

# Synthesis and Rietveld analysis of new thermoelectric oxides F-doped $\text{Na}_{1.6}\text{Co}_2\text{O}_4$

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A series of five bulk samples of  $\text{Na}_x\text{Co}_2\text{O}_{4-y}\text{F}_y$  ( $x = 1.6$ ,  $y = 0$  to  $0.20$ ) compounds was successfully synthesized by employing the solution precursor method using  $\text{CH}_3\text{COONa}$ ,  $\text{Co}(\text{CH}_3\text{COO})_2$  and  $\text{NaF}$  dissolved in aqua regia. The XRD study with the Rietveld analysis revealed that the lattice parameter  $a$  slightly decreased with increasing F content  $y$ , while the  $c$  increased with increasing  $y$ . The electrical conductivity ( $\sigma$ ) of the compounds continuously decreased with increasing  $y$ . The Seebeck coefficient ( $S$ ) once increased from  $y = 0$  to  $0.10$ , and decreased above  $y = 0.15$ . No improvement in the power factor ( $S^2\sigma$ ) was observed in the compositional range of  $0 \leq y \leq 0.20$ . The carrier concentration was unchanged over the compositional range of  $0 \leq y \leq 0.20$ . A drastic reduction in the thermal conductivity ( $\kappa$ ) of the compounds was observed by substituting O atoms with F atoms at the anion site in the  $\text{Na}_{1.6}\text{Co}_2\text{O}_4$  compounds.

Key words: thermoelectric materials, oxide, Rietveld analysis, thermal conductivity, anion substitution

## 1. INTRODUCTION

Thermoelectric power generation systems can directly convert heat into electrical energy without mechanical and chemical energy losses. Oxide thermoelectric materials have been expected as promising candidates for thermoelectric energy conversion in the high temperature region, because these materials are generally inexpensive, non-toxic, and stable at high temperature in air. Among them,  $\text{Na}_x\text{Co}_2\text{O}_4$  compounds are identified as a powerful  $p$ -type candidate material. Thermoelectric performance of materials is generally evaluated by using the dimensionless figure of merit,  $ZT$ , which is calculated by the equation  $ZT = S^2\sigma T/\kappa$ , where  $S$ ,  $\sigma$ ,  $T$  and  $\kappa$  are Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity of the material, respectively. The maximum  $ZT$  values of  $\text{Na}_x\text{Co}_2\text{O}_4$  reached 0.78 [1], which is a significantly high value in polycrystalline oxide thermoelectric materials. However, a further enhancement in the performance (at least  $ZT \geq 1.0$ ) is necessary in order to employ the  $\text{Na}_x\text{Co}_2\text{O}_4$  compounds to practical thermoelectric power generation systems.

Partial substitution at a certain atomic site in the candidate compounds with different elements is a well-known approach to improve the thermoelectric performance of the compounds. Although a number of studies have been carried out on substituting at various cationic site of  $\text{Na}_x\text{Co}_2\text{O}_4$  [2-4] in order to further enhance its thermoelectric performance, reports on anion substitution of the compound are scarce. This is probably due to difficulties in anionic substitution for the solid state reaction method using  $\text{NaCO}_3$  and  $\text{Co}_3\text{O}_4$  powders having been employed by many researchers [1-5]. A solution precursor method is also known to be

capable of synthesizing such ternary oxides, for example,  $\text{LiMn}_2\text{O}_4$  compounds, which is popular as an electrode material for lithium secondary batteries [6-9]. In particular, anionic substitutions of F and S atoms for the O sites in the material were successfully carried out by this method [6-8].

In this study, we tried to substitute F atoms for O atoms in the  $\text{Na}_x\text{Co}_2\text{O}_4$  compounds for the first time in order to improve the thermoelectric performance of the oxide. Our present goal is to establish preparative conditions of the  $\text{Na}_x\text{Co}_2\text{O}_{4-y}\text{F}_y$  compounds by employing the solution precursor method, and to evaluate the thermoelectric performance of the resulting materials.

