

The Effect of Ag Addition on Thermoelectric Properties of $\text{Ca}_3\text{Co}_4\text{O}_9$ Compound

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The $\text{Ca}_3\text{Co}_4\text{O}_9/\text{Ag}$ composite was synthesized by a solid-state reaction. The SEM observation reveals that Ag particles are dispersed and combined with $\text{Ca}_3\text{Co}_4\text{O}_9$ grains of several μm size. The electrical resistivity (ρ) of the composite is lower than that of the $\text{Ca}_3\text{Co}_4\text{O}_9$ compound and decrease with the increase of Ag content. It can be inferred that the highly conductive Ag particles between oxide grains make a contribution to reduce the ρ . The Seebeck coefficient (S) of the composite is also decreased by the Ag addition, although the small amount of Ag has little influence on the S value. The poor S value of Ag seems to have negative effect on the S of the composite. Since the reduction of the ρ is more significant than the degradation of the S , power factor is improved by the Ag addition of 10wt%.

Key words: oxide, layered cobaltite, composite, thermoelectric properties.

1. INTRODUCTION

Thermoelectric devices have recently attracted renewed interest in terms of their potential application to clean energy-conversion systems. The conversion efficiency of a thermoelectric material is evaluated by the figure-of-merit $Z = S^2/\rho\kappa$, where S is the Seebeck coefficient, ρ is the electrical resistivity and κ is the thermal conductivity. Thus, the materials to be used for the thermoelectric device should have a large S , and low ρ and κ simultaneously. Actually, the ZT value (where T is absolute temperature) of the thermoelectric material is required to exceed 1 for the practical application. Moreover, they should be harmless to the environmental and chemically stable in air at high temperatures. The recent discovery of large thermopower coexisting with low electrical resistivity in layered-cobaltite of Na_xCoO_2 and $\text{Ca}_3\text{Co}_4\text{O}_9$ (Co349) has opened the way to the exploration of oxide thermoelectric materials, which are generally stable at high temperatures in air atmosphere [1-5]. The single crystal of these cobalt oxides exhibits good thermoelectric performance along the ab -plane, $ZT > 1$ at 1000 K [2, 4], competitive with conventional degenerate semiconductors such as Bi_2Te_3 , PbTe and $\text{Si}_{1-x}\text{Ge}_x$.

However, the ZT value of the randomly oriented polycrystalline material is rather small because of the highly anisotropic properties of these layered cobaltites [6]. Therefore, texturation of polycrystalline bulk material is indispensable for the achievement of ZT high enough for practical application, as it is difficult to grow single crystals large enough for the construction of a thermoelectric device. For this purpose, some research groups have already reported the fabrication of textured

Co349 ceramics by reactive templated grain growth [7-9], magnetic alignment [10-12] or utilization of the combined effect of large single crystals and powder [13]. We have also demonstrated the validity of using large-grained Co349 powder as material for producing textured Co349 ceramics [14]. The resulting textured samples show reduced ρ compared to non-aligned sintered-Co349 materials.

However, ρ values of well-aligned ceramics are still about two times larger than the single-crystal along the ab -plane. Therefore, we should modify not only the grain alignment but also electron scattering at grain boundaries in order to decrease the ρ value of polycrystalline material. Since the Co349 does not melt but decompose at high temperature, it is difficult to reduce the number of grain boundaries by adjusting the sintering or annealing conditions such as the partial melting technique. On the other hand, it is expected that the addition of some material, which has the lower ρ than cobaltite, at the grain boundaries is effective to reduce the electrical resistance at the grain boundary. For instance, the addition of fine particles of metal would form electrically connected grains in the cobaltite/metal composite material. Based on this concept, it has been recently reported that the Ag addition on the polycrystalline Na_xCoO_2 can reduce the ρ value [15]. In the present study, we examined the effect of the Ag addition on thermoelectric properties of the Co349 bulk materials.

2. EXPERIMENTAL

Co349 powder was prepared by solid-state reaction. A mixture of Co_3O_4 (99.9 %) and CaCO_3 (99.5 %) at a

molar ratio of Ca:Co=3:4 was ground, calcined at 1073 K for 10 h in air, pulverized, and pressed into pellets, which were sintered at 1153 K for 20 h in an oxygen gas flow and ground into fine powder. In order to increase the grain size, the prepared Co349 powder was heated at 1123 K for 20 h in a 20wt% solvent consisting of K_2CO_3 and KCl at a molar ratio of 4:1 [14]. The powder was collected from the solidified materials by dissolving the solvent in distilled water in an ultrasonic washing machine.

