

Synthesis and Thermoelectric Properties of Doped NaCo₂O₄ with Transition Metal Cations

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ABSTRACT

We have investigated site-selective doping of Ni in order to experimentally explore the roles of the Na and Co sites of NaCo₂O₄. The selective doping is carried out by changing preparation procedures of the oxide. Cation "substitution" is intended by incorporating Ni(NO₃)₂ into a Co-deficient starting mixture of Na₂CO₃ and Co₃O₄ prior to the first heat treatment. Cation "exchange" is, on the other hand, carried out by heating a mixture of Ni(NO₃)₂ or Co(NO₃)₂ and a single phase sample of NaCo₂O₄, which has been prepared beforehand from a stoichiometric starting mixture. Comparison with control samples without addition of Ni(NO₃)₂ reveals that the "substituted" sample shows a significant decrease in the thermopower with keeping the electrical conductivity almost intact, while the "Ni exchanged" samples shows the lower electrical conductivity with leaving the thermopower unchanged. These results strongly suggest that Ni cations occupy different sites in the Ni-doped samples; disturbing Co-Co spin exchange at the Co site, and compensating holes at the Na site. "Co exchanged" samples shows the same phenomena with the "Ni exchanged" samples. These results strongly suggest that doped Co and Ni of the "exchanged" samples occupy the Na sites.

KEY WORDS: NaCo₂O₄, electrical conductivity, thermoelectricity, Seebeck coefficient, ion exchange

1 INTRODUCTION

The thermoelectric materials are using thermo power in the solids to exchanging heat energy to electrical energy. Recently, thermoelectric materials are used for deep space satellite, watch, and etc.

$$Z = S^2 \sigma / \kappa \quad (1)$$

The equation (1) shows figure of merit Z, which is the estimate criterion of thermoelectric materials. The S, σ , and κ are the Seebeck coefficient, electrical conductivity, and thermal conductivity, respectively, also $S^2 \sigma$ is called power factor that shows electrical thermoelectric properties. Generally speaking, the practical thermoelectric materials (such as Bi₂Te₃) are degenerate semiconductors, and these materials are very expensive, toxic, and not stable at high temperature, so very difficult in wide spread commercial use.

Oxides are inexpensive, nontoxic, and very stable at high temperature at air atmosphere.

NaCo₂O₄ shows outstanding thermoelectric properties among oxides. This is attributable to the high electrical conductivity, large Seebeck coefficient, and low thermal conductivity of the oxide.

The thermal conductivity of NaCo₂O₄ was little changed by ion-exchanging Na with Ba¹⁾. This suggests that ion exchange in NaCo₂O₄ would give negligible influence on the thermal conductivity. The thermal conductivity of NaCo₂O₄ was also hardly changed by "twice sintering", although the Seebeck coefficient and electrical conductivity were enhanced²⁾.

NaCo₂O₄ is an AMO₂ type cobalt oxide with distinct 2D layered crystal structure. The unit cell of NaCo₂O₄ is built up by sheets of edge-sharing CoO₆ octahedra, and the Na sites between the CoO₂ sheets are 50% occupied.

LiCoO₂ and LiNiO₂ are essentially the same as NaCo₂O₄ in their crystal structure. These Lithium compounds have

been attracting keen interests as cathode materials for 4V rechargeable lithium batteries³⁾. However, LiNiO₂ is not used in practical lithium batteries in spite of its large discharge capacity reaching 220mAh/g⁴⁾. It was already reported that stoichiometric LiNiO₂ is extremely difficult to prepare. In comparison of LiCoO₂ and LiNiO₂, Ni³⁺ is more reductive than Co³⁺, and hence LiNiO₂ easily forms Li defects due to volatility of Li salt during high temperature calcination. However, the lithium deficiency is not due to Li⁺ vacancies in the lithium layers, but to the presence of excess nickel occupying Li⁺ sites^{1,2)}.

The AMO₂ rocksalt type structure is subdivided by occupying pattern of the A site. Some investigators noticed that hexagonal system layered rocksalt structure is stable at >1.154 of the ratio of the ionic radii, R_A/R_M, and succeeded at using an ion-exchange method to obtain layered rocksalt structure LiFeO₂ from NaFeO₂^{7,8)}. From these results, there is strong possibility that the A site of NaCo₂O₄ can be exchanged by cations smaller than Na(1.00Å). This idea also seems to be supported indirectly by observation of ion exchange of Na by Ba and Bi¹⁾.

