Site-Selective Substitution by Transition Metal Cations for NaCo_2O_4 via Ion-Exchange

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遷移金属カチオンを用いたイオン交換による NaCo_2O_4 のサイト選択元素置換

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Incorporation of Ni ions into two different sites of the Na and Co sites of NaCo_2O_4 was carried out by the processes of conventional elemental substitution for Co ion and solid state ion exchange of mobile Na^+ ion. The changes of the lattice parameters of “substituted” and “exchanged” samples were different, suggesting that the Ni ions occupy different sites. The Ni-substituted sample for Co showed a significant decrease of Seebeck coefficient keeping the electrical conductivity almost intact, while Ni-exchanged samples for Na showed a lower electrical conductivity than that of the non-substituted sample with keeping the Seebeck coefficient unchanged. These results suggest that Ni cations introduced to the Co site decouples the Co–Co spin exchange, whereas those at the Na site compensates positive holes by providing conduction electrons.

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1. Introduction

Thermoelectric materials are functional solids which convert heat to electricity using thermoelectric effects, and have been applied to energy source for the deep space explorers and the remote appliances as energy sources. As a miniaturized device, the wrist watches powered by thermoelectric generators were also commercialized. Although conventional thermoelectric materials are commonly degenerated compound semiconductors such as Bi_2Te_3 , they have problems in practical use such as evaporation at high temperature, oxidative degradation under air atmosphere, and the potential serious environmental incompatibility due to the constituting heavy elements.

Oxides are generally stable at high temperature in air, non-toxic, inexpensive, and have been proven to be environment-friendly through a long history of oxide ceramics in human society. Recently, new thermoelectric materials such as skutterudite compounds and oxides have been reported. The crystal structure of NaCo_2O_4 , which is one of the best candidates among the oxide thermoelectrics, is a layered A_xBO_2 type ($0.5 < x < 1$) structure in which alkali ions such as Li, Na, and K occupy the A site, whereas the 3d transition metals such as Fe, Co, and Ni occupy the B site.⁽¹⁾ The low temperature thermoelectric properties of $\text{Na}_{0.7}\text{CoO}_2$ were first reported in 1983.⁽²⁾ After the report by Terasaki, et al. in 1997, the low temperature thermoelectric properties of single crystals and sintered bodies,⁽¹⁾ and influence of Co-site substitution by Mn, Ru, Ti, Rh, and Pd⁽³⁾ were reported. High temperature thermoelectric properties were also reported for single crystals⁽⁴⁾ and polycrystalline samples.⁽⁵⁾ We have reported a marked improvement of the thermoelectric performance of polycrystalline samples by developing a double-sintering method, in which doubly sintered samples showed a larger Seebeck coefficient and a higher electrical conductivity compared to single sintered samples.^(6,7) Furthermore, the band structure

of NaCo_2O_4 was calculated by the cluster method⁽⁸⁾ using discrete variational X -alpha molecular orbital calculation. It was also found that Ca-ion substitution for the Na site results in the lower electrical conductivity and higher Seebeck coefficient.⁽⁹⁾ A large electron specific heat coefficient⁽¹⁰⁾ and point-defect phonon scattering have been proposed to play an important role in NaCo_2O_4 .⁽¹¹⁾

Koshibae et al. proposed that anomalously large Seebeck coefficient of NaCo_2O_4 even at very high carrier concentrations comparable to metals can be explained by a large entropy flow due to Co^{3+} – Co^{4+} spin exchange accompanying the hole transport.⁽¹²⁾

The crystal structure of NaCo_2O_4 is almost the same as that of LiCoO_2 and LiNiO_2 , which are widely used as the cathode materials for lithium ion batteries.⁽¹³⁾ It was reported for LiNiO_2 that almost equal ionic radii of Ni^{3+} and Li^+ can cause cationic mixing at the Li site, and leads to degradation of the discharge capacity of LiNiO_2 .⁽¹⁴⁾ It is also known that in NaCo_2O_4 , Na^+ ion between the CoO_2 slabs is highly mobile and largely non-stoichiometric. In fact, the electrical conductivity of NaCo_2O_4 due to the Na^+ ionic conduction is of the order of 0.1 S/m at around 300°C, and reaches to 1.4 S/m at 800°C,⁽¹⁵⁾ which value approaching to the oxide ionic conductivity of partially stabilized zirconia, a well-known solid electrolyte for oxygen sensors and solid oxide fuel cells. These facts strongly suggest that selective substitution of the Na site of NaCo_2O_4 would be possible by ion-exchange, and that a direct comparison to conventional elemental substitution of the Co site would elucidate the roles of the Co ions in the thermoelectric performance of the oxide.

