Microstructure and Sintering Behavior of ZnO Thermoelectric Materials Prepared by the Pulse-Current-Sintering Method

Noboru Shikatani[1,a], Tatsuya Misawa[1,b], Yasunori Ohtsu[1,c], Hiroharu Fujita[1,d],
Yuji Kawakami[2,e], Takashi Enjoji[2,f]

[1]Saga University
[1]Honjo-machi Saga-shi Sagaken 840, Japan
[2]Industrial Technology Center of Saga
114 Yaemizo Nabeshima-machi Saga-shi Saga-ken 849-0932, Japan
[a]sikatani@emat.fit.ac.jp, [b]misawa@ep.ee.saga-u.ac.jp, [c]ohtsu@ep.ee.saga-u.ac.jp.
[d]fujita@plasma.ep.ee.saga-u.ac.jp, [e]kawakami@saga-itc.go.jp, [f]enjoji@saga-itc.go.jp

Abstract

Thermoelectric conversion efficiency of thermoelectric elements can be increased by using a structure combining n-type and p-type semiconductors. From the above point of view, attention was directed at ZnO as a candidate n-type semiconductor material and investigations were made. As the result, a dimensionless figure of merit ZT close to 0.28 (1073K) was obtained for specimens produced by the PCS (Pulse Current Sintering) method with addition of specified quantities of TiO_2, CoO, and Al_2O_3 to ZnO. It was found that the interstitial TiO_2 in the ZnO restrains the grain growth and CoO acts onto the bond between grains. The influence of the inclusion of TiO_2 and CoO onto the sintering behavior also was investigated.

Keywords : ZnO thermoelectric materials, Pulse-Current-Sintering method, Figure of merit, Crystal grain size

1. Introduction

Recently, oxide materials with markedly high heat tolerance compared with intermetallic compounds are considered to be promising as thermoelectric materials. On the basis of this background, ZnO-type materials are attracting much attention as thermoelectric materials for n-type oxide semiconductors, and many reports have been published on studies of these materials.[1, 2] However, there are problems to be resolved regarding thermoelectric materials of this type. For example, if Al_2O_3 doped ZnO materials are sintered in a regular electric furnace, high temperature (˜ 1673 K) is required to decrease the electric resistance of the materials. Furthermore, such high-temperature sintering causes an increase in thermal conductivity because the treatment is accompanied by grain growth due to the high temperature. In this study, we sintered a predetermined amount of micro-ZnO particles and their additives, Al_2O_3, TiO_2, and CoO, by PCS (sintering; ˜ 1400K) and obtained a specimen consisting of ultrafine crystal particles connected by necks because of the suppression of grain growth; the specimen has relatively good thermoelectrical characteristics.

2. Experimental and Results

We accurately measured the predetermined weight of the starting raw materials, ZnO, Al_2O_3, TiO_2 and CoO, and wet-mixed these materials using a ball mill for 24 h. After drying the specimen, we filled the graphite molds in a PCS apparatus (SPS-3.20MK-4) with a predetermined amount of mixed powder and sintered the powder by PCS at 1373-1423 K for 10 min in atmosphere at an applied pressure. To study the state of the microstructure of the sintered body, the apparent density was determined by the Archimedes method, the structure was examined by SEM, and the phase was identified by powder XRD analysis. The values of Z ($S^2/\rho \kappa$), which indicate the thermoelectric characteristics of a specimen, were obtained as follows: resistivity ρ, by the dc four probe method; Seebeck coefficient S, from the electromotive force induced by applying a temperature difference of 4-8 K across the specimen; and thermal conductivity κ, by the laser flush method using a disk-shaped specimen (ϕ10).

In this study, a dopant (Al_2O_3), which reduces resistivity, and sintering aids (TiO_2 and CoO) were used as additives to ZnO. As compositions (rate;mol), $100ZnO-2Al_2O_3$ (ZA), $100ZnO-2TiO_2-2Al_2O_3$(ZTA),$100ZnO-2CoO-2Al_2O_3$(ZCA), and $100ZnO-2TiO_2-2CoO-2Al_2O_3$ (ZTCA) were used. The thermoelectric materials were evaluated in terms of the microstructure of the sintered body, densification characteristics in specimens ZA and ZTCA, and thermoelectric characteristics.
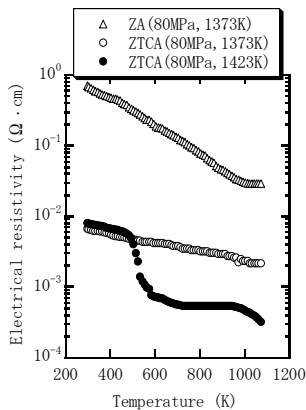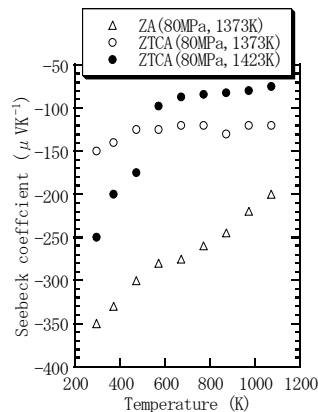
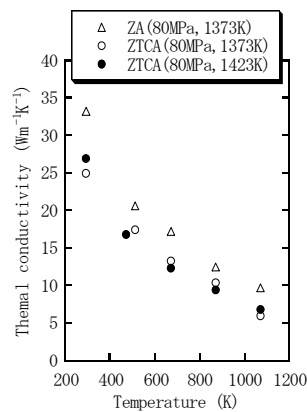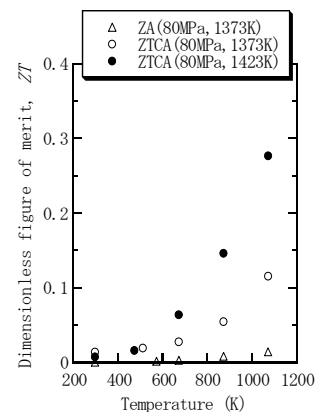**Fig. 1.** Correlation of T vs. ρ.   **Fig. 2.** Correlation of T vs. S.   **Fig. 3.** Correlation of T vs. κ.   **Fig. 4.** Correlation of T vs. ZT.