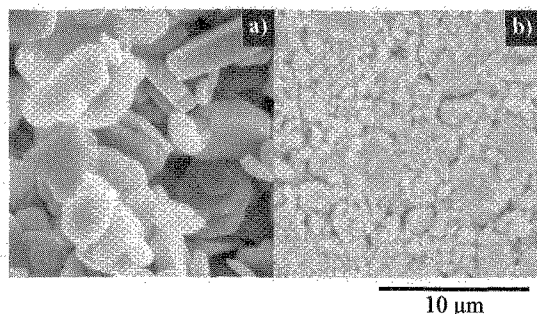


Fig. 1 SEM images of a) large-grained Co349 powder and b) Ag_2O powder.

The large-grained powder was mixed with fine Ag_2O powder at four different weight ratios to Co349: 0wt% (without Ag_2O), 5wt%, 10wt%, and 20wt%. Although Ag_2O grains of 3-4 μm size can be found, the size of the major part of Ag_2O particles is less than 1 μm , which is considerably smaller than Co349 grains of several μm size, as shown in Fig. 1. The mixtures were cold-pressed into 15 thin-disks, which were finally stacked under uniaxial pressure of 180 MPa. The layered pellets were then hot-forged at 1153 K for 20 h in air under uniaxial pressure of 10 MPa. The obtained samples were cut into a bar shape with a typical size of $2.5 \times 2.5 \times 10 \text{ mm}^3$ for the measurement of thermoelectric properties. In the present paper, the hot-forged samples made of the large-grained Co349 powders mixed with 0wt%, 5wt%, 10wt%, and 20wt% of Ag_2O are abbreviated as CA-0, CA-5, CA-10 and CA-20, respectively.

Crystallographic structure analysis was performed with X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation. The microstructures of the samples were observed with a scanning electron microscope (SEM) using both secondary electron and back scattered electron (BSE) modes. The constituent analysis was conducted using an energy-dispersive X-ray spectrometer (EDX). ρ was measured in air in the temperature range of 300-1073 K using a conventional four-probe dc technique. S was calculated from a plot of thermoelectric voltage against temperature differential as measured in air at 373-1073 K using an instrument designed by our laboratory. Two Pt-Pt/Rh (R-type) thermocouples were attached to both ends of the sample using silver paste and the Pt wires of

the thermocouples used as voltage terminals. Measured S values were reduced by those of the Pt wires to obtain the net S values of the samples.

3. RESULTS AND DISCUSSION

The XRD measurement was performed on the pressed surface of the hot-forged sample. As shown in Fig. 2, the XRD patterns of all the samples agree with the reported data for Co349 structure [6] except for weak diffraction peaks from secondary phase of Ag (marked \bullet) in the Co349/Ag composites. Since major strong peaks in every XRD patterns can be assigned to a $00l$ peak of Co349 structure, it can be inferred that the ab -plane of cobaltite grains are well aligned parallel to the pressed plane. In addition, the intensity ratio of the peaks attributed Co349 structure is almost the same in every sample, the degree of orientation of cobaltite grains seems not to be affected by the amount of Ag. Since all of the Ag-related peaks are agreed with metal Ag, it is confirmed that the starting material of Ag_2O is reduced by the hot-forging process. Moreover, the intensity of the peaks from Ag metal obviously increases with the increase of the mixed ratio of Ag_2O .

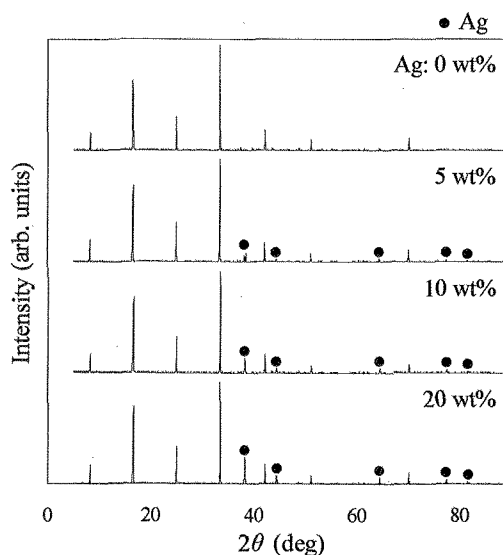


Fig. 2 XRD patterns ($\text{Cu K}\alpha$ radiation) of hot-forged Co349 sample and Co349/Ag composite. The measurement was performed on the polished pressed-plane.