## 2. EXPERIMENTAL DETAILS

Five solutions with nominal compositions of  $\text{Na}_x\text{Co}_2\text{O}_{4-y}\text{F}_y$  ( $y = 0, 0.05, 0.10, 0.15, 0.20$ ) were prepared by using  $\text{CH}_3\text{COONa}$ ,  $\text{Co}(\text{CH}_3\text{COO})_2$  and  $\text{NaF}$  dissolved in aqua regia. In this study, the nominal Na composition of  $x$  was adjusted at 1.6, whose value had been systematically optimized in the compositional range between 1.1 and 1.6 by the XRD study. Thus, the ratios of Na:Co:F in the five solutions were set as 1.6:2.0:y. The solutions were heated to dryness at  $80^\circ\text{C}$ , and the solids thus obtained were calcined at  $450^\circ\text{C}$  for 24 h as the first reaction. The reacted materials were crushed into fine powders by using an agate mortar. The powders were calcined again at  $750^\circ\text{C}$  for 14 h as the second reaction, and crushed again by using the mortar. The resulted powders were pressed into disks by using a CIP apparatus, and were sintered at  $930^\circ\text{C}$  for 24 h in air.

The powder XRD patterns for all the samples were measured from  $2\theta = 10$  to  $80^\circ$  at room temperature on a Rigaku RINT-2000 diffractometer with  $\text{Cu-K}\alpha$  radiation at 40 kV and 40 mA. A step scan condition with an

increment of  $0.01^\circ$  in  $2\theta$  was applied in the whole  $2\theta$  range. The electrical conductivity ( $\sigma$ ) and the Seebeck coefficient ( $S$ ) were measured for the sintered samples with a parallelepiped shape from room temperature to  $800^\circ\text{C}$  on an Ozawa Science RZ2001i thermoelectric property measurement system. The thermal conductivity ( $\kappa$ ) was measured for thin square samples on a Kyoto Electronics LFA-502 laser flash measurement system. The Hall measurement was also carried out by van der Pauw method in order to analyze the carrier concentration and the carrier mobility of the samples.

### 3. RESULTS AND DISCUSSION

#### 3.1 XRD measurements and Rietveld analysis

Figure 1 shows the powder XRD patterns of the five samples of  $\text{Na}_{1.6}\text{Co}_2\text{O}_{4-y}\text{F}_y$ . As shown in diffraction indexes in Fig. 1, all diffraction peaks of the five samples can be indexed by assuming a hexagonal structure with a space group of  $P6_3/mmc$  as presented by Balsys [10]. Peaks from impurities were invisible in these XRD patterns.

In this study, all the XRD patterns were refined by the Rietveld method using the multi-purpose-fitting system RIETAN-2000 [11]. In order to determine the quantities of impurity phases in the samples, a four-phase-fitting condition of  $\text{Na}_{1.6}\text{Co}_2\text{O}_4$ , Co, CoO and  $\text{Co}_3\text{O}_4$  was applied. A Pearson VII function, which is continuously variable from the Gauss function to Lorentz function, was selected as a peak profile function for all peaks.

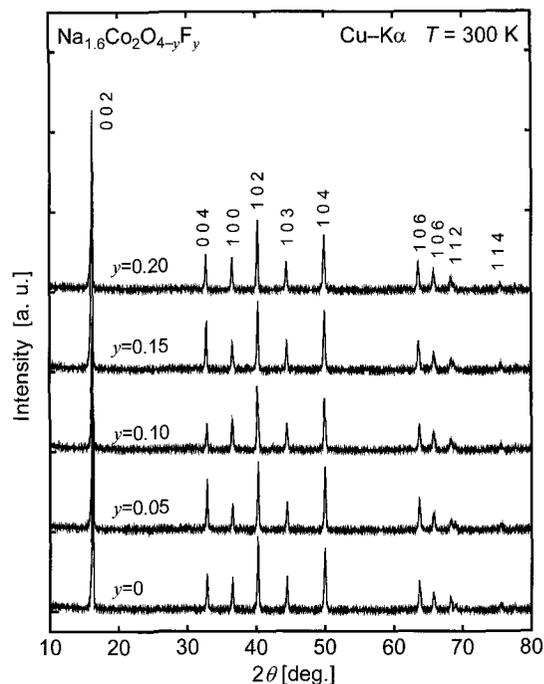


Fig. 1. Powder XRD patterns for the  $\text{Na}_{1.6}\text{Co}_2\text{O}_{4-y}\text{F}_y$  ( $0 \leq y \leq 0.20$ ) sintered samples.

