sawano, and Y. Nakamura, *Scientific Reports* 6 (2016) 22838
- (13) X. Hu, P. Jood, M. Ohta, M. Kunii, K. Nagase, H. Nishiata, M. G. Kanatzidis, A. Yamamoto, *Ene. & Env. Sci.* 9 (2016) 517
- (14) N. T. Hung, E. H. Hasdeo, A. R. T. Nugraha, M. S. Dresselhaus, and R. Saito, *Phys. Rev. Lett.* 117 (2016) 036602-1
- (15) G. Chen, M. S. Dresselhaus, G. Dresselhaus, J. -P. Fleurial, and T. Caillat, *Int. Mat. Rev.* 48 (2003) 45

- (16) M. S. Dresselhaus, M. Y. Lin, B. S. Cronin, O. Rabin, M. R. Black, G. Dresselhaus, T. Koga, *Semicond. Semimet.* 71 (2001) 1
- (17) C. Chang, C. Qin, A. Makino, A. Inoue, *J. Alloy. Comp.* 533 (2012) 67
- (18) H. Takiguchi, M. Aono, and Y. Okamoto, *Jpn. J. Appl. Phys.* 50 (2011) 041301
- (19) H. Takiguchi, *Dr. thesis* (2011)
- (20) <http://nanoc.imr.tohoku.ac.jp/research.html>
- (21) T. Takeuchi, *Mater. Trans.* 50 (2009) 2359–2365
- (22) N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, 1960), pp. 308–314
- (23) A. Yamamoto, and T. Takeuchi, *J. Electron. Mater.* 41 (2012) 1743
- (24) A. Yamamoto, H. Miyazaki, and T. Takeuchi, *J. Appl. Phys.* 115 (2014) 023708
- (25) A. Yamamoto, H. Miyazaki, M. Inukai, Y. Nishino, and T. Takeuchi, *Jpn. J. Appl. Phys.* 54 (2015) 071801
- (26) A. Yamamoto, S. Ghodke, H. Miyazaki, M. Inukai, Y. Nishino, M. Matsunami, and T. Takeuchi, *Jpn. J. Appl. Phys.* 55 (2016) 020301
- (27) T. Takeuchi, Y. Toyama, A. Yamamoto, H. Hazama, and R. Asahi, *Mater. Trans.* 51 (2010) 1127–1135
- (28) T. Takeuchi, T. Otagiri, H. Sakagami, T. Kondo, U. Mizutani, and H. Sato, *Phys. Rev. B* 70 (2004) 144202
- (29) T. Takeuchi, N. Nagasako, R. Asahi, and U. Mizutani, *Phys. Rev. B* 74 (2006) 054206
- (30) T. Takeuchi, T. Onogi, E. Banno, and U. Mizutani, *Mater. Trans.* 42 (2001) 933–938
- (31) M. Adachi, S. Fujii, M. Kiyama, Y. Yamamoto, T. Takeuchi, *The 77th Autumn Meeting in JSAP* (Sep. 2016), 15a-A35-5
- (32) M. Adachi, S. Fujii, M. Kiyama, Y. Yamamoto, S. Nishino, M. Omprakash, A. Yamamoto, A. Makino, and T. Takeuchi, *14th European Conference on Thermoelectrics*, PA12.10 (2016), Lisbon
- (33) V. Raghavan, *J. of Phase Equilibria and diffusion* 28 (2007) 192
- (34) A. Yamamoto, H. Miyazaki, M. Inukai, Y. Nishino, and T. Takeuchi, *Jpn. J. Appl. Phys.* 54 (2015) 072801
- (35) Young-Geun Leea, Moon-Kwan Choia,b, Il-Ho Kima and Soon-Chul Ur, *J. Cera. Process. Res.* 13 (2012) 816

Contributors

The lead author is indicated by an asterisk (*).

M. ADACHI*

- Doctor of Engineering
Group Manager, Transmission Devices Laboratory
2010 Paper Award in JSAP



M. KIYAMA

- Doctor of Engineering
Senior Assistant General Manager, Transmission Devices Laboratory



Y. YAMAMOTO

- Department Manager, Transmission Devices Laboratory



T. TAKEUCHI

- Doctor of Engineering
Professor
Toyota Technological Institute