Figure 3 shows SEM and BSE images of a fracture cross-section of CA-20. White spots in the BSE image (in Fig. 3b)) are corresponded with Ag particles. It can be observed that the cobaltite grains of several μm size are well aligned as predicted from the XRD patterns. It should be mentioned that a similar degree of orientation and grain size was observed in other samples. On the other hand, the amount of Ag particle apparently increases with the increase of the mixed ratio of Ag_2O in

starting powder. Though the average size of the Ag particle seems to be almost the same in every sample, the number of conjoined Ag particles seems to increase with the increase of Ag content. Although the Ag particles of several μm size can be found, the size of the major part of Ag particles is less than $3\ \mu\text{m}$. In addition, Ag particles are dispersed, and agglomerated Ag cluster larger than $10\ \mu\text{m}$ could not be found. It was confirmed that the content of the Ag in every sample was as much as the initial amount of Ag_2O in starting powder by EDX. From these results, it was verified that four samples have almost the same microstructure but different Ag content.

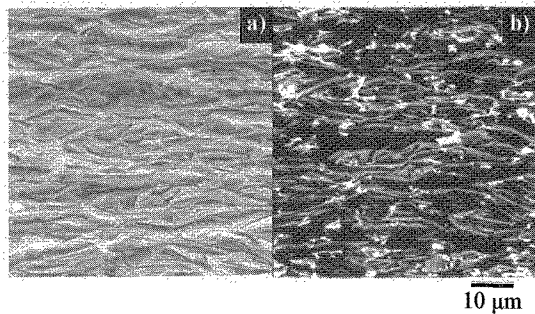


Fig. 3 a) SEM and b) BSE images of fracture transverse section of Co349/Ag composite at 20wt% of Ag. White spots in the BSE image corresponds with Ag particles.

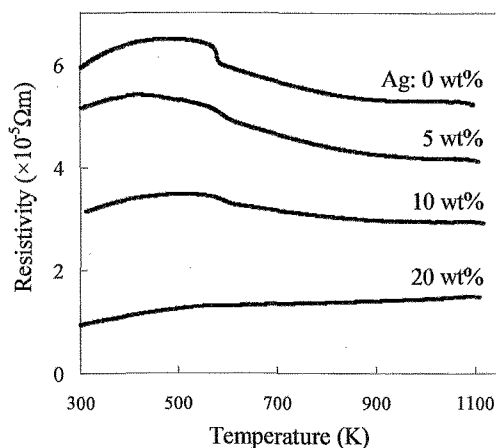


Fig. 4 T dependence of ρ along the pressed plane of the hot-forged Co349 and Co349/Ag composites.

As shown in Fig. 4, the average ρ value is reduced according to the Ag content. The T dependence of ρ is also changed with the amount of Ag. ρ of the CA-0 gradually decreases with the increase of temperature except for a broad maximum around 500 K and a steep decline at 570 K. A broad hump around 500 K could correspond to the behavior of ρ in the single crystal Co349 along the ab -plane [5]. However, since a steep section around 570 K is observed only in polycrystalline hot-forged samples, the rapid reduction could be related to ρ along the c -axis or to the electrical properties of the

grain boundaries. The reduction rate of ρ with the increase of temperature tends to decline with the increase of the Ag content. Eventually, the CA-20 shows metallic T behavior entire measurement temperature range. These results obviously indicate that the ρ of the Co349/Ag composite consists of the semiconducting Co349 and the metallic Ag behavior.

