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THERMOELECTRIC PROPERTIES OF OXIDE CERAMICS

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Abstract – Thermoelectric properties of several oxides were investigated. Al_2O_3-, TiO_2- or ZrO_2-doped ZnO showed large power factor over the wide temperature range. Fe_2O_3 showed large power factor by doping of TiO_2. BaO-doped RuO_2, $BaRuO_3$ and $CaRuO_3$ showed large power factor at high temperature. Improvement of electrical conductivity by doping was effective to increase power factor in these oxide materials.

Key words: *Thermoelectricity, Seebeck Effect, Power Factor, ZnO, Fe_2O_3, RuO_2*

INTRODUCTION

Thermoelectric generation is a direct conversion technique from thermal energy to electric energy. Fig. 1 shows materials that had been researched for thermoelectric generator [Uemura and Nishida, 1988]. The performance of thermoelectric materials was characterized by figure of merit Z,

$$Z = \alpha^2\sigma/\kappa \quad (1)$$

where α is the Seebeck coefficient, σ electrical conductivity and κ thermal conductivity. Consequently, large α and σ, and small κ are essential for thermoelectric materials. κ is in the same order of magnitude among similar materials. Then, power factor ($=\alpha^2\sigma$) can be used as an index for thermoelectricity. Thermoelectric generator has some advantages; 1) small internal resistance, which leads to large power supply, 2) ease to obtain high voltage by connecting some modules in series, even though it has small open circuit voltage for 1 module, 3) no noise and no vibration because of no moving parts, 4) ease of down sizing and getting light weight, 5) long lifetime [Uemura and Nishida, 1988]. On the other hand, there is a disadvantage that an energy conversion efficiency is low. However, both Carnot efficiency and a thermal-electric energy conversion efficiency increase at high temperature. Thus, some silicides ($FeSi_2$, $CrSi_2$, etc.) [Sakata and Nishida, 1976], SiC [Pai et al., 1991] and B_4C [Kawaguchi and Kawashima, 1993] have been investigated for high temperature thermoelectric materials. However, there is few research on oxide materials, which are stable at high temperature under air. In the present work, thermoelectric property of oxide materials which show a high electrical conductivity over wide temperature range was studied.

ZnO-BASED MATERIAL

1. Preparation and Measurement

Commercial ZnO powder (Hayashi Pure Chemical Ind., Ltd., 99.0%) and dopant oxide powder were dispersed in distilled water by ultrasonic agitation, and dried by a rotary evaporator. The powders were also prepared by co-precipitation or homogeneous precipitation. The mixed oxide powders were ground in an agate mortar, compacted into a rod (diameter : 5 mm, length : 20 mm) by isostatic pressing at 400 MPa and sintered at 1100°C or 1400°C for 2h in air. The density of sintered body was measured by Archimedes' method.

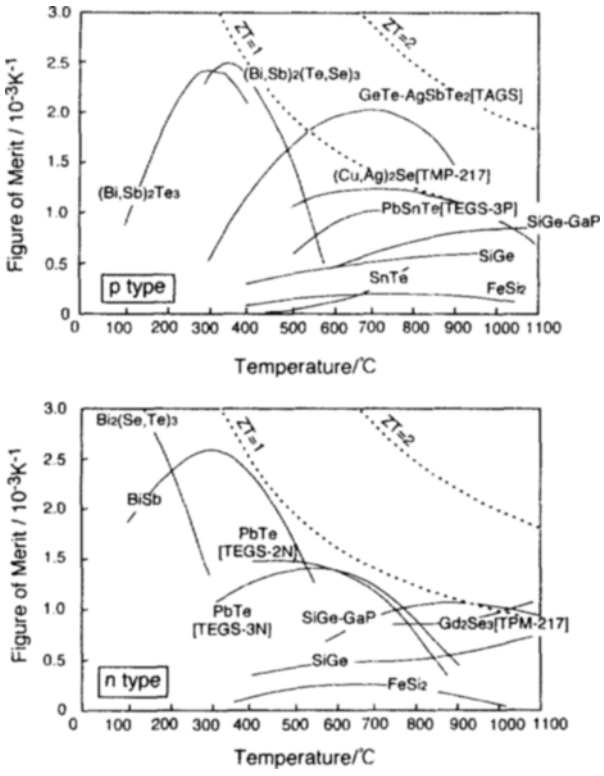

Fig. 1. Figure of merit of thermoelectric materials.