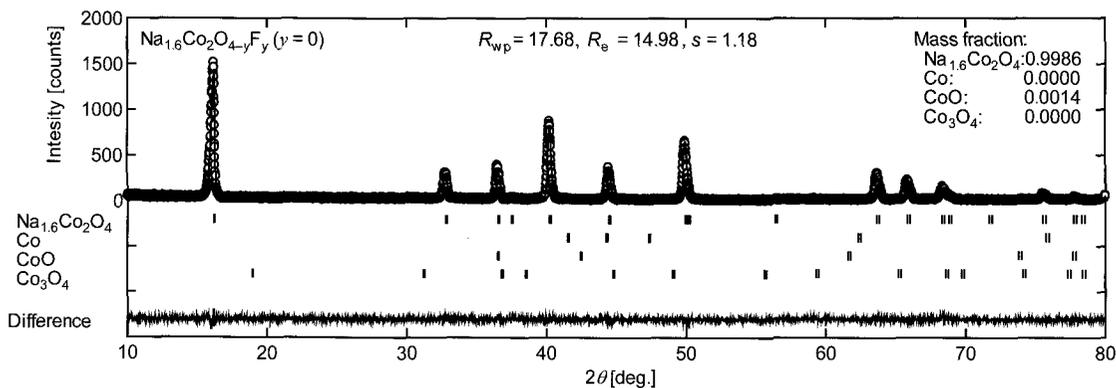
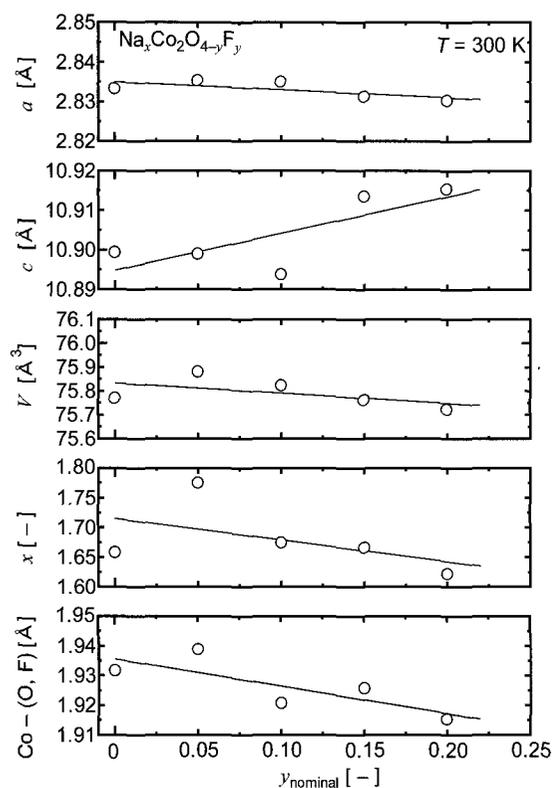


Fig. 2. The profile fitting simulated by the Rietveld analysis for the nominal composition of  $\text{Na}_{1.6}\text{Co}_2\text{O}_4$  ( $y = 0$ ) at  $300\text{ K}$ . The observed and simulated patterns are given by the open circles and solid line, respectively. Short vertical bars below the patterns indicate peak positions of possible reflections from  $\text{NaCo}_2\text{O}_4$ , Co, CoO and  $\text{Co}_3\text{O}_4$ . The difference between observed and calculated intensities is indicated at the bottom.

Figure 2 gives a typical refinement of the XRD patterns of the samples; the profile fitting by the Rietveld analysis for the sample at  $y = 0$  ( $\text{Na}_{1.6}\text{Co}_2\text{O}_4$ ). A satisfactory agreement was obtained between the measured and calculated patterns with a goodness of fit  $s = 1.18$ , as shown in Fig. 2. Since  $s$  values of other four refinements did not exceed 1.3, a quantitative discussion is possible for refined parameters including lattice parameters.

