Effects of Ag Addition on Microstructure and Thermoelectric Properties of Na$_{x}$Co$_2$O$_4$ Synthesized by Citric Acid Complex Process

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A thermoelectric Na$_{x}$Co$_2$O$_4$/Ag composite was synthesized by citric acid complex process using CH$_3$COOAg as an Ag source. The powder precursor after calcination was composed of plate-like Na$_{x}$Co$_2$O$_4$ grains and Ag particles. The Ag addition deteriorated crystallographic anisotropy of the sintered body. However, the electrical resistivity and the Seebeck coefficient of this composite were significantly smaller and slightly larger, respectively, than those of the sample without Ag, resulting in larger power factor. The Ag phase dispersed in the Na$_{x}$Co$_2$O$_4$ matrix contained about 5~17 at.% Co, which is considered to cause the increase in Seebeck coefficient.

Keywords: thermoelectric oxide, citric acid complex process, oxide-metal composite, crystallographic anisotropy, thermoelectric properties

1. Introduction

Thermoelectric power generation has been expected as a new technique to achieve energy savings and effective use of waste heat. The layered oxide Na$_{x}$Co$_2$O$_4$ shows large thermoelectric power in spite of the large carrier density ($\sim 10^{23}$ cm$^{-3}$) compared to that of the conventional thermoelectric materials. Generally, as one of the methods to improve thermoelectric performance, metallic phases are added to thermoelectric materials in order to decrease their electrical resistivity. In the case of the Na$_{x}$Co$_2$O$_4$ synthesized by the conventional solid state reaction method, Ag powder was directly added to the Na$_{x}$Co$_2$O$_4$ powder by using mechanical milling. In this case, the composite of the Na$_{x}$Co$_2$O$_4$ matrix and coarse Ag particles around 10$\mu$m in size was synthesized. The electrical resistivity and Seebeck coefficient of the sintered Na$_{x}$Co$_2$O$_4$ were reduced and enhanced, respectively, by the Ag addition, resulted in significant improvement of the power factor. On the other hand, it has been reported that the Na$_{x}$Co$_2$O$_4$ phase was synthesized by the citric acid complex (CAC) method. The CAC method, which is a chemical solution process similar to the polymerized complex method, is useful for obtaining a homogeneous and fine powder precursor, resulting in the large Seebeck coefficient of Na$_{x}$Co$_2$O$_4$. Based on these experimental results, it is expected that if a Na$_{x}$Co$_2$O$_4$/Ag composite can be obtained by the CAC process, the composite sample will show the significantly large power factor. Therefore, in the present study, synthesis of a Na$_{x}$Co$_2$O$_4$/Ag composite sample was tried by the CAC process and subsequent sintering, where CH$_3$COOAg was selected for an Ag source, and the effects of the CAC process on the microstructure and the electrical transport properties of the Na$_{x}$Co$_2$O$_4$/Ag composite were investigated.

2. Experimental Procedure

Sintered Na$_{x}$Co$_2$O$_4$ with and without 10 mass% Ag were synthesized by the following process. Citric acid was first dissolved in ion-exchange water by heating and stirring at 433 K. Subsequently, (CH$_3$COO)$_2$Co-4H$_2$O, CH$_3$COONa and CH$_3$COOAg in a mole ratio corresponding to the nominal composition of Na$_{1.6}$Co$_2$O$_4$ were added to this solution. The citric acid was mixed in the proportion of 3 moles for each mole of metal cation. The mixture was then stirred and condensed at 433 K for about 3.6 ks. During this heating process, the formation of the metal citrate complexes was promoted. As this solution condensed, it became highly viscous, and the viscous product was heated up to 723 K for about 7.2 ks in air by a mantle heater to form a dark mass precursor. This dark mass precursor was calcined at 1073 K for 10 ks in flowing O$_2$ gas in order to remove a residual organic matter completely and obtain the thermoelectric Na$_{x}$Co$_2$O$_4$ phase. The calcined powder precursor was compacted, and then sintered at 1153 K for 72 ks in air. The x value in Na$_{x}$Co$_2$O$_4$ of the sintered sample was about 0.7.

The phases and the microstructures of these samples were determined by XRD (X-ray diffraction analysis), SEM (scanning electron microscopy), and EDX (energy dispersive X-ray spectroscopy). The XRD analysis was performed on the pressed plane of the sintered compacts using Cu $K\alpha$ radiation. The Seebeck coefficient, $S$, and the electrical resistivity, $\rho$, were simultaneously measured along the pressed plane from room temperature to about 1100 K by the ordinary four probe dc method in a flowing air gas atmosphere using a computer-controlled equipment.

