Synthesis of Na$_x$Co$_2$O$_4$ thermoelectric oxide with crystallographic anisotropy by chemical solution process

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Abstract

The synthesis of the Na$_x$Co$_2$O$_4$ with a layered crystal structure was attempted by using the polymerized complex (PC) method or citric acid complex (CAC) method, both of which are a kind of chemical solution process. The effects of these chemical solution processes on the crystallographic anisotropy, microstructure and thermoelectric properties of the sintered Na$_x$Co$_2$O$_4$ were investigated and compared to those of the conventional SSR method. In the case of the PC method, the sintered body with higher chemical homogeneity and finer microstructure than those of the SSR sample was obtained, resulting in the high thermoelectric performance. However, the crystallographic orientation was almost the same as that of the SSR sample. On the other hand, in the case of the CAC method, a flaky powder precursor was formed by grain growth of the Na$_x$Co$_2$O$_4$ phase along the c-plane. The Na$_x$Co$_2$O$_4$ sample sintered from this powder precursor showed a high crystallographic anisotropy and good chemical homogeneity, so the CAC process was found to be quite effective for synthesizing a crystallographically oriented Na$_x$Co$_2$O$_4$ polycrystal with high thermoelectric performance.

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1. Introduction

Several electronic conductive oxides, such as (Zn$_{1-x}$Al$_x$)O, BaSrPbO$_3$, Na$_x$Co$_2$O$_4$ etc. have been recognized as potential candidates for a new thermoelectric material [1–6]. These thermoelectric oxides can be used at high temperatures without deterioration of their performance due to oxidation, and their production costs are comparatively low. The Na$_x$Co$_2$O$_4$ thermoelectric oxide shows three types of crystal structure depending on the $x$ value; P3 type ($\beta$-phase, $1.1 \leq x \leq 1.2$), P2 type ($\gamma$-phase, $1.0 \leq x \leq 1.4$) and O3 type ($\alpha$-phase, $1.8 \leq x \leq 2.0$) [7]. The P2 type $\gamma$-Na$_x$Co$_2$O$_4$ shows a large Seebeck coefficient despite its metallic conductivity and a good thermoelectric performance as an electrically conductive oxide at around $x = 1$ in Na$_x$Co$_2$O$_4$. The P2 $\gamma$-type Na$_x$Co$_2$O$_4$ thermoelectric material is a layered oxide composed of an electric conductive CoO$_2$ layer and an insulating Na layer, which are perpendicular to the c-axis. The sign of the Seebeck coefficient is positive, indicating a p-type thermoelectric material. The electrical resistivity of this phase exhibits significant anisotropy due to its crystal structure; the electrical resistivity along its c-axis is about ten times larger than that along its c-plane [4]. On the other hand, the production cost of the Na$_x$Co$_2$O$_4$ single crystal is quite high. Therefore, in order to reduce electrical resistivity, synthesis of the Na$_x$Co$_2$O$_4$ polycrystalline sintered body with high crystallographic orientation has been desired; the c-axis of each grain in the sintered body is required to be aligned along the pressing direction.

In the conventional solid state reaction (SSR) method, it is difficult to synthesize a sintered body with high crystallographic orientation and fine microstructure. Besides that, because of its SSR process, there is compositional inhomogeneity in the Na$_x$Co$_2$O$_4$ matrix, which is considered to result in deterioration of the thermoelectric performance. In a previous study [8], mechanical grinding and SPS (spark plasma sintering) were tried to synthesize the Na$_x$Co$_2$O$_4$ in order to prepare a fine microstructure, but the crystallographic anisotropy was ruined, resulting in a lower...
thermoelectric performance. In this study, we have applied
the polymerized complex (PC) method, which is a kind
of chemical solution process, in the synthesis of the Na$_{x}$Co$_2$O$_4$
ceramics. This technique was modified by Kakihana et al. to
prepare the oxide superconductors such as YBa$_2$Cu$_3$O$_y$ [9,
10]. This method is based on the stable formation of metal-
citrate complexes and the following polymerization
between ethylene glycol and citric acid complexed with
constituent metals, forming the polymeric product with a
three-dimensional network structure. Heating of the resul-
tant polymeric product in air causes a breakdown of the
polymer, which allows mixing of the constituent metals at
atomic level. Therefore, the PC method is expected to
provide samples with good chemical homogeneity com-
pared to the SSR sample. Besides that, the powder precursor
obtained by the PC process is generally fine, and sintering of
this powder precursor is expected to result in the Na$_{x}$Co$_2$O$_4$
sintered body with a fine microstructure.

