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Thermoelectric properties of $Na_xCo_2O_4$ with rare-earth metals doping prepared by polymerized complex method

Mikio Ito [a,*], Tomoya Nagira [b], Shigeta Hara [a]

[a] Department of Materials Science and Processing, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
[b] Department of Adaptive Machine Systems, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

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Abstract

Polycrystalline $(Na_{1-y}M_y)_xCo_2O_4$ (M = Dy and Yb; $y = 0.01$–0.05) samples were synthesized by the polymerized complex method. The effects of partial substitution of rare-earth metals for a Na-site on the thermoelectric properties of $Na_xCo_2O_4$ were investigated. Dy-substituted samples with $y = 0.03$ and 0.05 showed the decrease in the electrical resistivity compared to the non-substituted sample because of the enhanced c-axis orientation. The power factors of the Dy-substituted samples were higher than that of the non-substituted sample over the entire temperature range investigated (400–1073 K), and the maximum power factor, 1.5×10^{-3} W/m/K^2, was obtained at 1073 K for the sample with $y = 0.05$. The Yb-substitution caused the increase in the electrical resistivity and the Seebeck coefficient compared to the non-substituted sample over the entire temperature range, which is considered to be due to the reduction in the carrier density resulted from the Yb substitution for Na-site. The power factor of the sample with $y = 0.03$ was enhanced over the entire temperature range and the maximum power factor, 1.5×10^{-3} W/m/K^2 was obtained at 1073 K.

Keywords: $Na_xCo_2O_4$; Thermoelectric properties; Polymerized complex method; Rare-earth metal; Substitution effect

1. Introduction

With the rapidly worsening energy and environmental problems, thermoelectric power generation, which can directly convert thermal energy into electrical energy, has been expected as a promising energy conversion technique. Recently, metal oxides such as ZnO, Ca–Co–O, and $Na_xCo_2O_4$ systems [1–5] have been recognized as encouraging thermoelectric materials because they have good stability at high temperature and a low toxicity. The γ-$Na_xCo_2O_4$ has a layered structure, where the Na layer, randomly occupied by 50% Na ions in the regular sites, and the CoO_2 layer of the edge-sharing CoO_6 octahedra, are alternately stacked along the c-axis. Terasaki et al. reported that the γ-$Na_xCo_2O_4$ shows a large thermoelectric power in spite of its metallic conductivity [6]. A single crystal of γ-$Na_xCo_2O_4$ exhibits a crystallographic anisotropy in electrical resistivity, and the out-of-plane electrical resistivity is about one order greater than the in-plane electrical resistivity. Consequently, the high c-axis orientation in the direction perpendicular to the pressed plane for the polycrystalline sample is effective for the reduction in the electrical resistivity in the case of a measurement in the direction parallel to the pressed plane.

In order to improve the thermoelectric properties of $Na_xCo_2O_4$, the effects of various metals substitution for Na-site by the conventional solid-state reaction (SSR) method have been reported [3,7–9]. On the other hand, it was found that the rare-earth metals were hardly substituted for Na-site, and their contents in the $Na_xCo_2O_4$ phase were less than 1 at.%. These samples showed the lower Seebeck coefficient and higher electrical resistivity compared to the non-substituted sample because of the effect of the impurity

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[*] Corresponding author. Tel.: +81 6 6879 7506; fax: +81 6 6879 7506.
E-mail address: ito@mat.eng.osaka-u.ac.jp (M. Ito).

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phases, which are associated with the rare-earth metal atoms, such as rare-earth oxides. In this study, we used a polymerized complex (PC) method to increase the rare-earth metal content in the matrix phase. The PC method was originally outlined by Pechini [10] in the 1960s and modified by Kakihana et al. [11]. The advantages are the elimination of a possible phase segregation during the process of solvent removal and the elimination of steps such as centrifugation, filtration, washing, drying or fine control of the pH when fabricating the powder precursors. Consequently, it is expected that various metals can be more easily substituted for Na-site by utilizing the PC method than the conventional SSR method because PC method makes it possible to mix constituent atoms at the atomic level. In this study, we have chosen Dy and Yb, as a substitution rare-earth metal. The substitution of the rare-earth metal, which has a higher valence number compared to Na, would have significant effects on the thermoelectric performance. Based on this consideration, the influence of the PC method on the rare-earth metal content in the matrix phase and the effects of partial substitutions for the Na-site on the thermoelectric properties of $Na_xCo_2O_4$ were investigated.

