Effect of Partial Substitutions of Rare-earth Metals for Na-site on the Thermoelectric Properties of $\text{Na}_x\text{Co}_2\text{O}_4$ Prepared by the Polymerized Complex Method

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Polycrystalline $(\text{Na}_{1-y}\text{M}_y)_x\text{Co}_2\text{O}_4$ ($\text{M}=\text{Nd, Sm, Dy and Yb}$; $y = 0.01 \sim 0.05$) samples were synthesized by a polymerized complex method. The effects of partial substitution of rare-earth metals for a Na-site on the thermoelectric properties of $\text{Na}_x\text{Co}_2\text{O}_4$ were investigated, and their differences with the sample prepared by a conventional solid-state reaction (SSR) method were evaluated. In case of the Nd, Sm and Dy-substituted samples, each rare-earth metal content in the matrix phase was slightly higher than that of the sample prepared by the SSR method, resulting in the slight increase in the thermoelectric power. 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, and the sample with $y = 0.05$ showed the maximum power factor value of $1.5 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-2}$ at 1073 K. On the other hand, Yb-substituted samples with $y \leq 0.03$ were almost single $\text{Na}_x\text{Co}_2\text{O}_4$ phase. 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. For the Yb-substituted samples with $y \leq 0.03$, the c -axis orientation was enhanced with increasing the nominal Yb composition in conjunction with the rise in the lattice parameter, c . The Yb substitution caused the increase in the electrical resistivity and thermoelectric power 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, $1.5 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-2}$ was obtained at 1073 K.

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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 $\text{Na}_x\text{Co}_2\text{O}_4$ systems¹⁻⁵⁾ have been recognized as encouraging thermoelectric materials because they have good stability at high temperature and a low toxicity. $\text{Na}_x\text{Co}_2\text{O}_4$ 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. The crystal structure of $\text{Na}_x\text{Co}_2\text{O}_4$ is classified into the following three types: P3: $\beta\text{-Na}_y\text{CoO}_2$ ($0.55 \leq y \leq 0.6$), P2: $\gamma\text{-Na}_y\text{CoO}_2$ ($0.5 \leq y \leq 0.7$) and O3: $\alpha\text{-Na}_y\text{CoO}_2$ ($0.9 \leq y \leq 1$) based on the sodium nonstoichiometry.⁶⁾ Molenda *et al.* reported that the $\gamma\text{-Na}_x\text{Co}_2\text{O}_4$ shows a large thermoelectric power in spite of its metallic conductivity. A single crystal of $\gamma\text{-Na}_x\text{Co}_2\text{O}_4$ 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.⁷⁾ 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 case of a measurement in the direction parallel to the pressed plane.

Generally, it is considered that the Na-site substitution by some metals, which have a higher valence number than Na ion, lead to the decrease in a carrier density because the major carriers of $\text{Na}_x\text{Co}_2\text{O}_4$ are holes. In order to improve the

thermoelectric properties of $\text{Na}_x\text{Co}_2\text{O}_4$, the effects of various metals substitution for Na-site by the conventional solid-state reaction (SSR) method have been reported.^{3,8,9)} Yakabe *et al.* synthesized the sintered $\text{Na}_{0.95}\text{Ba}_{0.05}\text{Co}_2\text{O}_4$ sample and measured the thermoelectric properties.³⁾ Although the thermoelectric power slightly increased compared to the non-substituted sample, the electrical resistivity doubled over the entire temperature range resulting in the declination of the thermoelectric property. In our previous study,¹⁰⁾ we have investigated the effects of alkali-earth and rare-earth metals substitution for Na-site. It was possible to substitute Sr for Na-site and the Sr substitution caused the increase in the thermoelectric power, however, it led to the slight improvement in the thermoelectric property because of the marked increase in the electrical resistivity. On the other hand, it was found that the rare-earth-metals such as Nd, Sm and Yb were hardly substituted for Na-site, and their contents in the $\text{Na}_x\text{Co}_2\text{O}_4$ phase were less than 1 at%. These samples showed the lower thermoelectric power and higher electrical resistivity compared to the non-substituted sample because of the effect of the impurity phases which are associated with the rare-earth metal atoms. 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 Pechini¹¹⁾ in the 1960's and modified by Kakihana *et al.*¹²⁾ 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

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constituent atoms at the atomic level. We have chosen rare-earth-metals such as Nd, Sm, Dy and Yb, as a substitution metal. The substitution of the rare-earth metal, which has a higher valence number compared to the alkali-earth metals, would have much effect on the thermoelectric performance. 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 $\text{Na}_x\text{Co}_2\text{O}_4$ from 400 to 1073 K were investigated. Furthermore, their differences in the substitution effects with the samples prepared by the SSR method were evaluated.