3. Results and Discussion

Figure 1 shows the SEM photograph of the cross section of the calcined powder precursor with 10 mass% Ag. Most of the Na$_{x}$Co$_2$O$_4$ powders have a quite narrow shape of their cross section with a high aspect ratio, reflecting the layered crystal structure of Na$_{x}$Co$_2$O$_4$, indicating each Na$_{x}$Co$_2$O$_4$ particle grew along its c-plane during calcination. On the other hand, it was also found that Ag phase formed as coarse particles around 10$\mu$m in size after CAC process and...
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Calcination. The Ag phase did not precipitate separately from the Na$_2$Co$_4$O$_7$ particles, and agglomerated with several Na$_2$Co$_2$O$_4$ flakes, as shown in Fig. 1.

Figure 2 shows the XRD patterns of Na$_2$Co$_2$O$_4$ sintered bodies (a) without addition and (b) with 10 mass% Ag. The sample without Ag synthesized by the CAC process was composed of the Na$_2$Co$_2$O$_4$ single phase. When 10 mass% Ag was added, the sample was composed of the Na$_2$Co$_2$O$_4$ and Ag phases only, indicating that any reaction of Ag with Na$_2$Co$_2$O$_4$ did not occur. Thus, it was found that the Na$_2$Co$_2$O$_4$/Ag composite could be obtained by the CAC process using CH$_3$COOAg as an Ag source. Figure 3 shows the SEM photograph of the cross section parallel to the pressed plane of the Na$_2$Co$_2$O$_4$/Ag composite. It was expected that fine Ag particles precipitated during the CAC process where constituent metal ions can be mixed at atomic level. However, Ag phase already precipitated as coarse particles up to about 10 µm in size with the flaky Na$_2$Co$_2$O$_4$ powders prior to sintering, as shown Fig. 1. Therefore, after the sintering, the Ag phase remained coarse in the Na$_2$Co$_2$O$_4$ matrix. Those particle sizes of Ag phase were almost the same as those of the Na$_2$Co$_2$O$_4$/Ag composite synthesized by the conventional solid state reaction method and mechanical milling with Ag powders. EDX analysis also revealed that spectrum of Ag was hardly detectable in the Na$_2$Co$_2$O$_4$ matrix, indicating that most of Ag atoms from the mother material of CH$_3$COOAg were not substituted for Na and Co sites and precipitated as Ag particles.

As described above, the plate-like grains of Na$_2$Co$_2$O$_4$ phase were obtained by the CAC process and calcination. When this powder precursor is uniaxially compacted for the subsequent sintering, it is expected that each Na$_2$Co$_2$O$_4$ grain aligns along the pressing plane and the sintered body with large crystallographic anisotropy can be obtained. The electrical resistivity of the Na$_2$Co$_2$O$_4$ phase exhibits significant anisotropy due to its layered structure; the electrical resistivity along its c-axis is about ten times larger than that along its c-plane. Therefore, the synthesis of c-axis oriented polycrystal of Na$_2$Co$_2$O$_4$ is considered to be effective for reducing the electrical resistivity of a sintered body. Figure 4 shows the SEM photographs of the cross-section perpendicular to the pressed plane of sintered bodies (a) without Ag addition and (b) with 10 mass% Ag. It was found that the Na$_2$Co$_2$O$_4$ flaky grains were well aligned along the pressing plane in both samples. In the case of the Ag-added sample, as shown in Fig. 4(b), random-shaped Ag particles were dispersed in the aligned Na$_2$Co$_2$O$_4$ matrix. In order to evaluate the degrees of crystallographic anisotropy of these samples more accurately, the Lotgering factors, $f$, of these sintered compacts were calculated by using the peak intensity of their XRD patterns, namely, $f$ values were evaluated from the intensity of the $(hkl)$ peaks, $I(hkl)$, in the XRD patterns using an equation $f = (P - P_0)/(1 - P_0)$, where $P = \Sigma I((00\ell))/\Sigma I(hkl)$, and $P_0 = P$ for a crystallographically isotropic (randomly oriented) sample. In this study, $P_0$ was calculated from the peak data of the JCPDS card, No. 27-0682. When the c-axis direction of each grain is completely aligned along the pressing direction, the $f$ value is calculated to be 1, and $f = 0$ corresponds to an entirely isotropic sample. The sample without Ag addition showed the significantly large $f$ value, 0.9. On the other hand, in the
case of the sample with 10 mass% Ag, the $f$ value was calculated to be a smaller value, 0.7. As shown in Fig. 1, in the powder precursor after calcination, the Ag phase agglomerated with Na$_{x}$Co$_2$O$_4$ flakes. It is considered that such an agglomeration hindered alignment of the Na$_{x}$Co$_2$O$_4$ flaky powder during compaction. Besides that, the dispersion of Ag particles may also prevent anisotropic grain growth of Na$_{x}$Co$_2$O$_4$ grains along the pressed plane during sintering. However, in the case of the Na$_{x}$Co$_2$O$_4$/Ag composite (b), it seems that a number of pores was little and the Na$_{x}$Co$_2$O$_4$ grains adhered to each other very well as compared to the Na$_{x}$Co$_2$O$_4$ sample (a). In fact, the relative density of the Na$_{x}$Co$_2$O$_4$/Ag composite was about 96%, which was slightly larger than that of Na$_{x}$Co$_2$O$_4$ sample, 94%. It has been reported that the Seebeck coefficient was hardly affected by morphology of the sintered body, such as crystallographic anisotropy and grain size, etc.\[1,12\] On the other hand, this greater degree of densification in the Na$_{x}$Co$_2$O$_4$/Ag composite is considered to contribute to reduction in electrical resistivity.