In Figure 3, the lattice parameters of  $a$ - and  $c$ -axes and unit cell volume,  $V$ , of  $\text{Na}_{1.6}\text{Co}_2\text{O}_{4-y}\text{F}_y$  determined by the Rietveld analysis are indicated as a function of the F content,  $y$ . The solid lines are linear fits for the five samples by the least-squares method. As shown in Fig. 3,

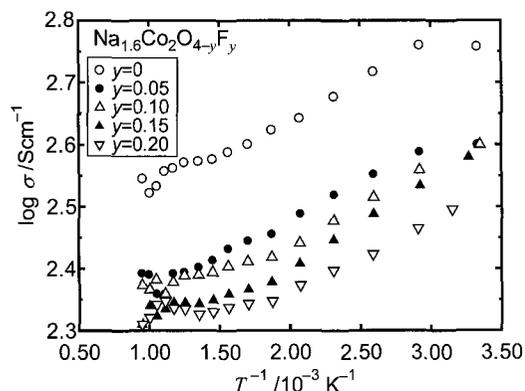
the  $a$  values decreased linearly with increasing F content,  $y$ , while the  $c$  values increased linearly with increasing  $y$ . As a result, the  $V$  values, which are calculated as  $V = a^2c \times \sin 120^\circ$ , slightly decreased with increasing  $y$ , at least in the F content range of  $y \leq 0.20$ . The Na content  $x$  and the interatomic distance between Co and (O, F) atoms in the  $\text{Na}_x\text{Co}_2\text{O}_{4-y}\text{F}_y$  compounds are also given in Fig. 3. As shown in Fig. 3, both  $x$  and the interatomic distance decreased with increasing F content,  $y$ . In addition, the  $x$  values of the samples are in between 1.6 and 1.7 except for the sample at  $y = 0.05$ , showing that the Na ratio was retained near the nominal composition of  $x = 1.6$ .



**Fig. 3.** The lattice parameters ( $a$ ,  $c$ ), unit cell volume ( $V$ ), Na content ( $x$ ) and interatomic distance of Co-(O, F) of  $\text{Na}_x\text{Co}_2\text{O}_{4-y}\text{F}_y$  as a function of the F content,  $y$ .

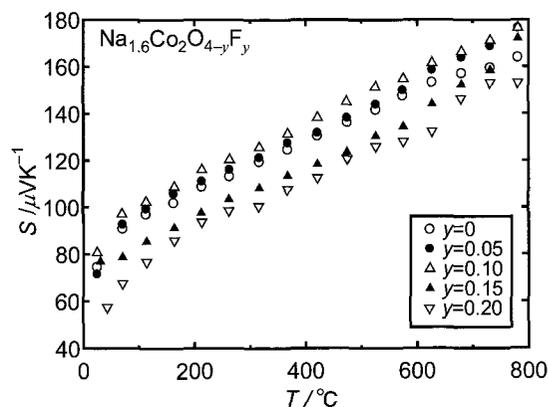
### 3.2 Thermoelectric properties

The temperature dependence of the electrical conductivity ( $\sigma$ ) of the  $\text{Na}_{1.6}\text{Co}_2\text{O}_{4-y}\text{F}_y$  compounds is given in Fig. 4. It is clear that all the  $\sigma$  values decreased with decreasing inverse temperature down to  $1/T = 1.2 \times 10^{-3} \text{ K}^{-1}$  (833 K), which is a typical metallic behavior in the  $\sigma$  vs.  $1/T$  curve. On the other hand, a semiconductor behavior was observed in the high temperature range of  $1/T \leq 1.2 \times 10^{-3} \text{ K}^{-1}$ . Interestingly, the magnitude of the conductivity shifted downward with increasing F content,  $y$ , as shown in Fig. 4. This tendency would be ascribed to a disturbance of the carrier conduction layer unexpectedly introduced by substituting O atoms in the  $\text{Na}_{1.6}\text{Co}_2\text{O}_4$  compounds with F atoms.



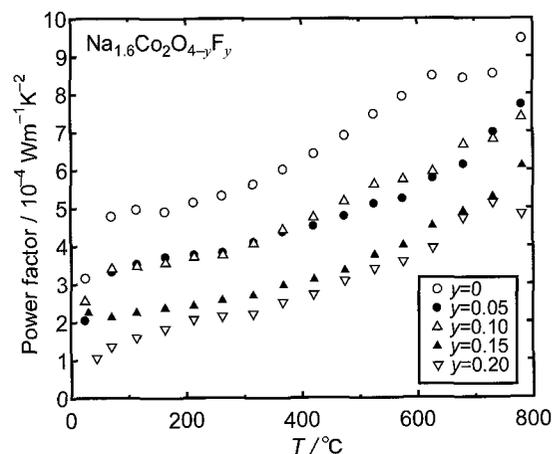
**Fig. 4.** Temperature dependence of the electrical conductivity,  $\sigma$ , of the  $\text{Na}_{1.6}\text{Co}_2\text{O}_{4-y}\text{F}_y$  compounds.