2. Experimental procedure

Polycrystalline samples of $(Na_{1-y}M_y)_xCo_2O_4$ (M = Dy and Yb; $y = 0.01$–0.05) were prepared by the polymerized complex method. Citric acid and ethylene glycol were added in the proportion of 4 and 180 mol, respectively, for each mole of metal cation. $NaNO_3$, $Co(NO_3)_2{\cdot}6H_2O$, $Dy(NO_3)_3{\cdot}6H_2O$ and $Yb(NO_3)_3{\cdot}4H_2O$ according to the nominal composition of $Na_{1.7-y}M_yCo_2O_4$ were dissolved in ethylene glycol by heating and stirring at 473 K. The solution was heated at 473–573 K. During the heating process, the formation of the polymer between ethylene glycol and the metal citrate complexes was promoted. When the colloidal solution was condensed, it became highly viscous. Viscous polymeric product was decomposed to a fine powder at 573–723 K. The powder precursor was calcined at 1073 K for 18 ks in air to enhance the crystallization and eliminate the organic contents. The calcined powder was compacted at a pressure of 5.6×10^2 MPa and then sintered at 1153 K for 72 ks in air. The x value in $Na_xCo_2O_4$ obtained in this study was about 1.1. The crystal structures of the samples were examined by X-ray diffraction (XRD) analysis using Cu Kα radiation. The lattice parameter was measured based on the result of powder XRD analysis. The electrical resistivity, ρ, and Seebeck coefficient, S, were measured in the direction parallel to the pressed plane from 400 to 1073 K in air by a conventional DC method, and then, the thermoelectric properties of the samples were evaluated by a power factor, P ($P = S^2/\rho$), in this study. The microstructure and composition of the samples were examined by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX).

3. Results and discussion

XRD analysis was performed on the sintered samples. All the diffraction peaks of the non-substituted sample can be assigned to the γ-$Na_xCo_2O_4$. There was no peak from Co_3O_4 phase in the XRD patterns of the Dy- and Yb-substituted samples, indicating that the Dy and Yb do not substitute Co sites. In the case of the $(Na_{0.97}Dy_{0.03})_xCo_2O_4$, there was a small peak from the Dy_2O_3 phase detected in the XRD pattern. On the other hand, $(Na_{0.97}Yb_{0.03})_xCo_2O_4$ was composed of the γ-$Na_xCo_2O_4$ phase without any impurity phase. However, when 5 at.% Yb was substituted, small peaks of Yb_2O_3 phase were appeared in the XRD pattern. Fig. 1 shows the SEM photographs of the cross-section of $(Na_{0.97}M_{0.03})_xCo_2O_4$ (M = Dy and Yb) samples. In the case of M = Dy, small Dy_2O_3 particles were widely dispersed in the $Na_xCo_2O_4$ matrix phase, which corresponded to the XRD results. EDX analysis showed that the Dy content in the $Na_xCo_2O_4$ matrix phase corresponded to $y = 0.01$–0.015, which was slightly higher than that in the case of the sample prepared by the conventional SSR method. On the other hand, the Yb content in the matrix phase from the EDX analysis mostly corresponded to the nominal composition. In the case of the Yb-substituted samples prepared by the SSR method, the lattice parameters, a and c, nearly remained constant with increasing y. This is considered to be due to the extremely small amount of Yb content in the matrix phase regardless of the nominal Yb