During heating for breakdown of the polymeric product,
growth of a plate-like powder precursor may occur because
of its layered crystal structure. Consolidation of the plate-
like powder precursor will allow alignment of the flaky
grains and provide a sintered body with high crystal-
lographic orientation. However, in the case of the PC
method, the formation of a polymeric product with a three-
dimensional network structure may suppress the growth of
plate-like grains. Based on this consideration, the citric acid
complex (CAC) method as another chemical solution
process was also tried to synthesize the Na$_{x}$Co$_2$O$_4$
compacts. In the CAC process, metal citrate complexes
without a network structure is formed by using water instead
of ethylene glycol. This chemical solution process without
polymer formation is expected to prepare a more plate-like
powder precursor and a sintered body with a larger
crystallographic anisotropy. Thus, in the present study, the
synthesis of the Na$_{x}$Co$_2$O$_4$ ceramics was tried using the PC
and CAC methods, and effects of these chemical solution
processes on the size, shape and chemical homogeneity of
powder precursors were investigated. Besides that, the
microstructure, crystallographic anisotropy and thermoelec-
tric properties of the sintered bodies were also evaluated,
and the effects of these processes on the characteristics of
the Na$_{x}$Co$_2$O$_4$ thermoelectric oxide were discussed and
compared to those of the conventional SSR process.

2. Experimental procedure

The γ-Na$_{x}$Co$_2$O$_4$ polycrystalline sintered bodies were
synthesized by the following process. In the case of the
conventional SSR method, Na$_2$CO$_3$ and Co$_3$O$_4$ powders
were mixed in the nominal composition of Na$_{1.2}$Co$_2$O$_4$. The
mixture was pressed into a pellet under a pressure of
5.6 × 10$^2$ MPa. Then, the pellet was calcined at 1153 K for 18
ks in air. We added 20% excess Na$_2$CO$_3$ powder into the calcined powder prior
to the sintering process, because Na tends to evaporate
during the heating process [11]. The synthesis of the samples by the PC method was summarized in Fig. 1. Citric
acid was first dissolved in ethylene glycol by heating and
stirring at 473 K. Subsequently, Co(NO$_3$)$_2$·6H$_2$O and
NaNO$_3$ in the mole ratio corresponding to a nominal
composition of Na$_{1.6-1.7}$Co$_2$O$_4$ were added to this solution.
Citic acid and ethylene glycol were mixed in the
proportion of 4 and 180 moles for each mole of metal
cation, respectively. The mixture was then stirred at
433 K for about 3.6 ks. During this heating process, the formation of the polymeric product with a three-
dimensional network structure was promoted. As the colloidal
solution was condensed, it became highly viscous, and this
viscous polymeric product was decomposed to a dark mass
precursor by heating at 723 K in mantle heater. This mass
precursor was calcined at 1073 K for 18 ks in order to obtain
the Na$_{1.6-1.7}$Co$_2$O$_4$ phase and eliminate the residual organic
contents. The calcined powder precursor was compacted
under a pressure of 5.6 × 10$^2$ MPa and then subjected to
sintering at 1153 K for 72 ks in air. 

