Huge thermopower of porous Y_2O_3

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Porous Y_2O_3 ceramic was found to show huge thermopower values up to -50 mV/K at 900–1000 K in vacuum, but not in air. Such huge thermopowers may be generated by the electron gas emitted from the internal surfaces of the pores and are associated with some unknown effects. The nondimensional thermoelectric figure of merit, ZT, of this porous ceramic was as large as ~ 0.95 at ~ 950 K, and hence, it can be used as a thermoelectric material. © *1997 American Institute of Physics.* [S0003-6951(97)03237-3]

A temperature difference applied across a solid generates an electromotive force, characterized by the thermopower of the solid. This phenomenon is called the Seebeck effect and is applied to thermoelectric power generation and temperature sensing. When a direct current is passed through a solid, the one end is cooled and the other end is warmed. This phenomenon is called the Peltier effect and is applied to both thermoelectric cooling and heating. Solid materials used for these applications require high electrical conductivity (σ), large thermopower (α), and low thermal conductivity (κ), so that they have large thermoelectric figures of merit, $Z(=\sigma\alpha^2\kappa^{-1})$, and hence, show high-energy conversion efficiencies (preferably, $ZT>1$, where T is the absolute temperature). Tellurides and selenides of Bi, Sb, Pb, etc., and SiGe alloys have so far been developed as high-Z materials.[1] Recently, investigations of materials such as $CoSb_3$ solid solutions[2,3] and superlattice structured thin films[4–6] have been actively carried out since they are expected to meet the criterion, $ZT>1$.

We have discovered that huge thermopower values of about -50 mV/K can be generated by porous yttrium oxide (Y_2O_3) ceramic at high temperatures (900–1000 K) in vacuum ($\sim 1.3\times 10^{-3}$ Pa) (See Fig. 1). In general, metals show only small thermopowers of the order of a few tens of μV/K and semiconductors show some hundreds of μV/K. Insulators typically have very large thermopower values, but the thermopower of insulators is hard to measure. Sher has reported that a porous body of (Ca, Sr, Ba)O solid solution having a low work function (~ 1.7 eV) also generates a large thermopower of about -2 mV/K at 1000 K in vacuum ($\sim 1.3\times 10^{-5}$ Pa).[7] In the present study, however, porous Y_2O_3 ceramic demonstrated one order of magnitude larger thermopower.

Porous Y_2O_3 ceramic was fabricated by common ceramic processing techniques. The starting powder of Y_2O_3 (Kojundo Chemical Laboratory, 99.9% pure) was mixed with 20–25 wt % liquid paraffin. The mixture was packed in a rubber bag, isostatically pressed at 196 MPa, and fired at 1723 K for 1 h in air. The porosity was measured in pure water by an Archimedes method. Electrical conductivity and thermopower were simultaneously measured under vacuum ($\sim 1.3\times 10^{-3}$ Pa) or in air. Details of the method of measurement for ceramic specimens are described elsewhere.[8]

The huge thermopower of porous Y_2O_3 ceramic is considered to be associated with the fact that Y_2O_3 possesses a rather low work function [~ 2.0 eV (Ref. 9)]. Namely, when the temperature is raised in vacuum, thermionic emission takes place from the internal surfaces of the pores giving rise to an electron gas filling the pores. The huge thermopower must have been generated by applying the temperature difference to the electron gas. As shown in Fig. 1, only a small thermopower was observed in air, which indicates that thermionic emission hardly took place because of the presence of air molecules. However, theoretical evaluation of the thermopower of the free electrons using a simplified equation[10] cannot explain such a huge thermopower, so that some other unknown effects must be responsible, though they remain to be clarified in future studies.

Our measurement indicates the electrical conductivity, σ, (dc four-probe technique) increases gradually with increasing temperature up to ~ 850 K under vacuum, and is approximately the same as that measured in air, as shown in Fig. 2. Above ~ 850 K σ suddenly increases, deviating sharply from the value measured in air. This observation

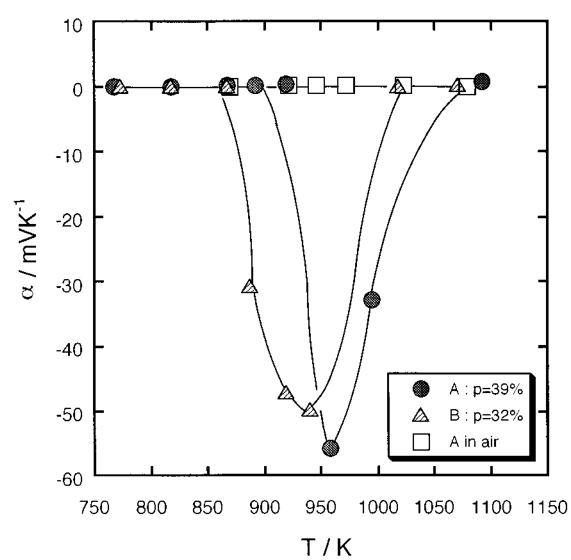

FIG. 1. Temperature dependencies of the thermopower, α, for two specimens, A and B, with different porosities, p. The values of α for specimen A measured in air are shown for comparison.