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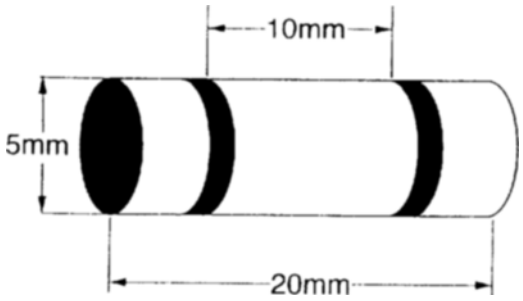

Fig. 2. Sample configuration for measurement.

Platinum paste was applied on the sintered body as shown in Fig. 2 and was fired at 1000°C for 1 hr in air. Thermoelectromotive force was measured by using a multimeter (Advantest Co., R6441B) under about 20°C difference for both ends of sample and Seebeck coefficient (α) was calculated. Electrical conductivity (σ) of sample was measured by 4-point method by using a potentiostat (Hokuto Denko Co. Ltd., HA-301) under the both ends of sample at the same temperature. These measurements were carried out from 300 to 1000°C in air. The performance of each sample was characterized by power factor ($=\alpha^2\sigma$) and the effects of dopants and sintering temperature were examined. Crystalline phase in sintered samples was analyzed by powder X-ray diffraction (XRD, Rigaku Co., Mini Frex).

2. Effect of Dopants

Power factors of ZnO doped with several oxides were shown in Fig. 3. Seebeck coefficients decreased by doping, except Nb_2O_5 at low temperature. Electrical conductivity, on the other hand, increased by doping, especially by doping of TiO_2. The sample doped with Nb_2O_5 shows a large power factor only at high temperature. On the other hand, TiO_2 doping gives large power factor over the wide temperature range. However, these power factors were 10-100 times smaller than that reported on Al_2O_3-doped ZnO [Tsubota et al., 1995].

3. Effect of Sintering Temperature

The effects of sintering temperature on the thermoelectricity of ZnO-TiO_2 and ZnO-Al_2O_3 systems were examined. Both TiO_2 and Al_2O_3-doped samples sintered at 1400°C showed smaller Seebeck coefficient and larger electrical conductivity than those sintered at 1100°C. This may be due to the densification of sintered body and the increase of Ti or Al which dissolved in ZnO lattice at higher sintering temperature. The power factors of these samples are shown in Fig. 4. TiO_2 doped sample sintered at 1400°C shows a smaller power factor than that sintered at 1100°C. On the other hand, Seebeck coefficient of Al_2O_3-doped sample sintered at 1400°C decreased remarkably, but a large power factor was obtained due to a remarkable increase in electrical conductivity at high temperatures.

4. ZnO-TiO_2 System

The effects of amount of TiO_2 dopant on the thermoelectricity of ZnO-TiO_2 system were examined. Fig. 5 shows the relation between power factor and TiO_2 content. Seebeck coefficient changed little with doping amount of TiO_2. Electrical conductivity showed a maximum at TiO_2 content of 0.1-0.2 mol% and power factor also showed a maximum. When TiO_2 content was above 0.2 mol%, electrical conductivity decreased. It may be due to the formation of high resistivity phase in samples. XRD on ZnO-TiO_2 systems showed the formation of Zn_2TiO_4. The amount of Zn_2TiO_4 formed increased with increase of TiO_2 content.

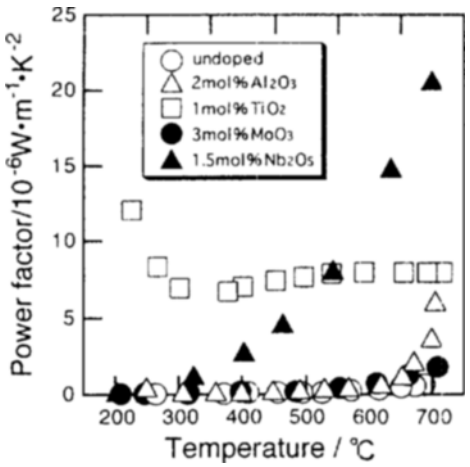

Fig. 3. The effect of dopants on power factor of ZnO sintered at 1100°C.