2. Experimental Procedure

Polycrystalline samples of $(\text{Na}_{1-y}\text{M}_y)_x\text{Co}_2\text{O}_4$ ($\text{M}=\text{Nd}$, Sm , Dy and Yb ; $y = 0.01\sim 0.05$) were prepared by the polymerized complex method. Citric acid and ethylene glycol were added in the proportion of 4 moles and 180 moles, respectively, for each mole of metal cation. NaNO_3 , $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{Nd}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, $\text{Sm}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, $\text{Dy}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ and $\text{Yb}(\text{NO}_3)_3\cdot 4\text{H}_2\text{O}$ according to the nominal composition of $\text{Na}_{1.7-y}\text{M}_y\text{Co}_2\text{O}_4$ 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 crystal structures of the samples were examined by X-ray diffraction (XRD) analysis using $\text{Cu K}\alpha$ radiation. The lattice parameter was measured based on the result of powder XRD analysis. The electrical resistivity and thermoelectric power were measured in the direction parallel to the pressed plane from 400 K to 1073 K in air by a conventional DC method. The microstructure and composition of the samples were examined by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The evaluation of the thermoelectric properties should be characterized by the figure of merit, $Z = \alpha^2/(\rho\kappa)$, where α is the thermoelectric power, ρ is the electrical resistivity and κ is the thermal conductivity. However, we could not measure the thermal conductivity in the direction parallel to the pressed plane due to the limitation of the experimental equipment using the laser flash method. Therefore, the thermoelectric properties of the samples were evaluated by a power factor, α^2/ρ , in this study.

3. Results and Discussion

Figure 1 shows the XRD patterns of the sintered $\text{Na}_x\text{Co}_2\text{O}_4$ sample and $(\text{Na}_{0.97}\text{M}_{0.03})_x\text{Co}_2\text{O}_4$ ($\text{M}=\text{Nd}$, Sm , Dy and Yb) samples. All the diffraction peaks of the non-substituted sample can be assigned to the $\gamma\text{-Na}_x\text{Co}_2\text{O}_4$. In case of $\text{M}=\text{Nd}$, Sm and Dy , several peaks of NdCoO_3 , SmCoO_3 and Dy_2O_3 were detected, respectively, as was the case with the SSR method. On the other hand, the Yb-substituted sample

Fig. 1 X-ray diffraction patterns for the sintered $\text{Na}_x\text{Co}_2\text{O}_4$ and $(\text{Na}_{0.97}\text{M}_{0.03})_x\text{Co}_2\text{O}_4$ ($\text{M}=\text{Nd}$, Sm , Dy and Yb).

was mostly composed of the $\gamma\text{-Na}_x\text{Co}_2\text{O}_4$ phase. However, the small peaks of Yb_2O_3 phase were detected in the samples with $y \geq 0.03$. Figure 2 shows the SEM photographs of the cross-section of $(\text{Na}_{0.97}\text{M}_{0.03})_x\text{Co}_2\text{O}_4$ ($\text{M}=\text{Nd}$, Sm , Dy and Yb) samples. In case of $\text{M}=\text{Nd}$, Sm and Dy , NdCoO_3 , SmCoO_3 and Dy_2O_3 phases were widely dispersed in each sintered sample, which corresponded to the XRD results. EDX analysis showed that each Nd, Sm and Dy content in the $\text{Na}_x\text{Co}_2\text{O}_4$ phase corresponded to $y = 0.01\sim 0.015$ which was slightly higher than that of the sample prepared by the SSR method. In case of the $\text{M}=\text{Yb}$, the Yb_2O_3 phase, which was detected in the XRD pattern, could not be observed. The Yb content in the matrix phase from the EDX analysis mostly corresponded to the nominal composition. In general, the ionic radius of rare-earth metals becomes smaller with increasing the atomic weight. Consequently, in case of Yb, which has the smallest ionic radius in Nd, Sm, Dy and Yb, the Yb content in matrix phase highly increased compared to the other rare-earth metal substitutions. From these findings, it was found that the PC method is an effective technique to substitute rare-earth metals for Na-site.