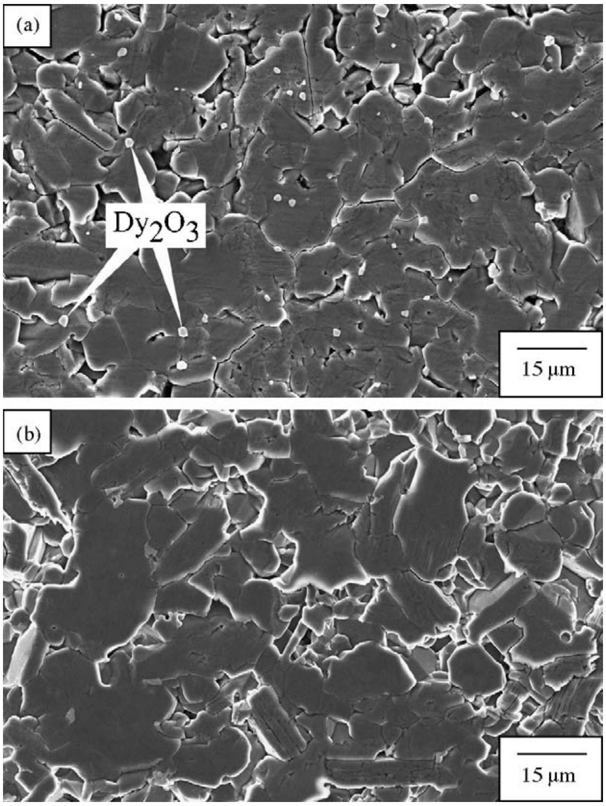

Fig. 1. SEM photographs of the sintered $(Na_{0.97}M_{0.03})_xCo_2O_4$ (M = (a) Dy and (b) Yb).

content. On the other hand, in case of the Yb-substituted samples prepared by the PC method, a and c decreased by 0.21% and increased by 0.43%, respectively, at $y = 0.03$. It can be concluded that the Yb-substitution caused the change of the lattice parameters. From these findings, it was found that the PC method is an effective technique to substitute rare-earth metals for Na-site.

Judging from the increase in the lattice parameter, c, by the Yb-substitution, it is considered that the layered structure extended along the c-axis, resulting in the change of the c-axis orientation. The degrees of c-axis orientation of the Yb-substituted samples were evaluated by Lotgering's method based on the results of the XRD analysis [12]. The factor f, which is called the Lotgering factor, is defined as:

$$f = \frac{P - P_0}{1 - P_0} \tag{1}$$

where $P = \sum I\,(0\,0\,l) / \sum I\,(h\,k\,l)$, $P_0 = \sum I_0\,(0\,0\,l) / \sum I_0\,(h\,k\,l)$ and $\sum I\,(0\,0\,l)$ and $\sum I\,(h\,k\,l)$ are the sum of the intensities of all the $(0\,0\,l)$ and $(h\,k\,l)$ reflections for the pressed plane, respectively. P_0 is the P value for a non-oriented sample. In this study, P_0 was calculated by the intensities of the powder diffraction pattern from the JCPDS card, No. 27–682. Based on the definition, f varies from 0 for a randomly oriented sample to 1 for a completely oriented sample. In the case of the non-substitution sample, f was calculated to be 0.68, and f of the Yb-substituted samples with $y = 0.03$ was evaluated to be 0.89. Thus, it is considered that the change of the lattice parameter influenced on f value: c-axis orientation of the sintered bodies.

The XRD analysis of Dy-substituted samples exhibited that the intensity of the (0 0 2) and (0 0 4) peaks corresponding to the ab-plane of the sintered $Na_xCo_2O_4$ samples was greater than that of the other peaks. This suggests that the c-axis of the crystal grains is aligned in the direction perpendicular to the pressed plane. The c-axis orientation of the Dy-substituted samples was also evaluated. The f values of the samples with $y = 0.01$, 0.03 and 0.05 were calculated to be 0.84, 0.92 and 0.94, respectively. The degree of c-axis orientation of the samples with $y = 0.03$ and 0.05 was higher than that of the Yb-substituted samples. The lattice parameter measurement showed that Dy-substitution increased the lattice parameter, c, by up to 0.50%, as well as in the case of the Yb-substitution. This result also supports that substitution of a rare-earth metal for Na-site is effective for obtaining a high degree of c-axis orientation. Fig. 2 shows the SEM photograph of the cross-section perpendicular to the pressed plane for the sintered $(Na_{0.95}Dy_{0.05})_xCo_2O_4$, which has the highest c-axis orientation. It was found that each crystal grain of the Dy-substituted sample, which had a large aspect ratio, was highly oriented and elongated in the direction parallel to the pressed plane. From these findings, we considered that the increase in the lattice parameter, c, by the substitution for Na-site led to the anisotropic crystal growth, resulting in the enhancement in c-axis orientation.

