International Journal of Thermophysics, Vol. 18, No. 2, 1997

Measurements of the Seebeck Coefficient of Thermoelectric Materials by an AC Method[1]

T. Goto,[2, 3] J. H. Li,[2] T. Hirai,[2] Y. Maeda,[4]
R. Kato,[4] and A. Maesono[4]

An ac method for measurement of the Seebeck coefficient was developed. Specimens were heated periodically at frequencies in the range 0.2–10 Hz using a semiconductor laser. The small temperature increase and the resultant thermoelectric power were measured with a Pt–Pt 13% Rh thermocouple (25 μm in diameter) through a lock-in amplifier. The Seebeck coefficient of a $Pt_{90}Rh_{10}$ foil measured by the ac method was in agreement with that obtained from the standard table. The optimum frequency and specimen thickness for the ac method were 0.2 Hz and 0.1–0.2 mm, respectively. The Seebeck coefficients of silicon single crystal and several thermoelectric semiconductors ($Si_{80}Ge_{20}$, PbTe, $FeSi_2$, SiB_{14}) measured by the ac method agreed with those measured by a conventional dc method in the temperature range between room temperature and 1200 K. The time needed for each measurement was less than a few tens of minutes, significantly shorter than that for a conventional dc method.

KEY WORDS: ac method; platinum rhodium alloy; Seebeck coefficient; semiconductors; silicon germanium alloy; thermoelectricity.

1. INTRODUCTION

Recently, thermoelectric power generation has attracted significant attention due to the necessity of having efficient energy consumption and developing long-term stable power supplies in space [1]. The efficiency of thermoelectric conversion depends strongly on the materials, which are characterized mainly by the Seebeck coefficient, electrical conductivity, and thermal conductivity. Although electrical and thermal conductivity

---

[1] Paper presented at the Fourth Asian Thermophysical Properties Conference, September 5–8, 1995, Tokyo, Japan.

[2] Institute for Materials Research, Tohoku University, Sendai 980-77, Japan.

[3] To whom correspondence should be addressed.

[4] SHINKO-RIKO Inc., Yokohama 226, Japan.

measurements have been well established, experimental difficulties are encountered in precise measurement of the Seebeck coefficient. In general, thermoelectric power (ΔE) is measured under steady-state conditions maintaining a small temperature gradient (ΔT) within the material [2], and the Seebeck coefficient (S) is determined from the following equation:

$$S = \lim_{\Delta T \to 0} \frac{\Delta E}{\Delta T} \tag{1}$$

The major experimental problem in the steady-state (dc) method is the elimination of spurious dc thermal emf's from the measuring circuit or the contacts between the specimen and the lead wires. Therefore, the Seebeck coefficients are usually determined from the gradient of the ΔE-versus-ΔT relationship, implying that the measurements are conducted at several values of ΔT. However, it is often difficult and time-consuming to maintain a small ΔT for a long time keeping the specimen under a constant temperature. Several rapid methods for measurement of the Seebeck coefficient have been proposed [3, 4]. Freeman and Bass [5] reported an ac method and measured the Seebeck coefficient of aluminum within an accuracy of 1%. They heated the specimen with a tungsten lamp at a frequency of 21 Hz and measured the thermoelectric power using a prototype lock-in amplifier. Their system appeared to have had a problem for thermoelectric semiconductors because the frequency (21 Hz) was possibly too high for materials with a low thermal diffusivity. The accuracy of the ac method depends on the frequency used; the lower the frequency, the higher the accuracy. On the other hand, a modern lock-in amplifier enables one to perform accurate measurements even at less than 1 Hz [6].

The present paper describes the development of a rapid and precise ac measuring system for the Seebeck coefficient and discusses the optimum measuring conditions for a metal and several thermoelectric semiconductors.

2. EXPERIMENTS

A schematic diagram of the ac measurement equipment and measuring circuit is shown in Fig. 1. Pt_{90}% Rh10%($Pt_{90}Rh_{10}$) alloy, Si single crystal (n type), $Si_{80}Ge_{20}$ alloy (0.2 at % B doped), PbTe single crystal, $FeSi_2$, and sintered SiB_{14} were used as specimens. The specimens were 10 to 15 mm in length, about 4 mm in width, and 0.1 to 0.6 mm in thickness. Two sets of fine Pt–Pt 13% Rh thermocouples (Type R; 25 μm in diameter) were attached to the specimens using silver paste. One end (hot junction) was periodically heated with a semiconductor laser in the frequency range