Figure 5 indicates the temperature dependence of the Seebeck coefficient ( $S$ ) from room temperature up to  $800^\circ\text{C}$  as a function of the F content,  $y$ , in the  $\text{NaCo}_2\text{O}_{4-y}\text{F}_y$  compounds. As shown in Fig. 5, the Seebeck coefficient of all the samples showed  $p$ -type conduction, and increased with increasing temperature up to  $800^\circ\text{C}$ . For the sample at  $y = 0$ , the  $S$  value was about  $70 \mu\text{V/K}$  at room temperature, and increased with increasing temperature, reaching  $160 \mu\text{V/K}$  near  $800^\circ\text{C}$ . These values agree well with the literature values for the sintered samples prepared by the solid state reaction [5]. It is notable that the magnitude of the Seebeck coefficient once shifted upward until  $y = 0.10$ , and turned to downward from  $y = 0.15$  to  $0.20$ .



**Fig. 5.** The Seebeck coefficient,  $S$ , of the  $\text{Na}_{1.6}\text{Co}_2\text{O}_{4-y}\text{F}_y$  compounds as a function of temperature.

Figure 6 shows the temperature dependence of the power factor,  $S^2\sigma$ , which is calculated from measured  $S$  and  $\sigma$  values presented in Figs. 4 and 5. For the sample at  $y = 0$ , the  $S^2\sigma$  value was near  $3 \times 10^{-4} \text{ W/mK}^2$  at room temperature, and increased with increasing temperature, reaching  $9 \times 10^{-4} \text{ W/mK}^2$  near  $800^\circ\text{C}$ . Since  $\sigma$  decreased strongly with increasing F content,  $y$ , the  $S^2\sigma$  value of the doped sample at the maximum  $y$  content of  $0.20$  decreased down to  $4.5 \times 10^{-4} \text{ W/mK}^2$  near  $800^\circ\text{C}$ , although  $S$  once increased in the compositional range of  $y = 0$  to  $0.10$ .



**Fig. 6.** The power factor ( $= S^2\sigma$ ) of the  $\text{Na}_{1.6}\text{Co}_2\text{O}_{4-y}\text{F}_y$  compounds as a function of temperature.

### 3.3 Hall measurements

The Hall measurements revealed that the Hall coefficients of all the five samples were positive, being in good accordance with the results of the Seebeck measurements as presented in Fig. 5.

Figure 7 summarizes the carrier concentration of the  $\text{Na}_{1.6}\text{Co}_2\text{O}_{4-y}\text{F}_y$  compounds obtained by the Hall measurements at room temperature using the equation of  $n = 1/eR_{\text{H}}$ , where  $e$  and  $R_{\text{H}}$  are elementary charge and the Hall coefficient, respectively. In this study, the carrier concentrations of the five samples were in the same magnitude around  $2.0 - 2.5 \times 10^{27} \text{ m}^{-3}$ , as shown in Fig. 7. This result suggests that the reduction in the hole concentration expected for F-doping at the O sites was somehow compensated possibly by the Na deficiency, resulting in the unchanged Co valence in the compounds over the compositional range of  $0 \leq y \leq 0.20$ .

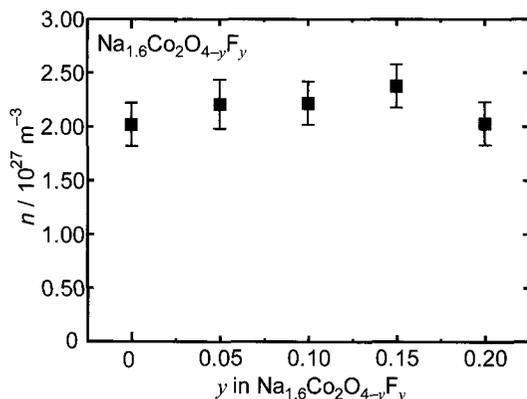


Fig. 7. The carrier concentration,  $n$ , of the  $\text{Na}_{1.6}\text{Co}_2\text{O}_{4-y}\text{F}_y$  compounds as a function of the F content,  $y$ .