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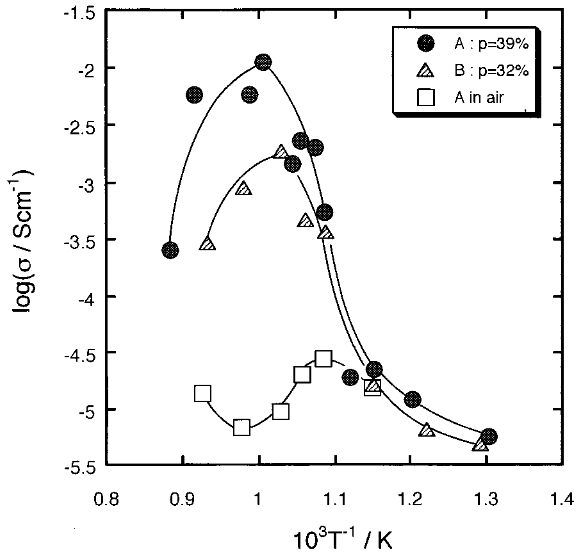

FIG. 2. Temperature dependencies of the electrical conductivity, σ, for two specimens, A and B, with different porosities, p. The values of σ for specimen A measured in air are shown for comparison.

clearly indicates that thermionic emission takes place above $\sim$850 K in vacuum but not in air. Both the electrical conductivity and the thermopower begin to decrease when the temperature is raised above $\sim$1000 K. The reason for this phenomenon is still unknown.

The thermal conductivity, κ, of specimen A with 39% porosity was measured under vacuum by a laser flash method. κ decreased slightly with increasing temperature and was as low as 1.42–1.62 $WK^{-1}\,m^{-1}$ at 700–1100 K, as shown in Fig. 3. Combination of the measured σ, α, and κ enabled us to calculate the values of Z for porous Y_2O_3 ceramic. The obtained Z was as large as $\sim 1.0\times 10^{-3}\ K^{-1}$ at 950 K ($ZT\sim 0.95$), almost meeting the above criterion, $ZT > 1$.

Although it should be possible to optimize for larger Z values in a wider temperature range, this material is expected to become a promising candidate for future thermoelectric energy conversion. The potential problem of integrating this material in working devices is that it only works at high temperatures in vacuum. However, this problem could be overcome if the devices can be suitably confined in a vacuum container, or if they are operated in space.

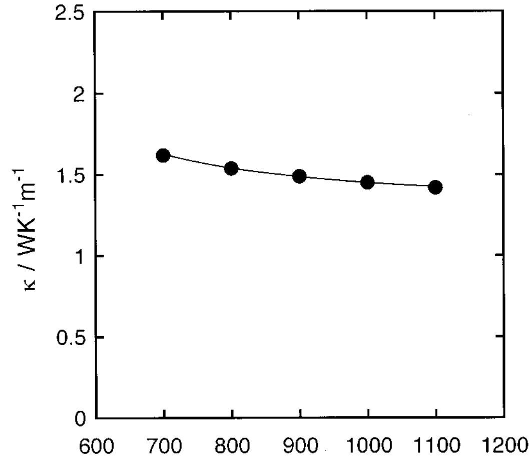

FIG. 3. Temperature dependence of thermal conductivity, κ, for specimen A with 39% porosity.

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[1] K. Uemura and I. Nishida, *Thermoelectric Semiconductors and Their Applications* (Nikkan Kogyo Shinbun, Tokyo, 1988).
[2] T. Caillat, A. Borschevsky, and J.-P. Fleurial, J. Appl. Phys. **80**, 4442 (1996); **79**, 8419 (1996).
[3] B. C. Sales, D. Mandrus, and R. K. Williams, Science **272**, 1325 (1996).
[4] L. D. Hicks T. C. Harman, X. Sun, and M. S. Dresselhaus, Phys. Rev. B **53**, R10 493 (1996).
[5] J. O. Sofo and G. D. Mahan, Appl. Phys. Lett. **65**, 2690 (1994).
[6] P. J. Lin-Chung and T. L. Reinecke, Phys. Rev. B **51**, 13 244 (1995).
[7] E. M. Sher, in *Proceedings of the 15th International Conference on Thermoelectrics*, edited by T. Caillat (IEEE, Piscataway, NJ, 1996), pp. 168–171.
[8] H. Ohta, W. S. Seo, and K. Koumoto, J. Am. Ceram. Soc. **79**, 2193 (1996).
[9] *Handbook of Chemistry—Fundamental Chemistry Edition* (Chemical Society of Japan, Tokyo, 1993), p. 490.
[10] F. G. Baksht, G. A. Dyuzhev, A. M. Martsinovskiy, B. Ya. Moyzhes, G. Ye. Pikus, E. B. Sonin, and V. G. Yur'yev, *Thermionic Converters and Low-Temperature Plasma* (U.S. Department of Energy, 1978), p. 16.