We studied the microstructure of sintered specimens of ZA, ZTA, ZCA and ZTCA. The particles in ZA specimens were approximately 1-3 μm in diameter, and pores are obse- rved locally between particles, showing poor sintering characteristics. The ZTA specimens prepared by adding TiO_2 to ZA consist of grains approximately 0.5-1 μm in diameter; the structure is orderly, and the grain growth is suppressed compared with that of ZA specimens. Grain growth and interparticle neck bonds are observed in ZCA specimens. The ZTCA specimens consist of orderly microparticles, and both boundary connected sections and neck bond sections are observed between particles. From the XRD patterns, we can identify a ZnO single phase and a $ZnAl_2O_4$ spinel phase in ZA, and a ZnO single phase and a mixed phase of $ZnTiO_4$ and $ZnAl_2O_4 \cdot CoZnTiO_4$ in ZTCA. The formation of the spinel phase of $ZnAl_2O_4$, which is related to the increase in the resistance of the specimen, is clearly observed in specimen ZA.

We then investigated the thermoelectric characteristics of specimens ZA and ZTCA in terms of resistivity, Seebeck coefficient, thermal conductivity, and dimensionless figure of merit. Fig. 1 shows the resistance-temperature characteristics. From these results, the resistivity of specimen ZA is 0.8 Ωcm at room temperature, and 0.03 Ωcm at 1100 K; the resistivity decreased markedly with increasing temperature. In the case of specimen ZTCA, the resistivity at room temperature was lower by two orders of magnitude than that of ZA. The microstructure of the specimens, which show low resistivity, consists of, as described, aggregates of particles, the diameter of which is 0.5-1 μm. The particles are bonded by necks. The high resistance of ZA compared with that of ZTCA is caused by the formation of the spinel phase of $ZnAl_2O_4$. On the other hand, as shown in Fig. 2, the absolute value of the Seebeck coefficient decreased with increasing temperature. This tendency matches well the decrease in resistivity shown in Fig. 1.

Figure 3 shows the relationship between the thermal conductivity and the temperature of the specimens. According to Fig. 3, the thermal conductivities of ZA and ZTCA decreased markedly with increasing temperature; the thermal conductivity of ZTCA decreased in all temperature regions measured, in comparison with that of ZA. The greater reduction in thermal conductivity in ZTCA than in ZA can be explained by 1) the blockage of the thermal conduction path due to the presence of spaces, and 2) the reduction of lattice thermal conductivity due to phonon scattering at crystal grain boundaries of fine particles.[3, 4]

Figure 4 shows the characteristics of the ZT that can be used for the evaluation of thermoelectric characteristics. In both ZA and ZTCA, ZT tended to increase with temperature; this phenomenon is clearly observed in ZTCA sintered at 1423 K. The maximum ZT of ZTCA sintered at 1423 K is approximately 0.28 (1073 K); this value is relatively high for ZnO-type thermoelectric materials.

3. Summary

The specimens consisting of ZTCA sintered at 1423 K for 10 min by PCS have relatively high values of ZT, approximately 0.28 (1073 K), for materials in the zinc oxide group. The reason for the relatively high ZT value can be 1) the reduction of thermal conductivity caused by the suppression of grain growth by the presence of TiO_2, or 2) the reduction of resistance caused by the formation of interparticle necks due to the presence of CoO.

4. References

1. M. Ohtaki, T. Tsubota, K. Eguchi and H. Arai：J. Appl. Phys., **79 [3]**,816-18(1996).
2. H. Ohta, W. Seo and K. Koumoto：J. Am. Ceram. Soc., **79 [8]**,193-96(1996).
3. C. M. Bhandari and D. H. Rower：Proc, 2nd International Conference on Thermoelectric Energy Conversion, p.32-35 (1978).
4. G. A. Slack and M. A. Hussain：J. Appl. Phys., **70 [5]**, 2694-718(1991)