Figure 3 shows the lattice parameters, a and c , for the Yb-substituted samples, which has the highest rare-earth metal content in the matrix phase, together with those of the Yb-substituted samples prepared by the SSR method. The lattice parameters, a and c , of the non-substituted samples prepared by the SSR method were smaller and higher, respectively, than those of the sample prepared by the PC method. Ono *et al.* reported that the lattice parameter, a , slightly increased, and c decreased with increasing the Na content(x) in $\gamma\text{-Na}_x\text{Co}_2\text{O}_4$.¹³⁾ According to their results, when the Na content in $\gamma\text{-Na}_x\text{Co}_2\text{O}_4$ decreased from 0.75 to 0.67, the lattice parameter, c , increased by 0.37%. In our previous study, the compositions of the samples prepared by the SSR and PC

Fig. 2 SEM photographs of the sintered $(\text{Na}_{0.97}\text{M}_{0.03})_x\text{Co}_2\text{O}_4$ ($\text{M}=\text{Nd}$, Sm , Dy and Yb).

Fig. 3 (a) a -axis and (b) c -axis parameters for the $(\text{Na}_{1-y}\text{Yb}_y)_x\text{Co}_2\text{O}_4$; $y = 0, 0.01, 0.03$ and 0.05 prepared by the SSR and PC method.

methods were $\text{Na}_{1.0}\text{Co}_2\text{O}_4$ and $\text{Na}_{1.1}\text{Co}_2\text{O}_4$, respectively.¹⁴⁾ Based on this fact, the increase in the lattice parameter, c , which was expected by the decrease in Na content, was almost same as our results. Therefore, it is considered that the

difference in the lattice parameters at $y = 0$ is attributed to that in the Na contents in $\gamma\text{-Na}_x\text{Co}_2\text{O}_4$. In 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 content. On the other hand, in case of the Yb-substituted samples prepared by the PC method, a and c decreased and increased, respectively, with increasing y , and showed the minimum and maximum values, respectively, at $y = 0.03$. We concluded that the Yb substitution caused the change of the lattice parameters. The increase in a and the decrease in c for $y > 0.03$ is considered to be due to the distortion of crystal structure, which result from the precipitation of the impurity phase due to the Yb substitution beyond the solution limit.

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 degree of c -axis orientation of the Yb-substituted samples was evaluated by Lotgering's method based on the results of the XRD analysis.¹⁵⁾ F , which is called the Lotgering Factor, is defined as

$$F = (P - P_0)/(1 - P_0)$$

where $P = \Sigma I(00\ell)/\Sigma I(hk\ell)$ and $P_0 = \Sigma I_0(00\ell)/\Sigma I_0(hk\ell)$, and $\Sigma I(00\ell)$ and $\Sigma I(hk\ell)$ are the sum of the intensities of all the (00ℓ) and $(hk\ell)$ reflections for the pressed plane, respectively. P_0 is the P value for a non-oriented sample. In this

Fig. 4 (a) a -axis and (b) c -axis parameters for the $(\text{Na}_{1-y}\text{Dy}_y)_x\text{Co}_2\text{O}_4$; $y = 0, 0.01, 0.03$ and 0.05 prepared by the PC method.

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 case of the non-substitution sample, F was calculated to be 0.68, and F of the Yb-substituted samples with $y = 0.01, 0.03$ and 0.05 were evaluated to be 0.76, 0.89 and 0.66. The degree of c -axis orientation of Yb-substituted samples was enhanced with increasing the lattice parameter, c , and the sample with $y = 0.03$, which has the longest lattice parameter, c , showed the highest F value. Consequently, it is considered that the change of the lattice parameter influenced on the c -axis orientation.