$\text{Na}_x\text{Co}_2\text{O}_4$  consists of two-dimensional  $\text{CoO}_2$  layers stacking along the (001) direction, and the Na atoms are sandwiched between the  $\text{CoO}_2$  layers [1]. It is considered that variations of unit cell volume ( $V$ ) of the  $\text{Na}_{1.6}\text{Co}_2\text{O}_{4-y}\text{F}_y$  compounds are affected mainly by three factors, *i.e.*, a reduction of the mean ionic radius at the anionic sites by the F-doping, an increment of repulsion between the  $\text{CoO}_2$  layers by the Na deficiency, and a fluctuation of the Co valence. However, it was found that the Co valence in the compounds was unchanged over the compositional range of  $0 \leq y \leq 0.20$ , and consequently the effects of both the ionic radius and the repulsion would be dominant to discuss the variation of  $V$ . An increment of repulsion between the negatively charged  $\text{CoO}_2$  layers with increasing Na deficiency would cause an elongation of the  $c$ -axis. On the other hand, a reduction in the interatomic distance of Co-(O, F) in the  $\text{CoO}_2$  layers by decreasing mean ionic radius at the anionic sites should lead to a shrinkage in the  $a$ -axis. This discussion is consistent with the results of the  $a$ ,  $c$ ,  $x$  and Co-(O, F) distance in the  $\text{Na}_x\text{Co}_2\text{O}_{4-y}\text{F}_y$  compounds obtained by the Rietveld analysis as shown in Fig. 3. It is therefore concluded that F-doping at the anion sites in the  $\text{Na}_{1.6}\text{Co}_2\text{O}_4$  compounds was successfully carried out by employing the solution precursor method using  $\text{CH}_3\text{COONa}$ ,  $\text{Co}(\text{CH}_3\text{COO})_2$  and  $\text{NaF}$  dissolved in aqua regia.

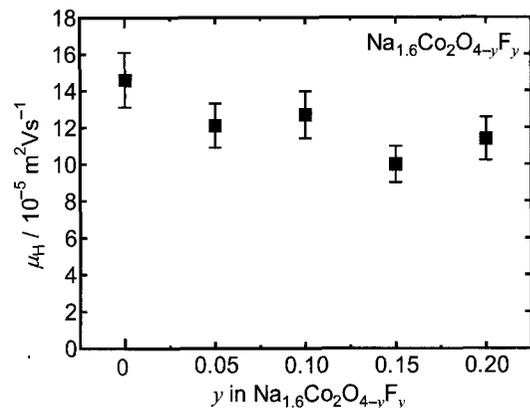


Fig. 8. The carrier mobility,  $\mu_{\text{H}}$ , of the  $\text{Na}_{1.6}\text{Co}_2\text{O}_{4-y}\text{F}_y$  compounds as a function of the F content,  $y$ .

Figure 8 gives the carrier mobility,  $\mu_{\text{H}}$ , of the five samples obtained by the equation  $\mu_{\text{H}} = \sigma/ne$ , where  $\sigma$ ,  $n$  and  $e$  are electrical conductivity, carrier concentration, and elementary charge, respectively. The  $\sigma$  and  $n$  values used here were presented in Fig. 4 and Fig. 7, respectively. Consequently,  $\mu_{\text{H}}$  of the samples gradually decreased with increasing F content,  $y$ , as shown in Fig. 8.

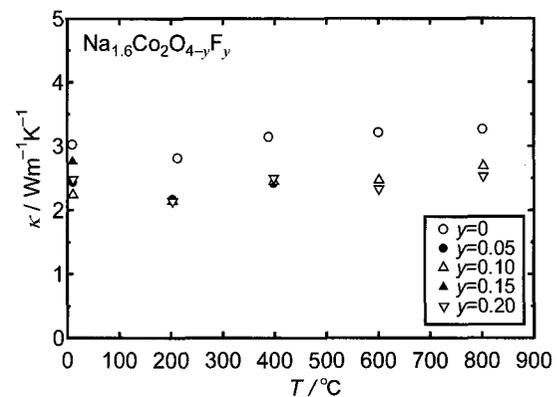


Fig. 9. The thermal conductivity,  $\kappa$ , of the  $\text{Na}_{1.6}\text{Co}_2\text{O}_{4-y}\text{F}_y$  compounds as a function of temperature.