NaCo₂O₄ shows the same crystal structure as that of LiNiO₂, and Ni can enter both the A and M site of LiNiO₂. In this paper, we have hence investigated the effect of doping Ni-ion and Co-ion to the Na site and the Co site of NaCo₂O₄ in order to explore the role of the Na and Co sites.

2 EXPERIMENTAL

All the samples were prepared by solid state reaction from the starting powder materials of Co₃O₄ (Kanto Chemical CO.,INC 99.99%), Na₂CO₃ (Kisida Chemical CO.,INC 99.95%), Co(NO₃)₂·6H₂O (Kisida Chemical CO.,INC 98%), and Ni(NO₃)₂·4H₂O (Kisida Chemical CO.,INC 98%) as shown in Fig. 1. The standard procedure to obtain single phase samples of non-doped and Ni doped NaCo₂O₄ is to mix starting materials and calcine twice at

800°C and sinter at 900°C with adding 10% excess Na_2CO_3 at each heating process. For Ni doping, $\text{Ni}(\text{NO}_3)_2$ was incorporated into a Co-deficient starting mixture before calcination. Amounts of doped Ni were 0.1 mol (10 mol%), and 0.05 mol (5 mol%) based on the composition formula of NaCo_2O_4 . We have named these samples SS, which means substituted samples, and the following numbers (-0, -5, -10) describes the amount of doped Ni in mol%. Cation “exchange” was carried out by heating a mixture of $\text{Co}(\text{NO}_3)_2$ or $\text{Ni}(\text{NO}_3)_2$ and a single phase sample of NaCo_2O_4 , which had been prepared beforehand from a stoichiometric starting mixture by calcining three times at 800°C with adding 10% excess Na_2CO_3 . The first heating of NaCo_2O_4 with $\text{Ni}(\text{NO}_3)_2$ or $\text{Co}(\text{NO}_3)_2$ was carried out at 600°C, and the resulting solid was pulverized and sintered again at 900°C without adding excess Na_2CO_3 . We named these samples D-EX-5 and -10. The D denotes that the samples experienced sintering twice, and EX means ion-exchanged samples. It should be noted that in our experiments the symbol “EX” is always accompanied by the suffix “D-”, because the ion exchange requires additional heat treatment and sintering. It should also be noted that we prepared Co and Ni exchanged samples, and we add Co for Co-ion exchanged samples and Ni for Ni-ion exchanged samples after the following numbers (-0, -5, -10). The different heating histories of SS and EX samples caused some difficulties to compare them directly. We have therefore synthesized substituted samples with the same heating history as that of the ion-exchanged samples. This procedure is to calcine the same materials as that of the SS samples three times at 800°C with adding 10% excess Na_2CO_3 and sintered at 600°C, then pulverize and sinter again at 900°C without adding excess Na_2CO_3 . These samples were denoted as, naturally, D-SS-0, -5, and -10. It should be noted that D-EX-0 is identical to D-SS-0, because the heat treatments denoted by D-EX and D-SS are completely the same; the difference is the way of Ni addition. The symbols denoting the samples are summarized in Table I. A powder X-ray diffraction study was carried out to identify crystal phases, and to measure lattice parameters. Specimens for the electrical measurements were cut out from the sintered bodies into a rectangular shape of about $3 \times 5 \times 14$ mm in size. The electrical conductivity was measured by 4-wire method. The thermoelectric power (Seebeck coefficient) was determined from the slope of the least-squares regression of ΔV

Table 1. The symbols denoting the procedures and amounts of doped Ni.

Symbol	Amount of doped Ni / mol		
	0	0.05	0.1
SS-	0	5	10
D-SS-	0	5	10
D-EX-	(D-SS-0)	5	10

vs. ΔT plotting, where ΔV is the voltage generated between both ends of specimen, across which various temperature difference ΔT (about 2K~10K) being applied. Scanning electron microscopic (SEM) observation was carried out on fracture surfaces of the sintered samples in order to examine crystal growth. Thermal conductivity measurement in room temperature was also carried out on sintered samples in order to find thermal conductivity difference between SS and EX samples.

3 RESULTS AND DISCUSSION

3.1 XRD study for crystal phases and measurement of lattice parameters

The results of X-ray diffraction of sintered samples are shown in Fig. 2. All the samples are identified to be single phase of NaCo_2O_4 , except D-SS-10. We confirmed a clear separation between (112) and (008) peaks at $2\theta = 69^\circ$ for D-SS-0, -5, -10, D-EX-5, and -10. The peak separation was not clear for SS-0, -5, -10. These results strongly suggest that repeated sintering leads to better peak separation.