\[
\begin{align*}
\text{NaNO}_3 + \text{Co(NO}_3)_2\cdot6\text{H}_2\text{O} & \text{ in citric acid + ethylene glycol} \\
\text{Stirring and condensing up to 573 K} & \\
\text{Polymerized Complex} & \\
\text{Pyrolysis up to 723 K in air} & \\
\text{Dark Mass Precursor} & \\
\text{Heating at 1073 K for 18 ks in air} & \\
\text{Calcined Powder Precursor} & \\
\text{Sintering at 1153 K for 72 ks in air} & \\
\text{Polycrystalline Na$_{x}$Co$_2$O$_4$ sintered body} & \\
\end{align*}
\]

Fig. 1. Flow chart for the polymerized complex procedure used to prepare the Na$_{x}$Co$_2$O$_4$ polycrystal.

During heating for breakdown of the polymeric product,
growth of a plate-like powder precursor may occur because
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like powder precursor will allow alignment of the flaky
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compared to those of the conventional SSR process.
promoted. As this solution condensed, it became highly viscous, and the viscous product was heated up to 723 K in air by a mantle heater to form a dark mass precursor. This dark mass precursor was calcined at 1073 K for 72 ks in air in order to remove a residual organic matter and obtain the $\gamma$-Na$_x$Co$_2$O$_4$ phase. In the CAC process, the period of calcination, 72 ks, which is longer than in the case of the PC process, was needed to crystallize the $\gamma$-Na$_x$Co$_2$O$_4$ phase completely. The calcined powder precursor was compacted and then pressurelessly sintered on the same condition as the PC method. In this paper, the samples prepared by the SSR, PC and CAC methods were referred to as a ‘SSR sample’, a ‘PC sample’ and a ‘CAC sample’, respectively. The phases and the microstructures of these samples were determined by X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX). 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 computer-controlled equipment.

3. Results and discussion

The SSR, PC and CAC powder precursors after the calcination were exposed to SEM observation. Fig. 2 shows the external appearances ((a), (c) and (e)) and the cross sections ((b), (d) and (f)) of the calcined SSR, PC and CAC powders, respectively. The XRD analysis showed that these calcined powders were composed of the $\gamma$-Na$_x$Co$_2$O$_4$ phase without any impurity phases. As shown in Fig. 2(a) and (b), the SSR powder was random in shape, because the powder was prepared by pulverization of the calcined compact using a mortar and pestle. On the other hand, in the case of the PC powder, although the each particle precipitated from the polymeric product with a three-dimensional network structure, many particles were flaky compared to the SSR

Fig. 2. SEM photographs of the external appearance ((a), (c) and (e)) and the cross section ((b), (d) and (f)) of the calcined SSR, PC and CAC powder precursor, respectively.
powder, indicating that the powder tends to grow along the c-plane reflecting its layered crystal structure. It was also found that the fine particles around 7–8 μm in size could be obtained by the PC process without pulverization that was required in the SSR method. In the case of the CAC process, as shown in Fig. 2(e), crystallographically anisotropic grain growth occurred and a significantly plate-like powder precursor compared to the PC powder was obtained. Fig. 2(f) also shows that most of the particles have a quite narrow shape of their cross section with a high aspect ratio. From these results, it was found that in the synthesis of an oxide with a layered crystal structure, the CAC process was quite useful for producing plate-like particles reflecting its crystal structure.

Fig. 3 showed the XRD patterns of the sintered (a) SSR, (b) PC and (c) CAC samples. All the samples maintained the γ phase after the sintering and no peaks from a second phase were detected. EDX analysis showed that the x values in Na$_x$Co$_2$O$_4$ of the SSR and PC samples were about 1.0 and 1.1, respectively. On the other hand, the CAC sample showed the smaller value of x, 0.7. In the CAC process, the period of calcination longer than that in the case of the PC method was needed for the γ phase formation. It is considered that the heating for longer period caused evaporation of a large amount of Na, resulting in the smaller x value. The relative densities of the SSR, PC and CAC samples were 93.0, 97.6 and 93.9%, respectively, which were comparatively high in spite of the fact that these samples were sintered pressurelessly.