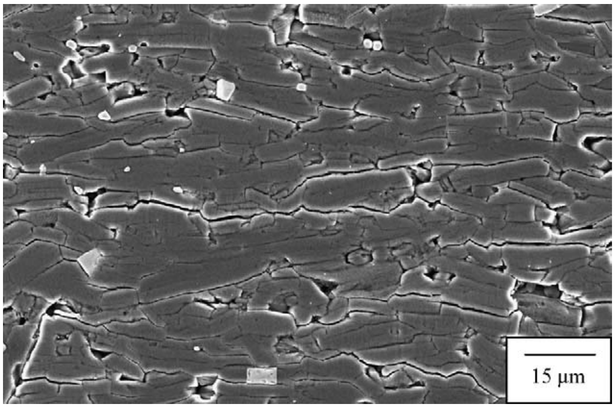

Fig. 2. SEM photograph of the cross-section perpendicular to the pressed plane of the sintered $(Na_{0.95}Dy_{0.05})_xCo_2O_4$.

Fig. 3 shows the temperature dependence of (a) the electrical resistivity, ρ, and (b) the Seebeck coefficient, S, of the sintered $Na_xCo_2O_4$ sample and the $(Na_{1-y}M_y)_xCo_2O_4$ (M = Dy and Yb) samples. In the case of M = Dy, the electrical resistivity decreased with increasing y. The increase in the carrier density generally provides the reduction in the electrical resistivity; however, it is considered that the carrier density decreased by the Dy substitution for Na-site. In addition, the impurity phase, Dy_2O_3, which was observed for all the Dy-substituted samples, is not a high conductor.

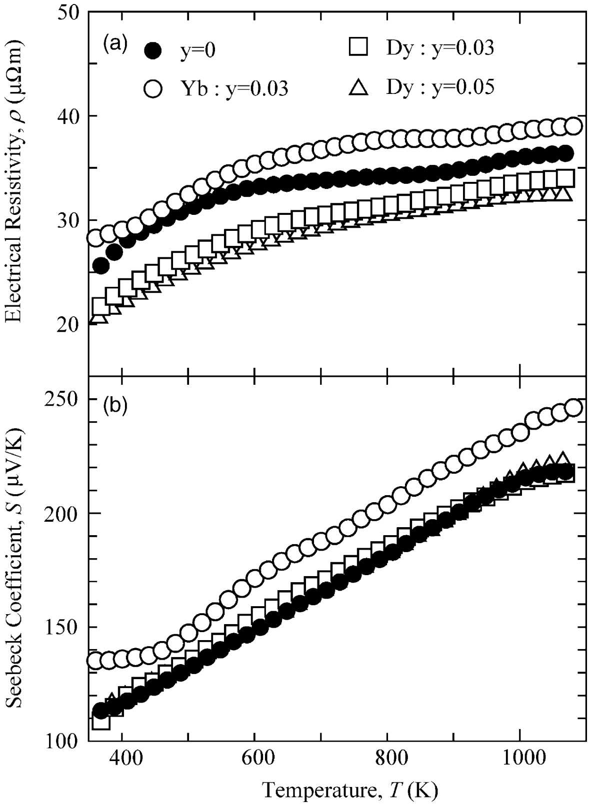

Fig. 3. Temperature dependence of (a) the electrical resistivity, ρ and (b) the Seebeck coefficient, S, for the $Na_xCo_2O_4$ and $(Na_{1-y}M_y)_xCo_2O_4$ (M = Dy and Yb).

From these results, the reduction in the electrical resistivity for the Dy-substituted sample is attributed to the enhancement in the degree of c-axis orientation. On the other hand, the Seebeck coefficient of the sample with $y = 0.03$ and 0.05 showed the Seebeck coefficient almost the same as that of the non-substituted sample. The maximum Dy content in the matrix phase corresponded to about $y = 0.015$, and therefore, it is assumed that the impurity phase obstructed the increase in the Seebeck coefficient caused by the reduction in the carrier density. In the case of M = Yb, the electrical resistivity increased compared to the non-substituted sample over the entire temperature range, in spite of the fact that the Yb-substitution enhanced the degree of c-axis orientation of the sintered body. This is considered to be caused by the reduction in the carrier density due to Yb solution. On the other hand, the Seebeck coefficient was enhanced by Yb-substitution. The increase in the Seebeck coefficient was consistent with the reduction in the carrier density.