The XRD analysis of Dy-substituted samples exhibited that the intensity of the (002) and (004) peaks corresponding to the ab -plane of the sintered $\text{Na}_x\text{Co}_2\text{O}_4$ samples was greater than that of the other peaks. This suggests that the c -axes of

the crystal grains are aligned in the direction perpendicular to the pressed plane. F of the samples with $y = 0.01, 0.03$ and 0.05 were evaluated to be 0.84, 0.92 and 0.94. The degree of c -axes orientation of the samples with $y = 0.03$ and 0.05 were comparable to the single crystal. As described above, the Yb-substituted sample with the longer lattice parameter, c , compared to the non-substituted sample, exhibited the high c -axis orientation. From this result, the lattice parameters of these Dy-substituted samples were measured from the results of powder XRD analysis. Figure 4 shows the lattice parameters, a and c for $(\text{Na}_{1-y}\text{Dy}_y)_x\text{Co}_2\text{O}_4$: $y = 0, 0.01, 0.03$ and 0.05 . The lattice parameter, a , decreased to $y = 0.01$, while c increased to $y = 0.03$ with increasing the nominal Dy content. EDX analysis revealed that the maximum Dy content in the matrix phase corresponded to about $y = 0.015$. The magnitude of the change in the lattice parameter, c , at $y = 0.015$ was remarkably higher than that of the change in c expected from a decrease in the nominal Na content. From these findings, it is concluded that the lattice parameters changed because of the Dy substitution for Na-site in case of the sample with $y \leq 0.015$. On the other hand, it is considered that the increase in the lattice parameter, c , for the sample with $y > 0.015$ is attributed to the decrease in the Na content in the matrix phase. As is the case with Yb, it was found that there could be the relationship between the lattice parameter and the c -axis orientation. Figures 5(a) and (b) show the SEM photographs of the cross-section perpendicular to the pressed plane for the sintered $(\text{Na}_{0.95}\text{Dy}_{0.05})_x\text{Co}_2\text{O}_4$, which has the highest c -axis orientation, and non-substituted sample, respectively. It was found that each crystal grain of the Dy-substituted sample was highly oriented and elongated in the direction parallel to the pressed plane, and the aspect ratio of the crystal grains was higher than that of the non-substituted. 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.

Figures 6, 7 and 8 show the temperature dependence of (a) the electrical resistivity, ρ , and (b) the thermoelectric power, α , of the sintered $\text{Na}_x\text{Co}_2\text{O}_4$ sample and $(\text{Na}_{1-y}\text{M}_y)_x\text{Co}_2\text{O}_4$ ($\text{M}=\text{Sm}, \text{Dy}$ and Yb) samples. In case of $\text{M}=\text{Sm}$, the temperature dependence of the electrical resistivity was

Fig. 5 SEM photographs of the cross-section perpendicular to the pressed plane of (a) the sintered $(\text{Na}_{0.95}\text{Dy}_{0.05})_x\text{Co}_2\text{O}_4$ and (b) the $\text{Na}_x\text{Co}_2\text{O}_4$.

Fig. 6 Temperature dependence of (a) the electrical resistivity and (b) the thermoelectric power for the $(\text{Na}_{1-y}\text{Sm}_y)_x\text{Co}_2\text{O}_4$; $y = 0, 0.03$ and 0.05 .

different from that of the non-substituted sample that indicates the metallic behavior. The Sm-substituted samples exhibited the maximal ρ value at 600 K and then ρ decreased. Moreover, the anomalous peak became prominent with increasing y . This is due to the impurity phase, SmCoO_3 , which transits from the insulator to the conductor at about 600 K.¹⁶⁾ The behavior of the electrical resistivity, which exhibited the anomalous peak at 600 K, was similar to that of $\text{M}=\text{Nd}$. On the other hand, the thermoelectric power slightly increased compared to the non-substituted sample. In general, the carrier density decreases by the trivalent rare-earth metal ion substitution for monovalent Na ion because the major carriers of $\text{Na}_x\text{Co}_2\text{O}_4$ are holes. The increase in the thermoelectric power is due to the reduction in the carrier density. In case of $\text{M}=\text{Dy}$, 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 that, the impurity phase, Dy_2O_3 , which was observed for all the Dy-substituted samples, is not high conductor. 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 thermoelectric power of the sample with $y = 0.01$ was slightly higher than that of the non-substituted sample. However, the sample with $y =$

Fig. 7 Temperature dependence of (a) the electrical resistivity and (b) the thermoelectric power for the $(\text{Na}_{1-y}\text{Dy}_y)_x\text{Co}_2\text{O}_4$; $y = 0, 0.01, 0.03$ and 0.05 .