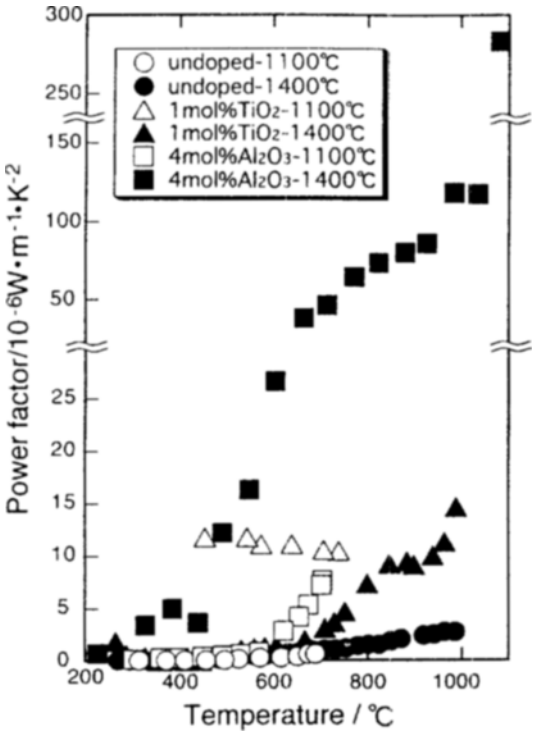

Fig. 4. The effect of sintering temperature on power factor of ZnO-TiO_2 and ZnO-Al_2O_3 systems.

5. ZnO-ZrO_2 System

The effects of amount of ZrO_2 on the thermoelectricity of ZnO-ZrO_2 system were examined. Fig. 6 shows the relation between power factor and ZrO_2 content. Both Seebeck coefficient and electrical conductivity showed a maximum at around 1 mol% ZrO_2. When ZrO_2 content was 1 mol%, power factor showed a maximum and was large over the wide tem-

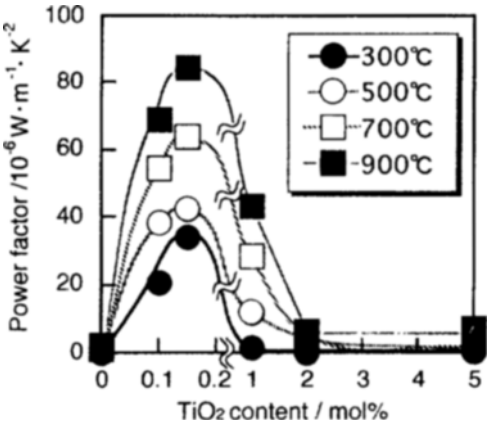

Fig. 5. The effect of amount of TiO_2 on power factor of ZnO-TiO_2 system sintered at 1400°C.

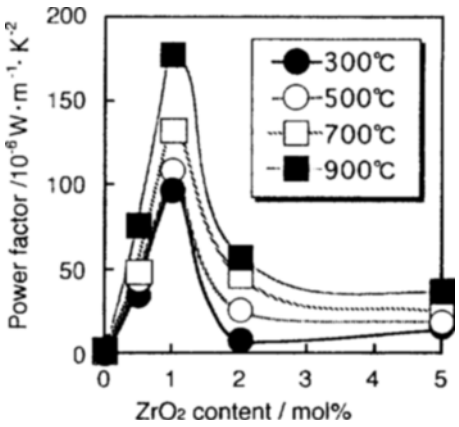

Fig. 6. The effect of amount of ZrO_2 on power factor of ZnO-ZrO_2 system sintered at 1400°C.

perature range.

Fe_2O_3-BASED MATERIAL

The effect of dopant on thermoelectricity of Fe_2O_3-based material was examined. Preparation method and measurement procedure were same as those of ZnO-based material. Commercial Fe_2O_3 (ISHIZU SEIYAKU Co., Ltd.) and dopant powders were mixed in ethanol and dried. The mixed oxide powders were ground in an agate mortar, compacted into a rod and sintered at 1200°C or 1400°C for 2 hr in air or N_2 atmosphere. Electrical measurements were carried out in air or N_2.