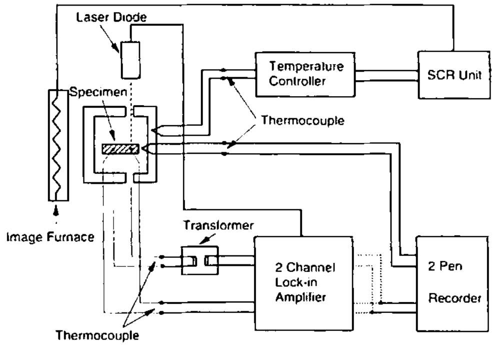

Fig. 1. Schematic diagram of the ac measuring equipment and circuit.

between 0.2 and 10 Hz. The temperature increase in the hot junction was 0.5–0.8 K depending on the frequency and the specific heat of the specimen. A higher frequency caused a smaller temperature increase at the hot junction. There was almost no temperature increase at the cold junction. The temperature difference between the hot and the cold junctions (ΔT) was obtained from the conversion of voltage to temperature using the standard table for a Pt–PtRh 13% thermocouple [7]. The thermoelectric power (ΔE) was measured between the Pt wires attached to the hot and cold junctions. The Seebeck coefficient (S) with respect to Pt was calculated as $S = \Delta E/\Delta T$. Temperatures of the junctions and thermoelectric powers were measured with a lock-in amplifier (Type LAD-1A, SHINKU-RIKO). The time constant of the lock-in amplifier was usually 5 or 10 s. The specimen temperature was raised to 1200 K using an infrared image furnace. The Pt–PtRh 13% thermocouple (0.3 mm in diameter) was placed just below the specimen to measure the average specimen temperature. The atmosphere was generally vacuum (at about 0.1 Pa) and occasionally Ar (at 67 kPa) to prevent sublimation of the specimen.

3. RESULTS AND DISCUSSION

Figure 2 shows the frequency dependence of ΔT for $Pt_{90}Rh_{10}$ foil (0.1 mm thick) at 293 and 673 K. The values of ΔT were almost independent of the frequency at $f = 0.2$–0.5 Hz and decreased with increasing frequency above 1 Hz. This trend was commonly observed for other materials. ΔT ranged between 0.4 and 0.8 K at $f = 0.2$ Hz, depending on the material and temperature.

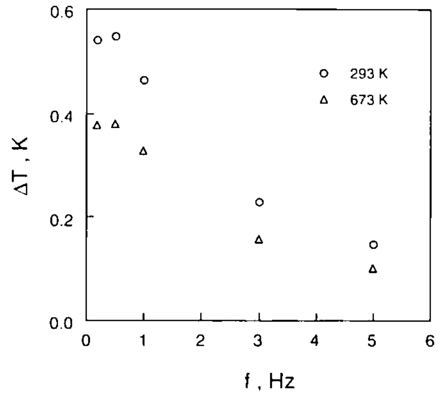

Fig. 2. Frequency dependence of temperature difference between the hot and the cold junctions (ΔT) for $Pt_{90}Rh_{10}$ at 293 and 673 K.

Figure 3 shows the temperature dependence of the Seebeck coefficient for the $Pt_{90}Rh_{10}$ foil with respect to Pt measured by the ac method and calculated using the standard table for Pt-$Pt_{90}Rh_{10}$ thermocouple (type S) [7]. The measured values were almost independent of frequency and were approximately $2\,\mu V \cdot K^{-1}$ greater than the calculated values. This slight difference may be caused by the disagreement between the standard values

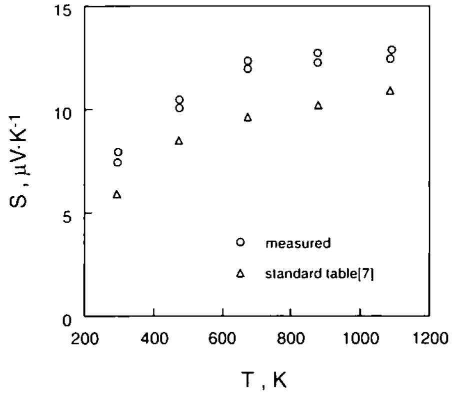

Fig. 3. Temperature dependence of the Seebeck coefficient of $Pt_{90}Rh_{10}$ measured by the ac method and the values obtained from the standard table for the Pt-$Pt_{90}Rh_{10}$ thermocouple (type S) [7].

[7] and the thermoelectric powers of very fine wires of Pt and PtRh 13% (25 μm in diameter).