The lattice parameters of the samples are shown in Fig. 3a and b as a function of the amount of doped cation. A general trend can be seen, in which the c-axis expands with increasing amount of doping, while the a-axis contracts at the same time, especially in the Co-ion exchanged samples. The c-axis of Co-ion exchanged samples shows linear increase by increasing amount of doping, while the a-axis shows linear contracts. Another tendency is that the Ni-double sintered samples (D-SS-10, D-EX-5Ni, and D-EX-10Ni) have considerably shorter c-axis as seen in Fig. 3a. These results strongly suggest that 1) Co ion-exchanging and Ni-doping leads to expansion in the c-axis regardless of the substituted or ion-exchanged samples, and 2) repeated sintering in Ni-doped samples causes contraction of the c-axis. The latter would be caused by volatilization of Na between the CoO_2 sheets during repeated sintering, whereas the former seems to be due to incorporation of Ni into the unit cell of NaCo_2O_4 . In the D-EX-5Ni and D-EX-10Ni samples the amount of Ni increase, the c-axis slightly contracts. This phenomenon can not be seen in the Co ion-exchanged samples. It must occurred by difference between Co-ion and Ni-ion. Interesting exception is the a-axis of the ion-exchanged samples (D-EX). The a-axis length of these samples showed negligible variation as seen in Fig. 3b, whereas that of the substituted samples (SS and D-SS) showed significant contraction with Ni-doping. Variation in the a-axis is considered to be caused mostly by distortion of the CoO_6 octahedra in the CoO_2 layers. It is therefore suggested that the SS samples incorporate Ni into the CoO_2 layers, while the EX samples do not. This is consistent with our expectation in which stoichiometric substitution of Ni for Co in the starting mixtures leads to partial elemental substitution of the Co sites, whereas post-treatment of single phase sample of NaCo_2O_4 with Ni nitrate at high temperature would result in ion-exchange of Na with Ni as observed for the Li site in

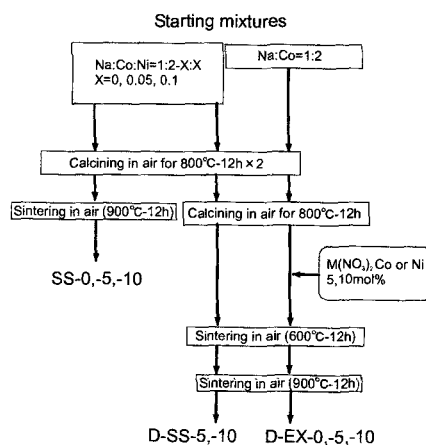


Fig. 1 The preparation process of samples

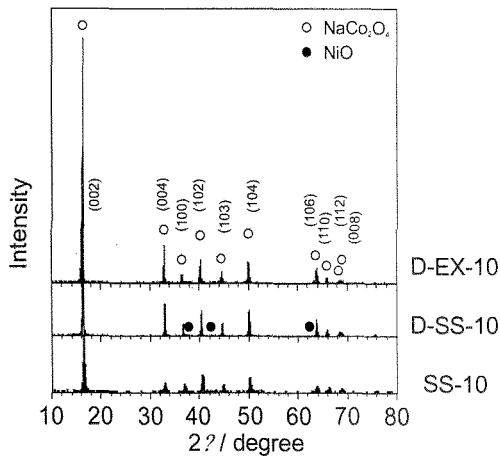


Fig. 2 The XRD patterns of sintered samples.

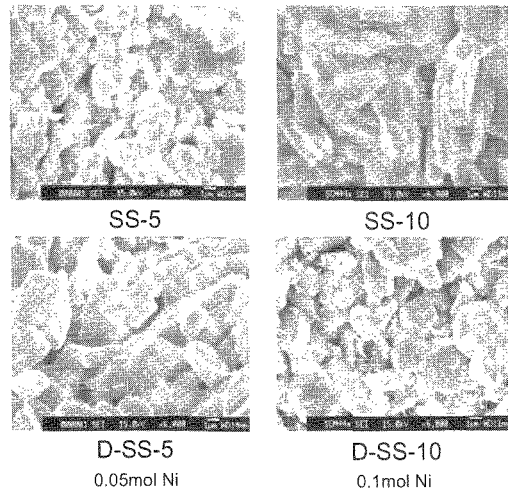


Fig.4 SEM images of the Ni substituted samples.