Figure 5 shows the temperature dependence of (a) the electrical resistivity, $\rho$, and (b) the Seebeck coefficient, $S$, of the sintered samples with and without 10 mass% Ag. The Ag addition resulted in the deterioration of crystallographic anisotropy of the sintered body, which is considered to increase the electrical resistivity as compared to the well-aligned sample without Ag addition. However, the electrical resistivity of the Na$_{x}$Co$_2$O$_4$/Ag composite was significantly smaller than that of the sample without Ag over the measured temperature range. Thus, the addition of Ag, a good electrical conductor, was found to be quite effective on reducing $\rho$ values of Na$_{x}$Co$_2$O$_4$. As shown in Fig. 4, the crystallographic anisotropy of the Na$_{x}$Co$_2$O$_4$/Ag composite was smaller than that of the Na$_{x}$Co$_2$O$_4$ sample without Ag. If the decrease in $f$ value caused by Ag addition did not occur, smaller $\rho$ values of the Na$_{x}$Co$_2$O$_4$/Ag composite would have been obtained, resulting in further improvement of its thermoelectric performance. On the other hand, as shown in Fig. 5(b), the Seebeck coefficient was slightly increased by the Ag addition. Generally, addition of a metallic phase to thermoelectric materials decreases their Seebeck coefficient. In fact, when Ag powder was directly added to the Na$_{x}$Co$_2$O$_4$ CAC powder by mechanical milling, the Seebeck coefficient was
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The Na$_x$Co$_2$O$_4$ cannot be explained only by the dispersion of Ag particles in the Na$_x$Co$_2$O$_4$ matrix. In order to discuss this experimental result, EDX analysis on Ag particles was performed. The EDX analysis revealed that the spectra of Co were detected on the Ag phase in the composite, and the Co content in each particle was around 5–17 at.%. The result of EDX analysis indicates that the Co concentration in the Na$_x$Co$_2$O$_4$ matrix slightly decreased as compared to the sample without Ag, resulting in a little increase in Na content in the Na$_x$Co$_2$O$_4$ phase. It has been reported that the increase in Na content in the Na$_x$Co$_2$O$_4$ phase was considered to reduce its carrier density and enhance the Seebeck coefficient. From the result of the EDX analysis, it is considered that the slight improvement of the Seebeck coefficient was caused by the precipitation of Ag particles containing Co during the CAC process. Although the reduction in carrier density also causes an increase in the electrical resistivity, the effect of existence of the metallic phase on the decrease in $\rho$ values was considered to be superior to that of the reduction in carrier density of the Na$_x$Co$_2$O$_4$/Ag composite. The power factor, $P$, was calculated using $S$ and $\rho$ values in the equation $P = S^2/\rho$. Figure 6 shows the temperature dependence of the power factor, $P$, of the samples with and without 10 mass% Ag. The power factor of the Na$_x$Co$_2$O$_4$/Ag composite was significantly larger than that of the sample without Ag, because the electrical resistivity and the Seebeck coefficient were markedly reduced and slightly enhanced, respectively, by the Ag addition. The maximum $P$ value in this study, 2.53 mW/mK$^2$, was obtained for the Na$_x$Co$_2$O$_4$/Ag composite at 1060 K, which was by about 80% larger than that of the sample without Ag. Thus, the CAC process using CH$_3$COOAg as an Ag source is quite effective for improving the thermoelectric properties of Na$_x$Co$_2$O$_4$/Ag composites.

4. Conclusion

The Na$_x$Co$_2$O$_4$/Ag composite was synthesized by the CAC process using CH$_3$COOAg as an Ag source. The sample was composed of the Na$_x$Co$_2$O$_4$ matrix and coarse Ag particles. The plate-like Na$_x$Co$_2$O$_4$ grains obtained by CAC process and calcination were aligned along the pressed plane, resulting in c-axis oriented Na$_x$Co$_2$O$_4$ polycrystal. However, Ag addition deteriorated the crystallographic anisotropy of the sintered body. On the other hand, the Ag addition was quite effective on reducing the electrical resistivity. It was also found that the Seebeck coefficient was slightly enhanced by the Ag addition. From these results, the power factor of the Na$_x$Co$_2$O$_4$/Ag composite was significantly larger than that of the sample without Ag, and 2.53 mW/mK$^2$ was obtained for this sample at 1060 K. Thus, the CAC process and Ag addition were quite effective for improving the electrical transport properties of Na$_x$Co$_2$O$_4$.

Acknowledgements

This study was partially supported by Industrial Technology Research Grant Program in ’04 from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

REFERENCES