The power factor, P, was calculated using the Seebeck coefficient, S, and the electrical resistivity, ρ, in the equation $P = S^2/\rho$. Fig. 4 shows the temperature dependence of the power factor of the sintered $Na_xCo_2O_4$ sample and the $(Na_{1-y}M_y)_xCo_2O_4$ (M = Dy and Yb) samples. In the case of M = Dy, the power factor of all the substituted samples was higher than that of the non-substituted sample over the entire temperature range because of its electrical resistivity smaller than that of the non-substituted sample. The sample with $y = 0.05$ showed the maximum power factor value of 1.5×10^{-3} W/m/K^2 at 1073 K. In the case of M = Yb, the sample with $y = 0.03$ showed the higher power factor over the entire temperature range compared to the non-substituted sample, which resulted from the increase in the Seebeck coefficient. The maximum power factor, 1.5×10^{-3} W/m/K^2 was obtained for the sample $y = 0.03$ at 1073 K, which was the same value obtained for the Dy-substituted sample with $y = 0.05$. As mentioned above, in the case of the conventional SSR process, the substitution content in the matrix phase was remarkably fewer than that of the nominal composition. The power factor of these samples synthesized by the SSR process was significantly reduced because of the decrease in the Seebeck coefficient and increase in the electrical resistivity, which result from the existence of the impurity phase. In this study, it was found that the PC method is useful for the rare-earth metal substitution for Na-site, resulting in the improvement of the thermoelectric properties of $Na_xCo_2O_4$.

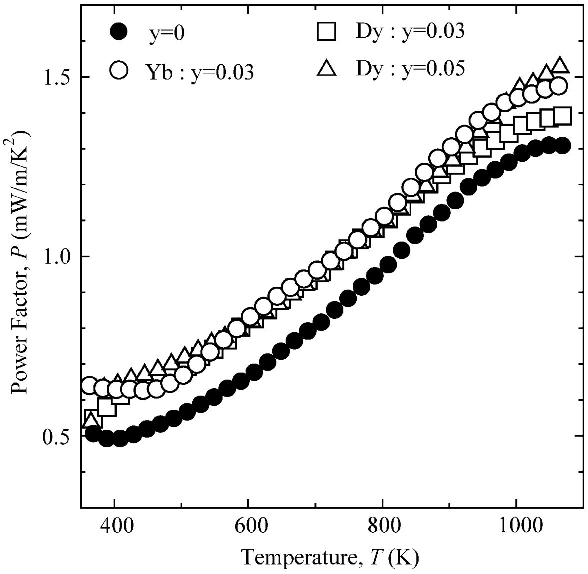

Fig. 4. Temperature dependence of the power factor, P, for the $Na_xCo_2O_4$ and $(Na_{1-y}M_y)_xCo_2O_4$ (M = Dy and Yb).

4. Conclusion

$Na_xCo_2O_4$ thermoelectric oxides partially substituted by the rare-earth metals (Dy and Yb) for Na-site were synthesized by the polymerized complex method, and effects of Na-site partial substitutions on the thermoelectric properties of $Na_xCo_2O_4$ were investigated in the temperature range 400–1073 K. For M = Dy, the rare-earth metal content in the matrix phase slightly increased compared to the samples prepared by the conventional SSR method. In case of the Dy-substituted samples with $y = 0.03$ and 0.05, the electrical resistivity remarkably decreased over the entire temperature range compared to the non-substituted sample. This is due to the enhancement of the c-axis orientation caused by the anisotropic crystal growth resulted from increase in the lattice parameter, c. The power factors of the Dy-substituted samples were higher than those of the non-substituted sample over the entire temperature range, and the sample with $y = 0.05$ showed the maximum power factor value of 1.5×10^{-3} W/m/K^2 at 1073 K. On the other hand, for the Yb-substituted sample, the maximum Yb content in the matrix phase corresponded to $y = 0.03$ from the EDX analysis. The value was remarkably higher than that of the sample prepared by the SSR method. The Yb-substituted samples with $y \leq 0.03$ showed the enhancement in c-axis orientation with increasing the nominal Yb content in conjunction with the rise in the lattice parameter, c. The electrical resistivity and Seebeck coefficient increased compared to the non-substituted sample over the entire temperature range, which is ascribed to the decrease in the carrier density caused by the Yb substitution for Na-site. The power factor of the sample with $y = 0.03$ was enhanced over the whole temperature range, and the maximum power factor, 1.5×10^{-3} W/m/K^2, was also obtained at 1073 K.

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