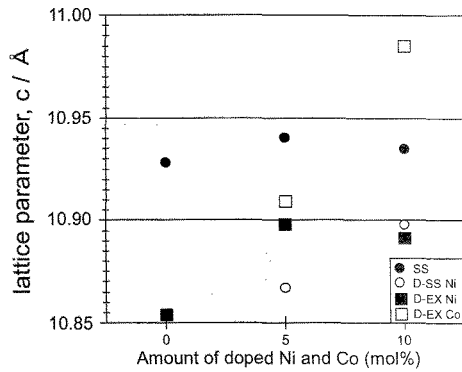


Fig. 3a c-axis lattice parameter of the samples.

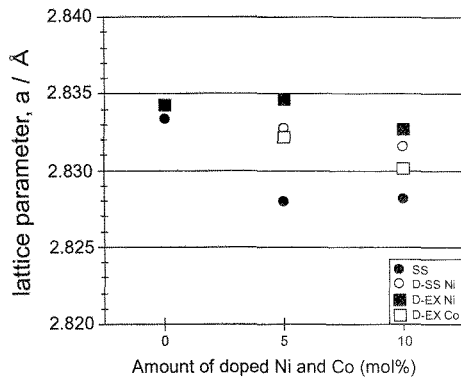


Fig. 3b a-axis lattice parameter of the samples.

LiNiO₂. The ionic radius of Ni²⁺(0.63Å) is larger than that of Co³⁺(0.61Å) and smaller than Na⁺(1.00Å). Since the c-axis of the substituted samples are longer than that of the exchanged samples, it is likely that Ni is substituted in the Co site. Due to the smaller ion radius of Ni than Na, the exchanged samples showed little change in length of the c-axis. A contradictory result of the a-axis of D-SS-10 is probably due to segregation of doped Ni as NiO at grain boundaries, as which was strongly suggested by XRD and SEM observation.

3.2 SEM images

SEM images of all the samples are shown in Fig. 4. In comparison of the SS-5 and the D-SS-5 in Fig. 4, the grain

size of the single sintered samples (SS-5) are smaller than that of the double sintered sample (D-SS-5), and is more porous than D-SS-5. These results are probably attributed to the difference in the heating history. Repeating of sintering process would contribute to larger grain size and more dense microstructure.

In the SEM image of D-SS-10, we found web like structure at the surfaces of the grains. This kind of structure was never observed in other samples. We found the peaks assigned to NiO in XRD patterns only for D-SS-10. From this result, probably this web like structure is excess NiO.

3.3 Thermoelectric properties

The electrical conductivity (σ) and Seebeck coefficient (S) of the samples are shown in Fig. 5a~5b. The electrical conductivity of all samples in Fig. 5a shows metal-like behavior except D-EX-10Co. D-EX-0 showed the highest σ , while SS-5 and -10 showed virtually the same σ as SS-0. D-EX-10Co showed lowest σ in all the samples.

Enhancement in σ of D-EX-0 is consistent with our previous report³⁾ on the improved thermoelectric perfor-

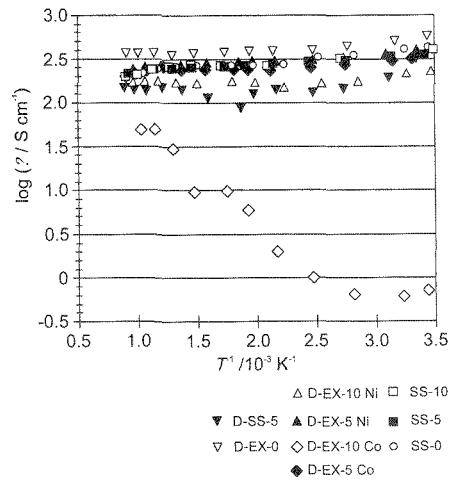


Fig. 5a Temperature dependence of the electrical conductivity of the samples.