In order to substitute the different cation sites of NaCo_2O_4 selectively, we have employed two different reaction pathways. One is conventional partial substitution of a particular cation A by another cation B, by mixing appropriate amount of raw materials with conforming the total cation stoichiomet-

ry as $A_{1-x}B_x$ ($0 < x < 1$). In the present study, A is Co and B is mainly Ni with $x = 0.05$ – 0.2 . We denote this method and the samples prepared in this way as “substitution” reaction and “substituted” samples, respectively.

The other one is exchange of mobile cations via solid state reaction by heating a mixture of the sample and a metal salt (usually nitrate) of the substituent cation. Several researcher have reported that Na^+ ion in NaCo_2O_4 can be substituted by other metal cations easily and selectively, even those with the higher valence, via solid state ion-exchange reactions. Doumerc et al. prepared AgCoO_2 by heating a mixture of AgNO_3 and LiCoO_2 at 350°C for 4 days.¹⁶⁾ Cushing and Wiley used $\text{Ca}(\text{NO}_3)_2$ and NaCoO_2 to prepare CaCoO_2 . They heated a mixture of $\text{Ca}(\text{NO}_3)_2$ and NaCoO_2 at 310°C for 2 d and they stated that this was ion-exchanging and was topotactic, evidenced by the fact that the XRD patterns of the samples before and after the reaction almost unchanged, only showing a slight extension in the c -axis length of the crystal structure.¹⁷⁾ Ishikawa et al. recently reported that this reaction was also capable of synthesizing $\text{Sr}_{0.35}\text{CoO}_2$ layered oxide.¹⁸⁾ In this study, we have employed nickel nitrate for ion-exchange of Na by Ni, and denote the samples prepared by this method as “exchanged” samples.

2. Experimental

All samples were prepared by solid state reactions. Ni-substituted samples, $\text{Na}(\text{Co}_{1-x}\text{Ni}_x)_2\text{O}_4$, were prepared from the starting powder mixtures of Co_3O_4 (99.95% Kanto Chemical Co.), Na_2CO_3 (99.95% Kishida Chemical Co.) and $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (98% Kishida Chemical Co.). As shown in Fig. 1, the starting mixtures were calcined twice at 800°C and sintered at 900°C with adding 10 mol% excess Na_2CO_3 at each heating process. This preparation procedure has been commonly used to obtain single phase samples of non-doped NaCo_2O_4 , and is denoted as “S” in this paper. The substituted samples ($\text{NaCo}_{2-x}\text{Ni}_x\text{O}_4$) thus obtained are denoted as $S-x$ ($x = 0, 5, 10$), where x is the amount of doped Ni in mol% per formula unit.

Cation “exchange” was carried out by the procedure “D” in Fig. 1, by firing at 600°C peletized mixtures of $\text{Ni}(\text{NO}_3)_2$ or $\text{Co}(\text{NO}_3)_2$ and a single phase sample of NaCo_2O_4 prepared beforehand by calcining three times at 800°C with adding 10% excess Na_2CO_3 . The resulting solid was pulverized and sintered at 900°C without adding excess Na_2CO_3 . The ion-exchanging was carried out only for the samples without Ni substitution, and the samples thereby obtained were denoted as $D-0-x\text{Ni}$ ($\text{Na}_{1-x}\text{Ni}_x\text{Co}_2\text{O}_4$) or $D-0-x\text{Co}$ ($\text{Na}_{1-x}\text{Co}_x\text{Co}_2\text{O}_4$), where x is the amount of the added metal nitrates in mol% per formula unit. We have also prepared Ni-substituted samples with the same thermal history as that of the ion-exchanged samples, by following the procedure “D” in Fig. 1 omitting the addition of metal nitrates for ion-exchange. These samples are denoted as $D-0$, -5 , and -10 ($\text{NaCo}_{2-x}\text{Ni}_x\text{O}_4$). The symbols denoting the samples are summarized in Table 1.