Freeman and Bass [5] pointed that the temperature gradient around the hot junction could cause the discrepancy between the dc and the ac methods. When a material is periodically heated, the temperature in the immediate vicinity of the hot junction falls off as x/λ, after transient phenomena have diminished, where x is the distance from the hot junction, and λ is given by the following equation [8]:

$$\lambda = \sqrt{\frac{D}{\pi f}} \tag{2}$$

where D is the thermal diffusivity of the material, and f is the frequency. In their experiments, the hot junction was heated at a frequency of 21 Hz and chromel–alumel thermocouple (50 μm in diameter) was used. The values of λ for the chromel–alumel ($\lambda_{\mathrm{Ch\text{-}Al}}$) is 0.1 mm, and the diameter of thermocouple wires is approximately 50% of λ. In the present experiments, for Pt at room temperature, $D = 0.25\ \mathrm{cm^2 \cdot s^{-1}}$ [9], thus $\lambda_{\mathrm{Pt}} = 6.3$ mm at $f = 0.2$ Hz. The diameter of the Pt wire (50 μm in diameter) is only 0.8% of λ for Pt, which is small enough for the precise temperature measurement in the ac method. Therefore, temperature distribution around the hot junction is quite uniform in the present system. As shown in Fig. 2, a lower frequency yields a larger ΔT, which causes greater thermoelectric power. The higher signal-to-noise ratio also must have contributed to the more precise measurements in the lower frequency region.

Figure 4 shows the temperature dependence of the Seebeck coefficient (S) for Si single-crystal plates. The values of S for specimens 0.10 and

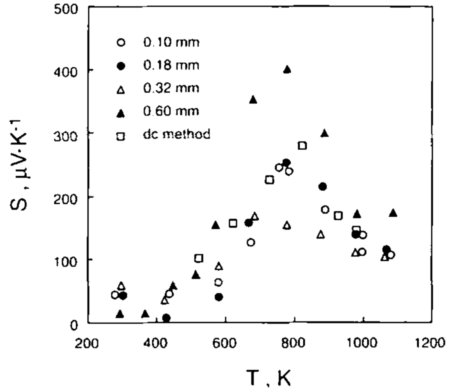

Fig. 4. Temperature dependence of the Seebeck coefficient of Si single crystals.

0.18 mm in thickness were in good agreement with the values obtained by the dc method. The values for 0.32- and 0.60-mm thicknesses are slightly smaller and greater than the other values, respectively.

When an ac thermal energy is supplied to a plate at a frequency (f), the thickness of the plate should be far thinner than the thermal diffusion length (λ^{-1}). Equation (3) should be satisfied to maintain a one-dimensional temperature gradient in the plate.

$$(d/\lambda) \ll 1 \tag{3}$$

where λ is given by Eq. (1), and d is the plate thickness. Since D is $1.06\ \mathrm{cm^2 \cdot s^{-1}}$ for Si at room temperature [10], $\lambda^{-1} = 0.08\ \mathrm{mm^{-1}}$ at $f = 0.2$ Hz. Therefore, $d/\lambda = 0.016$ for the specimen of $d = 0.2$ mm, which satisfies Eq. (3). Although the appropriate thickness depends on the material, the thickness of 0.1–0.2 mm is usually thin enough for the ac method.

Figure 5 shows the frequency dependence of the Seebeck coefficient (S) for $\mathrm{Si_{80}Ge_{20}}$ thermoelectric semiconductor at 873 K. The values of S for 0.60 mm in thickness increased with increasing frequency; however, the values for 0.30 and 0.10 mm in thickness are in good agreement with those of the dc method. For $\mathrm{Si_{80}Ge_{20}}$, since $D = 0.02\ \mathrm{cm^{-1} \cdot s^{-1}}$ at room temperature [11], $d/\lambda = 0.05$ for the specimen of $d = 0.10$ mm at $f = 0.2$ Hz. This may satisfy Eq. (3) in the case of $\mathrm{Si_{80}Ge_{20}}$. A thickness of 0.60 mm may be too thick, which could cause the inhomogeneous temperature distribution within the specimen. Figure 6 shows the temperature dependence of S values for $\mathrm{Si_{80}Ge_{20}}$. The S values of 0.30 and 0.10 mm in thickness agreed with those by the dc method in the whole temperature range.

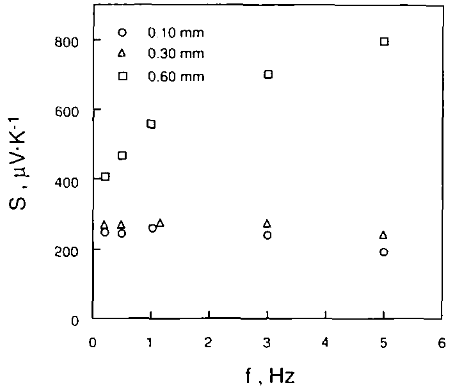

Fig. 5. Frequency dependence of the Seebeck coefficient of $\mathrm{Si_{80}Ge_{20}}$ at 873 K.

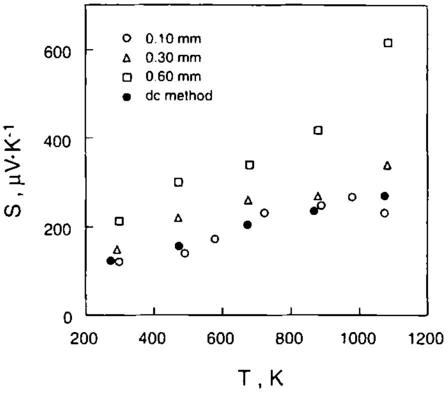

Fig. 6. Temperature dependence of the Seebeck coefficient of $Si_{80}Ge_{20}$.