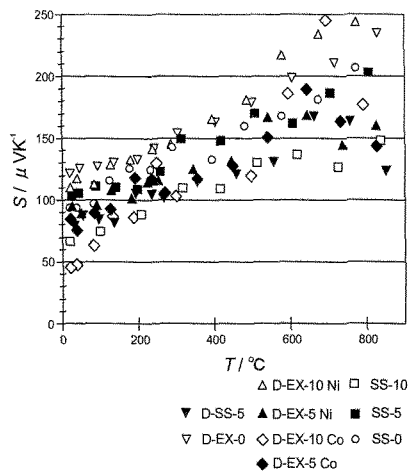


Fig. 5b Temperature dependence of the Seebeck coefficient of the samples.

mance of the doubly sintered samples. There is a significant difference in microstructure of SS-0, -5 and -10, but there is no difference in electrical conductivities. These results show that there is no influence of the microstructures on the electrical conductivities within this range of microstructure variation. The concentration dependences are observed in both the Co-ion, and the Ni-ion exchanged samples. If the Co-ion in the Co exchanged samples occupied the Co sites, the σ must be the same with D-EX-0. These results strongly suggest that the Co-ion and the Ni-ion of ion exchanged sample will occupy the Na site.

The Seebeck coefficients of the samples are shown in Fig. 5b. D-EX-10Ni showed the same S as D-EX-0. The Ni substituted samples (SS-5, -10) showed smaller value than the double sintered sample (D-EX-0). All -5 samples (SS-5, D-SS-5, D-EX-5Ni, and D-EX-5Co) show almost the same S , which lies in between D-EX-0 and SS-10 samples. SS-10 and D-EX-10Co showed the lowest S of all the samples.

The Ni concentration dependence can be seen in the SS samples. The promising thermoelectric properties of NaCo_2O_4 are considered to be attributable to electron exchange between Co^{3+} and Co^{4+} . When the Ni^{2+} ion substituted in the Co site, the carrier (hole) density will increase, but Ni^{3+} are more reductive than Co^{3+} , Ni^{2+} is not easy to exchange electron like Co^{3+} . This would cause lowering of the mobility, and hence S . Enhancement of the carrier density and lowering in mobility can compensate each other. This would be the reason of the fact that the SS samples showed almost the same σ , but decrease in S . When the Co^{3+} and Ni^{2+} ion substituted in the Na site, it will dope electrons into the CoO_2 layer without disturbing the Co-Co electron exchange. This would account for the lower σ of D-EX-10 and its almost the same S as D-EX-0.

3.4 Thermal conductivity at room temperature

Thermal conductivities of the samples are shown in Fig. 6. Thermal conductivities of SS samples at room temperature increase by increasing amount of doped Ni. The Co-ion exchanged samples showed opposite dependence with SS samples. The D-EX-5Ni, D-EX-10Ni samples shows same thermal conductivities with SS samples. These results suggest that increase of unit cell volume and c-axis result in decrease of κ . The thermal conductivity difference between SS-0 and D-EX-0 suggests that increase of

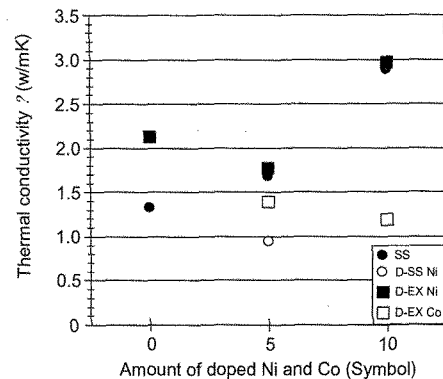


Fig. 6 Thermal conductivity of the the samples.

heat treatment result in enhancement of planar structure inside of the crystal^(2,9).

4 CONCLUSIONS

The Co-ion exchanged NaCo_2O_4 and three types of Ni-doped NaCo_2O_4 were obtained. The Ni-substituted samples showed almost the same σ , but decrease in S compared to the non-doped sample. The Ni-exchanged samples, on the other hand, showed lower σ , but showing almost the same S . The Co-ion exchanged samples showed the same concentration dependence with Ni-ion exchanged samples in σ . The Ni-substituted samples incorporate doped Ni into the Co site, resulting in increased carrier density and lowered mobility which compensating each other. Most of Ni and Co doped into the exchanged samples occupies the Na site, doping electrons into the CoO_2 layer but undisturbing Co-Co electron exchange. This is a plausible explanation of the exchanged sample which shows lower σ than double sintered sample, but showing almost the same S .

The thermal conductivities of all the Ni-doped samples increases by increase amount of Ni. Co-ion exchanged samples shows the opposite depending from Ni-doped samples. These results suggest that enhancement of c-axis and unit cell volume afford low κ .

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