A powder X-ray diffraction study was carried out on a Rigaku RINT-2000 diffractometer with the $\text{Cu K}\alpha$ radiation. Measurements of the lattice parameters were carried out by using Si as an internal standard. Specimens for the electrical measurements were cut out from the sintered samples into a rectangular shape of about $3 \times 5 \times 5$ mm in size. The electrical conductivity, σ , was measured by the 4-wire method. Seebeck coefficient, S , was determined from the slope of the least-squares regression of ΔV vs. ΔT plotting, where ΔV is the voltage generated between both ends of the specimen, across which various temperature difference ΔT (about 2 K–10 K)

Fig. 1. Preparation processes of $\text{NaCo}_{2-x}\text{Ni}_x\text{O}_4$ ($S-x$, $D-x$; $x = 0, 5, 10$ in mol% per formula unit) and $\text{Na}_{1-x}\text{M}_x\text{Co}_2\text{O}_4$ ($D-0-x\text{M}$; $\text{M} = \text{Ni, Co}$).

Table 1. Summary of the Symbols Denoting the Samples of $\text{NaCo}_{2-x}\text{Ni}_x\text{O}_4$ ($S-x$, $D-x$; $x = 0, 5, 10$ mol%) and $\text{Na}_{1-x}\text{M}_x\text{Co}_2\text{O}_4$ ($D-0-x\text{M}$; $\text{M} = \text{Ni, Co}$)

Amount of added Ni or Co /mol%	Ni-substitution		Ni-exchange	Co-exchange
	S	D	D	D
0	S-0	D-0	←	←
5	S-5	D-5	D-0-5Ni	D-0-5Co
10	S-10	D-10	D-0-10Ni	D-0-10Co

being applied. Scanning electron microscopic (SEM) observation was carried out on a JEOL JSM-6340F for fracture surfaces of the sintered samples. Thermal conductivity measurement was carried out at room temperature by laser flash method on a Kyoto Electronics LFA-502.

3. Results and discussion

The XRD profiles of the samples are shown in Fig. 2. All of the samples were identified as single phase of NaCo_2O_4 except the sample $D-10$. There was virtually no change in the XRD patterns of the samples before and after the ion-exchange reaction, only the peak separation of (112) and (008) at $2\theta = 68$ – 69° becoming more significant for the $D-0$ and the Ni-exchanged samples ($D-0-5\text{Ni}$, 10Ni), while the peak separation was hardly resolved for the S samples. The well-resolved peak separation of (112) and (008) may be attributed to a decrease in disorders and defects in the layered crystal structure due to the repeated firing.

Changes in the lattice parameters of the samples are shown in Fig. 3. It is clear that the c -axis extended by 0.005–0.013 nm for the ion-exchanged samples by 10 mol%, while the a -axis shrank only slightly by 0.0004 nm. Although both $S-0$ and $D-0$ contain no substituent transition metal ions, a difference of about 0.008 nm was observed for the c -axis length. This would be due to volatilization of Na during the repeated sintering for the sample $D-0$. This contraction of the c -axis would also account for the better separation of (112) and (008) peaks for the samples prepared by the procedure “D.”

Fig. 2. XRD patterns of $\text{NaCo}_{2-x}\text{Ni}_x\text{O}_4$ (S - x , D - x ; $x=0, 5, 10$) and $\text{Na}_{1-x}\text{M}_x\text{Co}_2\text{O}_4$ (D - 0 - $x\text{M}$; $\text{M}=\text{Ni}, \text{Co}$).

Fig. 3. (a) c -axis lattice parameter of $\text{NaCo}_{2-x}\text{Ni}_x\text{O}_4$ (S - x , D - x ; $x=0, 5, 10$) and $\text{Na}_{1-x}\text{M}_x\text{Co}_2\text{O}_4$ (D - 0 - $x\text{M}$; $\text{M}=\text{Ni}, \text{Co}$). (b) a -axis lattice parameter of $\text{NaCo}_{2-x}\text{Ni}_x\text{O}_4$ (S - x , D - x ; $x=0, 5, 10$), and $\text{Na}_{1-x}\text{M}_x\text{Co}_2\text{O}_4$ (D - 0 - $x\text{M}$; $\text{M}=\text{Ni}, \text{Co}$).