0.03 and 0.05 showed the almost same thermoelectric power as the non-substituted sample. The maximum Dy content in the matrix phase corresponded to about $y = 0.015$, therefore, it is assumed that the impurity phase obstructed the increase in the thermoelectric power caused by the reduction in the carrier density. In case of $\text{M}=\text{Yb}$, the electrical resistivity increased compared to the non-substituted sample over the entire temperature range. This is considered to be due to the reduction in the carrier density as well as the effect of the impurity phase. The reason why the sample with $y = 0.03$ showed the same electrical resistivity as the sample with $y = 0.01$ is the higher c -axis orientation for the sample $y = 0.03$. On the other hand, the thermoelectric power increased with increasing y , and the sample with $y = 0.03$, which was mostly composed of the γ - $\text{Na}_x\text{Co}_2\text{O}_4$ phase, exhibited the highest thermoelectric power. The increase in the thermoelectric power was consistent with the reduction in the carrier density. The thermoelectric power of the sample with $y = 0.05$ was lower than that of the sample with $y = 0.03$. This is considered to be the influence of the impurity phase, YbCoO_3 .

Figures 9 and 10 show the temperature dependence of the power factor of the $(\text{Na}_{1-y}\text{M}_y)_x\text{Co}_2\text{O}_4$ ($\text{M}=\text{Dy}$ and Yb) samples. In case of $\text{M}=\text{Dy}$, the power factor of all the substituted samples was higher than that of the non-

Fig. 8 Temperature dependence of (a) the electrical resistivity and (b) the thermoelectric power for the $(\text{Na}_{1-y}\text{Yb}_y)_x\text{Co}_2\text{O}_4$; $y = 0, 0.01, 0.03$ and 0.05 .

Fig. 9 The temperature dependence of the power factor, $\alpha^2\rho^{-1}$, of the sintered $(\text{Na}_{1-y}\text{Dy}_y)_x\text{Co}_2\text{O}_4$; $y = 0, 0.01, 0.03$ and 0.05 .

substituted sample over the entire temperature range because of the increase in the thermoelectric power for the sample with $y = 0.01$ and the decrease in the electrical resistivity for the sample with $y = 0.03$ and 0.05 . The sample with $y = 0.05$

Fig. 10 The temperature dependence of the power factor, $\alpha^2\rho^{-1}$, of the sintered $(\text{Na}_{1-y}\text{Yb}_y)_x\text{Co}_2\text{O}_4$; $y = 0, 0.01, 0.03$ and 0.05 .

showed the maximum power factor value of $1.5 \times 10^{-3}\text{ Wm}^{-1}\text{K}^{-2}$ at 1073 K. In case of $\text{M}=\text{Yb}$, 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 thermoelectric power. The maximum power factor, $1.5 \times 10^{-3}\text{ Wm}^{-1}\text{K}^{-2}$ was obtained for the sample $y = 0.03$ at 1073 K in this study. In our previous study, the Dy and Yb substituted samples were prepared by the solid-state reaction method. As mentioned above, the substitution content in the matrix phase was remarkably fewer than that of the nominal composition. The power factor of all substituted samples significantly reduced because of the decrease in the thermoelectric power and increase in the electrical resistivity, which result from the existence of the amount 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 $\text{Na}_x\text{Co}_2\text{O}_4$.

4. Conclusion

$\text{Na}_x\text{Co}_2\text{O}_4$ thermoelectric oxides partially substituted by the rare-earth metals (Nd, Sm, 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 $\text{Na}_x\text{Co}_2\text{O}_4$ were investigated. For $\text{M}=\text{Nd}$, Sm and Dy, each rare-earth metal content in the matrix phase slightly increased compared to the samples prepared by the conventional SSR method. These substitutions caused the slight increase in the thermoelectric power. In case of the Dy-substituted sample 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 that of the non-substituted sample over the entire temperature range, and the sample with $y = 0.05$ showed the maximum power factor value of $1.5 \times$

$10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$ at 1073 K. On the other hand, for the Yb-substituted sample, the maximum Yb content in the matrix phase corresponded to $y \approx 0.03$ 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 thermoelectric power 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 entire temperature range, and the maximum power factor, $1.5 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$ was obtained at 1073 K.

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