Fig. 4 shows the SEM photographs of the cross section perpendicular to the pressed plane of the sintered (a) SSR, (b) PC and (c) CAC samples. In the case of the SSR sample, the grains were coarse and there were also several pores about 10 μm in size. In the case of the PC sample, though the grains were large compared to the calcined powder shown in Fig. 2(c) and (d), the flaky shape was almost maintained after sintering. It was also found that these particles were finer than those in the SSR sample. On the other hand, the grain size of the CAC sample was significantly smaller than that of the PC sample. Thus, the Na$_x$Co$_2$O$_4$ polycrystalline sintered body with a fine microstructure could be obtained by the CAC process. The reason why the grain size of the sintered CAC sample became small, in spite of the fact that the size of the calcined particles and the sintering condition in the CAC process

![Fig. 3. XRD patterns of the sintered bodies synthesized by the (a) SSR, (b) PC and (c) CAC processes.](image)

![Fig. 4. SEM photographs of the cross section perpendicular to the pressed plane of the sintered bodies synthesized by the (a) SSR, (b) PC and (c) CAC processes.](image)
were almost the same as those in the PC process, has not been clarified yet, but breaking particles during compacting because of their plate-like shape with a high aspect ratio may contribute to the formation of the fine microstructure. Besides that, it was found that the plate-like grain were well aligned along the pressed plane (horizontal direction in the SEM photograph), indicating that the sintered body possesses a large crystallographic anisotropy. Generally, the degree of crystallographic orientation of these samples is evaluated from the intensity of the $(h k l)$ peaks, $I(h k l)$, in the XRD patterns using the Lotgering factor [12], $f = (P - P_0)/(1 - P_0)$, where $P = \Sigma I(00l)/\Sigma I(h k l)$, 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 directions of grains are completely aligned along the pressing direction, the $f$ value is calculated to be 1. The crystallographic anisotropy of these SSR, PC and CAC samples were evaluated using the Lotgering factor, $f$. In the case of the conventional SSR method, it has been reported that in spite of its random shape of the starting powder, an anisotropic grain growth due to compacting pressure occurred, resulting in a certain amount of crystallographic orientation in the sintered body [5]. The $f$ value of the SSR sample prepared in this study showed a comparatively high value, 0.7, supporting that the anisotropic grain growth. In the case of the PC sample, though the alignment of the flaky powder was observed in Fig. 4(b), the $f$ value was about 0.7, which was almost the same as that of the SSR sample. On the other hand, the CAC sample showed a significantly large $f$ value, 0.9, indicating that a polycrystalline sintered body with a large crystallographic anisotropy can be synthesized by adopting the CAC process. In order to obtain a crystallographically oriented polycrystal, samples are usually produced by sintering under applied pressure, such as hot pressing, spark plasma sintering, hot forging, etc. However, in this study, it was found that a highly oriented sintered body with a large $f$ value could be obtained by pressureless sintering of the plate-like powder precursor with a high aspect ratio synthesized through the CAC process.

Fig. 5 shows the temperature dependence of the Seebeck coefficient, $S$, of the SSR, PC and CAC samples. The Seebeck coefficient of all the samples increased with increasing temperature, showing a metallic behavior. The $S$ values of the PC sample were significantly larger than those of the SSR sample over the entire temperature range. The CAC sample, in spite of its lower Na content, also showed the Seebeck coefficient markedly larger than that of the SSR sample, and those values were almost the same as those of the PC sample. The EDX analysis on these samples revealed that in the case of the SSR sample, several local areas with high Na content up to about $x = 1.4$ were detected in the $\gamma$-Na$_2$Co$_2$O$_4$ phase matrix, indicating inhomogeneity of the SSR sample. On the other hand, in the case of the PC and CAC samples, the Na/Co ratio at a local area in the $\gamma$ phase matrix was found to scarcely vary. This fact suggests that the compositionally homogeneous sintered bodies compared to the SSR sample could be obtained because of mixing of constituent metals at atomic level during their chemical solution processes of the PC and CAC methods. Based on these experimental results, the large Seebeck coefficient of the PC and CAC samples is probably due to the chemical homogeneity of the sintered compact.