Although the ionic radii of Ni and Co ions are much smaller than that of Na ion, the extension of the c -axis length was the most remarkable for the ion-exchanged samples particularly for those with the Co ions. These results may be accounted for an increased repulsion between Co in the CoO_2 layer and the A site cations with larger positive charges, which are incompletely screened by O^{2-} anions. A slight but general trend of the contraction of the a -axis with increasing doped metal content

x would be due to relaxation of the deformation strain of the CoO_2 slabs consisting of the CoO_6 octahedra elongated along the ab plane. The contrasting tendency in the lattice parameters for the D - x samples and the D - 0 - $x\text{Ni}$ samples strongly suggest that Ni-ion in these two series of the samples occupy different sites. In fact, a similar tendency of the c -axis and a -axis lengths for ion-exchanged sample was also reported for $\text{Sr}_{0.35}\text{CoO}_2$.¹⁸⁾ From these results, we consider that the Ni-ion occupies the Co site in the D - x samples and occupies the Na site in the ion-exchanged samples.

Figure 4 shows the SEM photographs of the S - x and D - x samples. The microstructure of the D - x samples was more dense than that of the S - x samples, probably due to the repeated sintering. A web-like structure seen in D -10 is considered to be NiO deposited at grain boundaries, as detected in the XRD profile of the sample.

The temperature dependence of the electrical conductivity is shown in Fig. 5. All the samples except D - 0 -10Co showed the metal-like behavior in which the conductivity decreases with increasing temperature. The S - x samples showed almost no change in the electrical conductivity even with increasing amount of Ni. The highest conductivity was observed for the sample D - 0 . Noteworthy, the electrical conductivity of the samples ion-exchanged with Ni and Co was obviously lower than that of the D - 0 . Substitution of the Na sites by the higher valent cations would compensate the positive hole carriers. Moreover, σ of the D - 0 was obviously higher than that of the S - 0 . Possible improvement in crystallinity and in the grain boundary conditions due to the repeated sintering might be responsible for the increase in σ of the D - 0 .

The temperature dependence of the Seebeck coefficient is shown in Fig. 6. The positive S values clearly show that the charge carriers in the samples are positive holes. The Seebeck coefficient decreased with increasing amount of the substituent cations for the S - x , D - x , and D - 0 - $x\text{Co}$ samples. For the S - x and D - x samples, it should be noted that S decreases with increasing x , while σ remained almost unchanged. If the Co^{3+} - Co^{4+} spin exchange is assumed as the origin of the large Seebeck coefficient of the oxide as proposed by Koshibae et al.,¹²⁾ the decrease in S can be explained in terms of decoupling of the spin exchange by the Ni substitution. Whereas the S values of the D - 0 and the D - 0 -10Ni samples were larger than that of the S - 0 , the sample D - 0 -5Ni showed almost the same S value as that of the S - 0 . The improvement in the crystallinity by the repeated sintering for the D samples is expected to increase the Seebeck coefficient. Moreover, the ion-exchange of Na by Ni would deplete the positive holes, resulting in the increase of the S values. However, this would also lower the carrier mobility due to impurity scattering. These counteracting effects would account for the smaller S values of the sample D - 0 -5Ni.

The temperature dependent power factor, $S^2\sigma$ of the samples are shown in Fig. 7. Since the D - 0 showed the highest value of the σ and also high S value over the measured temperature range, the highest power factor of $2.0 \times 10^{-3} \text{ W} \cdot \text{K}^{-2} \cdot \text{m}^{-1}$ at 800°C was obtained for the sample D - 0 . Although the electrical conductivity of the D - 0 -10Ni was lower than that of the D - 0 , the sample D - 0 -10Ni showed the highest S value of $250 \mu\text{V/K}$ and its power factor was $10 \times 10^{-4} \text{ W} \cdot \text{K}^{-2} \cdot \text{m}^{-1}$ at 800°C .

The thermal conductivity, κ at room temperature is shown in Fig. 8 as a function of the amount (x) of substituent metal cations Ni or Co. It is clearly seen that the κ decreased with x for the D - x and D - 0 - $x\text{Co}$ samples, whereas the κ of the S - x samples increased with x . The difference between the κ for the

(a)

(b)

Fig. 4. (a) SEM images of the Ni-substituted samples which denoted as $S-x$ ($\text{NaCo}_{2-x}\text{Ni}_x\text{O}_4$ $x=0, 5, 10$) and $D-x$. (b) SEM images of the ion-exchanged samples which denoted as $\text{Na}_{1-x}\text{M}_x\text{Co}_2\text{O}_4$ ($D-0-x\text{M}$; $x=0, 5, 10$; $\text{M}=\text{Ni}, \text{Co}$).