After sintering, only Fe_3O_4 phase was detected. Seebeck coefficient of samples doped with ZrO_2 or WO_3 decreased with increase of temperature. On the other hand, that of TiO_2-doped sample changed little with temperature. Electrical conductivity of these samples were increased by doping. Fig. 7 shows the effect of dopant on power factor of Fe_3O_4 sintered at 1200°C in N_2. The TiO_2-doped sample showed the largest power factor. Electrical conductivity of all samples increased by sintering at 1400°C than at 1200°C. This may be due to increase of density and degree of reduction of Fe_3O_4. The reduction was also accelerated by sintering in N_2, resulting in an increased power factor.

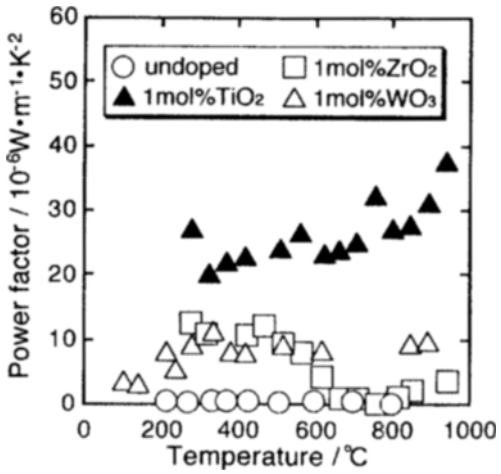

Fig. 7. The effect of dopants on power factor of Fe_3O_4 sintered at 1200°C in N_2 (measurement in N_2 atmosphere).

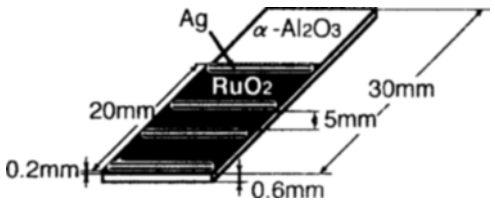

Fig. 8. RuO_2 film and electrodes for thermoelectric measurement.

RuO_2-BASED MATERIAL

Commercial RuO_2 powder (SHOEI CHEMICAL INC.) and dopant were mixed in ethanol. The mixed powder was heated in air at 900°C for 2h and ground in an agate mortar. The powder was mixed with organic vehicle (ethyl cellulose and terpineol), and the resulting paste was applied onto α-alumina substrate and fired in air at 900°C for 2h. The thickness of film was about 0.2 mm. Ag paste was applied on the film as electrode and fired at 800°C in air for 0.5h. Sample configuration for thermoelectric measurement is shown in Fig. 8.

BaO-doped RuO_2 showed a large power factor at high temperature because of increase in Seebeck coefficient. All of other (CoO, MgO, Ag_2O, CuO, Fe_2O_3, Al_2O_3, Bi_2O_3, Y_2O_3, Nb_2O_5 and MoO_3) showed smaller power factor than undoped RuO_2. The effect of amount of BaO on power factor is shown in Fig. 9. Seebeck coefficient increased with BaO content and showed a maximum at BaO content of 2 mol%. Electrical conductivity decreased with increase of BaO content due to the formation of highly resistive $BaRuO_3$ phase. As the results, power factor showed a maximum at 2 mol%-BaO-doping.

When BaO content was 50 mol%, only $BaRuO_3$ phase was detected by XRD. Fig. 10 shows power factor of $BaRuO_3$, $CaRuO_3$ and 2 mol%-BaO-doped RuO_2. $CaRuO_3$ showed larger Seebeck coefficient and electrical conductivity than $BaRuO_3$, and showed large power factor (4×10^{-4} $W\cdot m^{-1}\cdot K^{-2}$ at 900°C). These results suggest that there is a possibility to find a potential thermoelectric material among oxides with perovskite structure.