Fig. 6 shows the temperature dependence of the electrical resistivity, $\rho$, of the SSR, PC and CAC samples. The $\rho$ values of all the samples monotonously increased with increasing temperature, indicating a metallic behavior as well as in the case of the Seebeck coefficient. The PC sample shows the $\rho$ values slightly higher than those of the SSR sample over the entire temperature range. This is probably due to carrier scattering caused by its fine microstructure compared to that of the SSR sample. On
the other hand, in spite of the fact that the CAC sample had the significantly fine microstructure shown in Fig. 4(c), the electrical resistivity was slightly lower than that of the PC sample. The CAC sample possesses the large crystallographic anisotropy corresponding to $f = 0.9$, as described above. The alignment of the c-plane of each grain along the pressed plane contributes to the reduction in the electrical resistivity. In the CAC sample, it is considered that the reduction in the $\rho$ values due to the grain alignment effectively suppressed the increase in the electrical resistivity due to carrier scattering caused by the fine microstructure. Generally, thermoelectric materials are required to have a fine microstructure in order to decrease thermal conductivity, which is indispensable to enhancing their thermoelectric performance. From the results obtained in this study, it was found that the Na$_{x}$Co$_{2}$O$_{4}$ polycrystal without an increase in the electrical resistivity despite the fine microstructure could be synthesized by the CAC method.

Power factor, $P$, of these samples was calculated from the Seebeck coefficient, $S$, and the electrical resistivity, $\rho$, in the equation $P = S^2/\rho$. Fig. 7 shows the temperature dependence of the power factor of the SSR, PC and CAC samples. The power factor of the PC sample is significantly larger than that of the SSR sample over the entire temperature range. The large $P$ values were attributable to the large Seebeck coefficient, though the electrical resistivity was slightly high compared to the SSR sample. The CAC sample also showed the large power factor, which was almost the same as that of the PC sample, in spite of its smaller $x$ value. Thus, it is evident that the chemical solution process is quite effective for enhancing the thermoelectric properties of Na$_{x}$Co$_{2}$O$_{4}$. It has been reported that a smaller $x$ value in Na$_{x}$Co$_{2}$O$_{4}$ resulted in the smaller Seebeck coefficient and the higher electrical resistivity [13]. Therefore, in the case of the CAC sample, it is expected that the thermoelectric performance can be further enhanced by the synthesis of the Na$_{x}$Co$_{2}$O$_{4}$ polycrystal with a larger amount of Na.

4. Conclusion

The synthesis of the Na$_{x}$Co$_{2}$O$_{4}$ thermoelectric oxide was tried using the chemical solution process; the PC and CAC methods. The chemical solution process was found to be effective for synthesizing the sintered body with chemical homogeneity better than that of the conventional SSR sample. The chemical homogeneity of the PC and CAC samples is considered to increase the Seebeck coefficient significantly, resulting in the large power factor compared to that of the SSR sample. In the case of the CAC method, the plate-like powder precursor with a high aspect ratio composed of the $\gamma$-Na$_{x}$Co$_{2}$O$_{4}$ phase was obtained. The sintered body from the powder precursor possessed a large crystallographic anisotropy with the Lotgering factor, $f = 0.9$, and a fine microstructure. The large crystallographic anisotropy was effective for suppressing an increase in the electrical resistivity due to carrier scattering caused by the fine microstructure. Thus, the CAC method was quite effective for synthesizing the crystallographically oriented Na$_{x}$Co$_{2}$O$_{4}$ oxide with compositional homogeneity and a fine microstructure, and for enhancing the thermoelectric performance.

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