In the ac measurements, the specimen thickness should be thin enough to satisfy Eq. (3), particularly for low-thermal diffusivity materials. Although the mechanical strength may determine the smallest thickness, it is usually not difficult to prepare specimens of $d = 0.1$–0.3 mm which seem thin enough for the ac measurements. In each measurement, at $f = 0.2$ Hz, a stable thermoelectric power was established within a few tens of minutes after the specimen temperature was stabilized. The dc method often takes several hours because the measurements have to be conducted at several

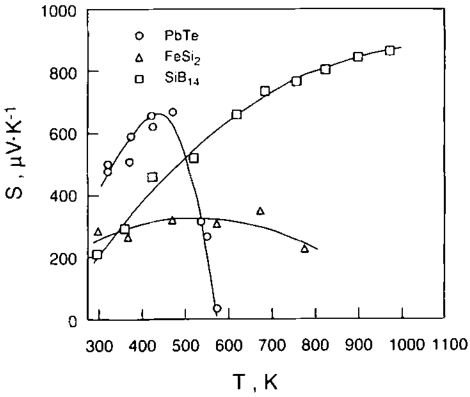

Fig. 7. Temperature dependence of the Seebeck coefficient of PbTe, $FeSi_2$, and SiB_{14} measured by the ac method.

values of ΔT to eliminate spurious emf's. Therefore, the present ac method is also advantageous for the rapid measurement of Seebeck coefficient. Figure 7 shows the temperature dependence of the Seebeck coefficient obtained by the ac method for several thermoelectric semiconductors. We confirmed that these results obtained by the ac method agreed well with those by the dc method.

4. CONCLUSION

We have successfully constructed a precise and rapid ac system for measuring the Seebeck coefficient using a high precision lock-in amplifier, high-power semiconductor laser, and fine Pt–PtRh 13% thermocouple (25 μm in diameter). The optimum measuring frequency and thickness of specimens were 0.2 Hz and 0.1–0.3 mm, respectively. The Seebeck coefficient of Pt90% Rh10% foil measured by the ac method was in agreement with the values obtained from the standard table. The Seebeck coefficients for several semiconductors such as Si, $Si_{80}Ge_{20}$, PbTe, $FeSi_2$, and SiB_{14} measured by the ac method agreed well with those by a conventional steady-state (dc) method.

ACKNOWLEDGMENTS

This research was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture under Contracts NP0601 and 06453081 and, also, by the Special Coordination Funds for Promoting Science and Technology from the Science and Technology Agency of Japan. We extend our appreciation to Professors K. Matsubara (Yamaguchi University) and Y. Noda (Tohoku University) and Drs. M. Imai (Komatsu Electronic Metals), T. Noguchi (Vacuum Metallurgical), and L. Chen (National Aerospace Laboratory) for supplying specimens of $FeSi_2$, PbTe, Si, $Si_{80}Ge_{20}$, and SiB_{14}, respectively.

REFERENCES

1. C. Wood, in *Mater. Res. Soc. Symp. Proc., Vol. 97* (Mater. Res. Soc., Pittsburgh, 1987), pp. 335–346.
2. R. R. Heikes and R. W. Ure, *Thermoelectricity* (Interscience, New York, 1961).
3. J. E. Ivory, *Rev. Sci. Instrum.* **33**:992 (1962).
4. G. R. Caskey and D. J. Sellmyer, *Rev. Sci. Instrum.* **40**:1280 (1969).
5. R. H. Freeman and J. Bass, *Rev. Sci. Instrum.* **41**:1171 (1970).
6. I. Hatta, Y. Sasuga, R. Kato, and A. Maesono, *Rev. Sci. Instrum.* **56**:1643 (1985).
7. R. L. Powell and G. W. Burns, *National Bureau of Standards Monograph 125, Suppl. 1* (U.S. Government Printers, Washington, DC, 1975).

8. H. S. Carslow and J. C. Jaeger, *Conduction of Heat in Solids*, 2nd ed. (Oxford University Press, London 1959), pp. 92–132.
9. J. J. Martin, P. H. Sidles, and G. C. Danielson, *USAEC Rept. IS-1261, Conf-651020-2* (1965), pp. 1–11.
10. H. R. Shanks, P. D. Maycock, P. H. Sidles, and G. C. Danielson, *Phys. Rev.* **130**:1743 (1963).
11. J. W. Winslow, *USNRDL-TR-67-83*, (1967), pp. 1–107.

Printed in Belgium