$S-0$ and the $D-0$ would be attributed to the improved crystallinity of the $D-0$ due to the repeated sintering. However, the x dependence of the κ was totally different for the $S-x$ and the $D-x$ samples. All the “ D ” samples at $x=5$ showed a decrease in the κ compared to $x=0$, while the κ of the samples at $x=10$ increased, except $D-0-10\text{Co}$. These results imply that Ni in the samples at $x=10$ would not com-

Fig. 5. Temperature dependence of the electrical conductivity of $\text{NaCo}_{2-x}\text{Ni}_x\text{O}_4$ ($S-x$, $D-x$; $x=0, 5, 10$) and $\text{Na}_{1-x}\text{M}_x\text{Co}_2\text{O}_4$ ($D-0-x\text{M}$; $\text{M}=\text{Ni}, \text{Co}$).

Fig. 6. Temperature dependence of the Seebeck coefficient of $\text{NaCo}_{2-x}\text{Ni}_x\text{O}_4$ ($S-x$, $D-x$; $x=0, 5, 10$) and $\text{Na}_{1-x}\text{M}_x\text{Co}_2\text{O}_4$ ($D-0-x\text{M}$; $\text{M}=\text{Ni}, \text{Co}$).

Fig. 7. Temperature dependence of the power factor of $\text{NaCo}_{2-x}\text{Ni}_x\text{O}_4$ ($S-x$, $D-x$; $x=0, 5, 10$) and $\text{Na}_{1-x}\text{M}_x\text{Co}_2\text{O}_4$ ($D-0-x\text{M}$; $\text{M}=\text{Ni}, \text{Co}$).

Fig. 8. Thermal conductivity of $\text{NaCo}_{2-x}\text{Ni}_x\text{O}_4$ ($S-x$, $D-x$; $x=0, 5, 10$) and $\text{Na}_{1-x}\text{M}_x\text{Co}_2\text{O}_4$ ($D-0-x\text{M}$; $\text{M}=\text{Ni}, \text{Co}$).

pletely incorporated in the crystal lattice. Accordingly, the D -0-10Co showed the much smaller κ than that of D -0-10Ni. The D -0-10Co showed large increase in the lattice parameter c , and decrease in a as seen in Fig. 3. A similar tendency was also reported by Cushing¹⁷⁾ and Ishikawa.¹⁸⁾ These facts also suggest an incomplete solubility of Ni into the oxide lattice. The drastic decrease in the σ of D -0-10Co and the changes of the lattice parameters mentioned above strongly suggest that Co successfully occupies the Na site of the oxide even at $x=10$.

4. Conclusions

We have prepared two types of Ni substituted samples of NaCo_2O_4 by two different method; one is the conventional partial substitution of the Co site, and the other one is solid state ion-exchange of mobile Na ions by Ni or Co. The extension of the c -axis length was the most remarkable for the Ni and Co ion-exchanged sample. These results may be attributed for an increased repulsion between Co in the CoO_2 layer and the Ni or Co ions with larger positive charges incompletely screened by O^{2-} anions.

The results of σ showed that selective substitution of the Na sites by higher valent cations such as Ni and Co via ion-exchange would compensate the positive hole carriers. The difference of the σ between the D -0 and the S -0 is attributed to the improvement in the crystallinity and grain boundary conditions due to the repeated sintering.

For both S - x and D - x samples the S value decreases with increasing x , while the σ remained almost unchanged. If the Co^{3+} - Co^{4+} spin exchange is assumed as the origin of the large Seebeck coefficient of the oxide, the decrease in S can be explained in terms of decoupling of the spin exchange by the Ni substituent.

The κ values decreased with increasing x for the D - x and D -0- x Co samples, whereas the κ of the S - x samples increased with x . The difference of the κ between S -0 and D -0 would be attributed to the improved crystallinity due to the repeated sintering. The Ni in the samples at $x=10$ would not completely incorporated in the crystal lattice of the oxide, resulting in a small amount of impurity phase such as NiO with higher κ values.

The drastic decrease in σ observed for the D -0-10Co coupled with the largest increase in the lattice parameter c suggest that Co successfully occupies the Na site of the oxide even at $x=10$.

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