Figure 9 indicates the temperature dependence of the thermal conductivity,  $\kappa$ , of the  $\text{Na}_{1.6}\text{Co}_2\text{O}_{4-y}\text{F}_y$  compounds. As shown in Fig. 9,  $\kappa$  was virtually unchanged over the temperature range from room temperature up to 800 °C. It should be noted that F-doping markedly reduced the  $\kappa$  values by 18 - 25%. This is obviously attributed to reduction in the lattice thermal conduction, and probably due to an enhancement of phonon scattering by substitution of O atoms with F atoms.

### 3.4 Dimensionless figure of merit (ZT)

Finally, the  $ZT$  values of the five samples were evaluated by using the measured thermoelectric parameters  $S$ ,  $\sigma$ ,  $T$  and  $\kappa$ . The temperature dependence of the  $ZT$  is given in Fig. 10. For the non-doped sample,  $ZT$  was 0.03 at room temperature, and increased with increasing temperature, reaching 0.31 at 800 °C.

Although F-doping resulted in the marked reduction in  $\kappa$ , the doping lowered the  $ZT$  values. This is due to the decrease in the  $S^2\sigma$  values of the F-doped samples, as presented in Fig. 6. Additional approaches such as cation doping are necessary to improve the thermoelectric performance in the  $\text{Na}_{1.6}\text{Co}_2\text{O}_{4-y}\text{F}_y$ .

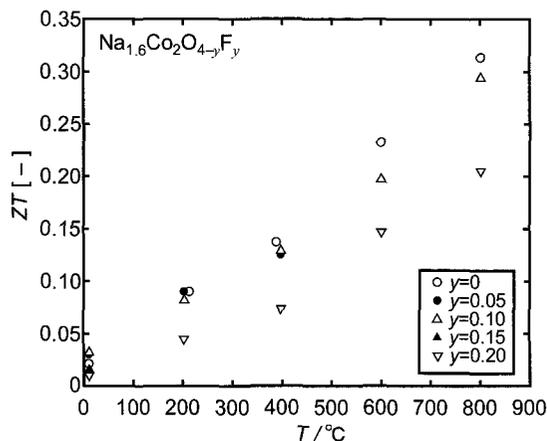


Fig. 10. The dimensionless figure of merit,  $ZT$ , of the  $\text{Na}_{1.6}\text{Co}_2\text{O}_{4-y}\text{F}_y$  compounds as a function of temperature.

#### 4. CONCLUSIONS

We have successfully synthesized the  $\text{Na}_{1.6}\text{Co}_2\text{O}_{4-y}\text{F}_y$  compounds in the compositional range of  $y = 0$  to 0.20. It was found that the solution precursor method using  $\text{CH}_3\text{COONa}$ ,  $\text{Co}(\text{CH}_3\text{COO})_2$  and  $\text{NaF}$  dissolved in aqua regia was capable of synthesizing the compounds at high purity. The  $a$ -axis was slightly contracted with increasing F content,  $y$ , while the  $c$ -axis was extended, resulting in a small reduction in the unit cell volume,  $V$ . The electrical conductivity ( $\sigma$ ) of the compounds simply decreased with increasing  $y$ . The Seebeck coefficient ( $S$ ) once increased between  $y = 0$  and 0.10, and then decreased from  $y = 0.15$  to 0.20. The power factor ( $S^2\sigma$ ) monotonically decreased with increasing  $y$ . The carrier concentration was unchanged over the compositional range of  $y = 0$  to 0.20. The thermal conductivity ( $\kappa$ ) of the compounds was markedly reduced by F-doping. The dimensionless figure of merit ( $ZT$ ) of the  $\text{Na}_{1.6}\text{Co}_2\text{O}_{4-y}\text{F}_y$  compounds simply decreased by F-doping within the nominal compositional range of  $y = 0$  to 0.20. The significant reduction of  $\kappa$  observed here will be helpful for development of the  $\text{Na}_{1.6}\text{Co}_2\text{O}_{4-y}\text{F}_y$  compounds as practical thermoelectric materials.

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(Received January 3, 2008; Accepted May 14, 2008)