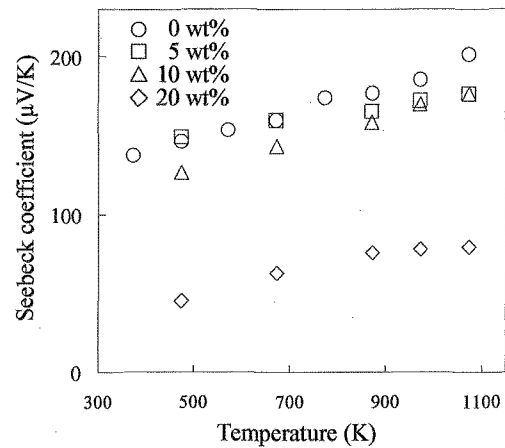


Fig. 5 T dependence of S along the pressed plane of the hot-forged Co349 and Co349/Ag composites.

The S value in every sample increases with the increase of temperature. This T dependence is similar to the single crystal Co349. Contrary to the Ag concentration dependence of ρ , the Ag addition weakly affect on the S value except for the S of CA-20, which is less than half the value of CA-0. Since the S of the Ag metal is low, less than $10\ \mu\text{V/K}$, it is obvious to assume that the Ag addition reduces S value. However, the difference in the degree of Ag addition impact on the S value of CA-20 and other composites needs further explanation. We propose that the Ag particle plays two kinds of roll in the composite: the electrical connection among cobaltite grains and the bypass of the carrier transport. It is presumed that the former have little influence on the S value because the thermopower of each Co349 grains can be added like series circuit. However, the latter can nullify the thermoelectric voltage of Co349 grains like short-circuit. If the Ag particles are well-separated and quite small compared to the oxide grains, the latter effect could be neglected. Conversely, if Ag particles are close to each other or agglomerated into a cluster larger than Co349 grains, the carriers will tend to transport through the Ag metal passes, resulting in the significant reduction of S . From the BSE observation, two kinds of Ag particle size are found: less than $2\ \mu\text{m}$ and several μm , which is as large as Co349 grains. Although it is difficult to quantitatively estimate the density of these two kinds of particles from the BSE image, it can be observed that the density of the

agglomerate Ag particles increases with the increase of the Ag content. Therefore, it can be supposed that the metallic conduction is dominant in the CA-20 due to the large Ag clusters, whereas the small and dispersed Ag particles seem not to disturb the thermoelectric effect of Co349 grains in the CA-5 and -10.

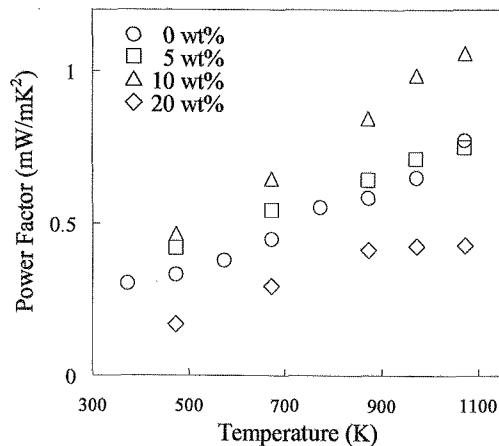


Fig. 6 T dependence of PF along the pressed plane of the hot-forged Co349 and Co349/Ag composites.

The thermoelectric power factor ($PF=S^2/\rho$) was calculated from measured ρ and S values. The PF value in every sample increases with the increase of temperature. Because the Ag addition on Co349 reduces ρ and S simultaneously, PF of the CA-5 is as high as CA-0. Moreover, the PF of CA-20 is about half the value of CA-0 because of the significant decrease in S . On the other hand, the considerable reduction of ρ without the serious deterioration in S enhances PF in the CA-10. The PF of CA-10 reaches 1 mW/mK at 1073 K, which is the highest value of Co349 bulk materials.

4. CONCLUSION

The Co349/Ag composites with different Ag content were synthesized by a hot-forging method using the mixture of large grained Co349 of several μm size and Ag_2O powder of submicron size. Because of the lower ρ and S of the metal Ag compared to Co349, the ρ and S was simultaneously reduced by the Ag addition. The appropriate amount of Ag addition, at 10wt% in this study, could improve the PF because of the significant reduction of ρ without the serious deterioration of S . Since the metal Ag has much higher κ value than Co349,

the κ of the composite should be measured in order to assess the effect of the Ag addition on the Z value. However, if we have a fixed temperature difference and ignore the conversion efficiency, high-power thermoelectric device could be produced with the Co349/Ag composite.

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