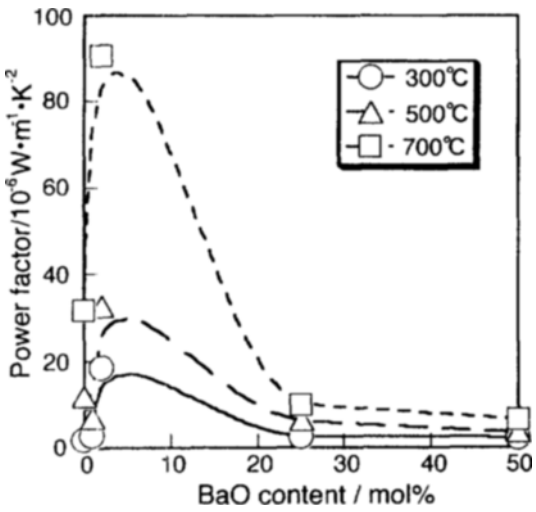

Fig. 9. The effect of amount of BaO on power factor of RuO_2-BaO system sintered at 900°C.

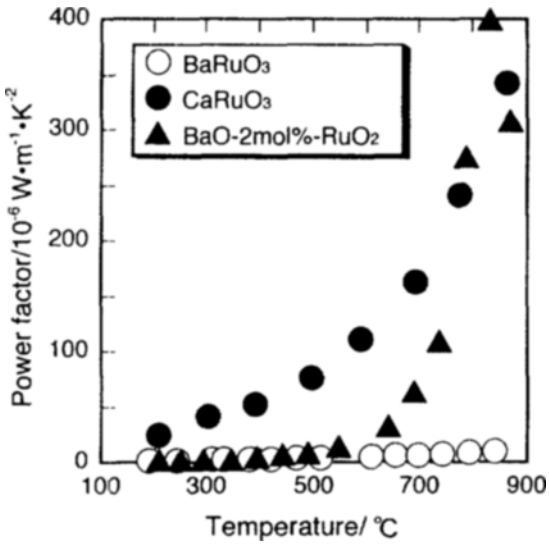

Fig. 10. Temperature dependence of power factor of $BaRuO_3$, $CaRuO_3$ and 2 mol%-BaO-doped RuO_2 sintered at 900°C.

CONCLUSIONS

The results in the present work were summarized as follow:

1. Al_2O_3, TiO_2 or ZrO_2 doped ZnO showed a large power factor at the wide temperature range. Fe_2O_3 showed large power factor by doping with TiO_2, but its figure was small compared with ZnO system. In these oxide materials, improvement of electrical conductivity by doping was effective to increase power factor.

2. There is a possibility to find a potential thermoelectric material among perovskite-structure oxide.

ACKNOWLEDGMENT

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NOMENCLATURE

Z : figure of merit [K^{-1}]
α : Seebeck coefficient [$V \cdot K^{-1}$]
σ : electrical conductivity [$S \cdot m^{-1}$]
κ : thermal conductivity [$W \cdot m^{-1} \cdot K^{-1}$]

REFERENCES

Kawaguchi, M. and Kawashima, T., "Basic Thermoelectric Properties for New Graphite-like Materials of Composition BC_XN(X=1,3) Prepared by Chemical Vapour Deposition (CVD) Method", in Proceeding of 12th International Conference on Thermoelectrics (ICT), Yokohama, Japan, edited by K. Matsuura, p. 268-271, November 1993.

Pai, C. H., Sasaki, Y., Koumoto, K. and Yanagida, H., "Reaction Sintering of Polycarbosilane-Impregnated Compact of Silicon Carbide Hollow Particles and the Resultant Thermoelectric Properties", *J. Am. Ceram. Soc.*, **74**, 2922 (1991).

Sakata, T. and Nishida, N., "Thermoelectric Properties of Semiconducting 3d-Transition Metal Disilicides", *Bulletin Jpn. Institute Metals*, **15**, 11 (1976).

Tsubota, T., Otaki, M., Eguchi, K. and Arai, H., "Transport Properties and Thermoelectric Figure of Merit of ZnO-based Mixed Oxide", in Proceedings of Fall Meeting of the Ceramic Society of Japan, p. 281, 1995.

Uemura, K. and Nishida, I., "Thermoelectric Semiconductors and Their Applications", Nikkan Kogyo Shinbun Press, Tokyo, Japan, p. 1-10 (1988).