Na-site substitution effects on the thermoelectric properties of NaCo$_2$O$_4$

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There appears a growing interest to a hunt for new thermoelectric (TE) materials reflecting urgent needs for a new energy-conversion system in harmony with our environments. A TE material generates electric power in the presence of temperature gradient through the Seebeck effect, and pumps heat in the presence of electric current through the Peltier effect. A serious drawback is the low conversion efficiency: It is characterized by the so-called “figure of merit” $Z = S^2/\rho \kappa$, where $S$, $\rho$, and $\kappa$ are the thermopower, resistivity and thermal conductivity of a TE material, respectively. In other words, a good TE material is a material that shows large $S$, low $\rho$ and low $\kappa$. However, a high value of $Z$ is difficult to realize, because the three parameters cannot be changed independently. To overcome this difficulty, a number of new concepts and new materials have been examined.

Recently, we have observed that a layered cobalt oxide NaCo$_2$O$_4$ exhibits unusually large $S$ (100 $\mu$V/K at 300 K) accompanied by low $\rho$ (200 $\mu$2cm at 300 K) along the direction parallel to the Co$_2$O$_3$ planes. NaCo$_2$O$_4$ belongs to a layered Na bronze Na$_x$Co$_2$O$_4$, which was studied as a cathode for sodium batteries. During the characterization, Molenda et al. first found a large $S$ in Na$_{0.7}$Co$_2$O$_4$. Although they noticed that $S$ was anomalously large, they did not mention a possibility for a TE material. Their samples were polycrystals, the resistivity of which was 2-4 m$\Omega$cm at 300 K, much higher than that of our crystals. Our finding is that the carrier density ($n$) is of the order of $10^{21} - 10^{22}$ cm$^{-3}$, and is two orders of magnitude larger than $n$ of conventional TE materials. This is difficult to understand in the framework of a conventional one-electron picture, and may indicate a way to get a good TE material other than the conventional approach. We have proposed that strong electron-electron correlation plays an important role in the enhancement of the thermopower of NaCo$_2$O$_4$.

Even in a correlated system, we can expect that a conductor of low $n$ will have a large $S$, because the diffusive part of $S$ is the transport entropy $\kappa T / E_F$, where $E_F$ is the Fermi energy. Thus it would be tempting to improve the TE properties in NaCo$_2$O$_4$ by decreasing $n$. We easily think of three ways to change $n$ in NaCo$_2$O$_4$, i.e., (i) doping of excess Na$^+$, (ii) the substitution of Ca$^{2+}$ for Na$^+$, and (iii) the change of the oxygen content. Among them, we will discard the idea of (iii), because it will seriously deteriorate the conduction paths consisting of Co and O. Here we report on the resistivity and thermopower of Na$_{3-x}$Co$_2$O$_4$ and Na$_{1.1-x}$Ca$_4$Co$_2$O$_4$ to study the doping effects.

We prepared polycrystalline samples of Na$_{1+x}$Co$_2$O$_4$ and Na$_{1.1-x}$Ca$_4$Co$_2$O$_4$ by solid state reaction. Since Na is volatile, we added 10% excess Na. Namely we expected the starting composition of Na$_{1.1}$Co$_2$O$_4$ to be Na$_{2}$Co$_2$O$_4$. An appropriate mixture of Na$_2$CO$_3$, CaCO$_3$, and Na$_2$O was thoroughly ground, sintered at 860–920°C for 12 h in air. The sintered powder was then pressed into a pellet, and sintered again at 800–920°C for 6 h in air.

The x-ray diffraction (XRD) was measured using a standard diffractometer with Fe K$_\alpha$ radiation as an x-ray source in the $\theta - 2\theta$ scan mode. Note that Cu K$_\alpha$ radiation is not suitable for this compound, because it emits the fluorescent x-ray of Co to make a high noise in the XRD pattern. $\rho$ was measured through a four-probe method, in which the electric contacts with a contact resistance of 1 $\Omega$ were made with silver paint (Dupont 4922). $S$ was measured using a steady-state technique. Temperature gradient ($\sim$0.5 K/cm) was generated by a small resistive heater pasted on one edge of the sample, and was monitored by a differential thermocouple made of copper-constantan. A thermopower of voltage leads was carefully subtracted. Temperature ($T$) was controlled from 4.2 to 300 K in a liquid He cryostat, and was monitored with a CERNOX resistance thermometer.

Figure 1 shows typical XRD patterns of the prepared samples. Almost all the peaks are indexed as the P2$_1$/c phase reported by Jansen and Hoppe, though a tiny trace of impurity phases is detected as marked with * in Fig. 1. Note that all the XRD patterns are nearly the same, which means that XRD is not very powerful for the sample characterization. Thus the best way to characterize the samples is to measure their thermoelectric properties directly. Usually an impurity phase including...
Na will be Na$_2$O, and exist as deliquesced NaOH (Na$_2$O + H$_2$O). We think, however, that Na$_2$O is not a major impurity phase for the present case. The samples are stable enough to handle in air, and the contact resistance and the surface do not deteriorate against several-hour exposure to the air.

Figure 2(a) shows $\rho$ for Na$_{1+x}$Co$_2$O$_4$ plotted as a function of $T$. Both the magnitude and the $T$ dependence are consistent with previous studies. All the samples show a metallic conduction down to 4.2 K without any upturn at low temperatures. This suggests that the conduction paths are not disturbed by the doped excess Na. The $T$ dependence of $\rho$ roughly resembles the in-plane resistivity for single-crystal NaCo$_2$O$_4$ implying that the conduction of polycrystals is mainly determined by the in-plane conduction. Note that $\rho$ for $x=0$ is higher than $\rho$ for $x=0.1$, which suggests that a small amount of Na is evaporated through the sintering process.

Contrary to the change of $\rho$ with $x$, $S$ for Na$_{1+x}$Co$_2$O$_4$ is nearly independent of $x$ as shown in Fig. 2(b). This indicates that $n$ remains intact by doping Na. It is, at first sight, unusual why the doped monovalent Na$^+$ does not change $n$. We point out two possibilities: One is that the excess Na is excluded from the crystal to increase the resistance at the grain boundary, and the other is that it is in the grain to make an insulating phase nearby. Note that NaCo$_2$O$_4$ (corresponding to $x=1$) is an insulator. In both cases, excess Na cations decrease the number of conduction paths to reduce the effective cross section for the current.

Making a remarkable contrast to Fig. 2(a), Figure 3 (a) shows a drastic change of $\rho$ for Na$_{1.1-x}$Ca$_x$Co$_2$O$_4$ with $x$. Above 50 K, while $\rho$ for $x=0$ shows a positive curvature, $\rho$ for $x=0.35$ shows a negative curvature to saturate near 300 K. Unlike the case of the excess Na, the residual resistivity, though not well-defined, tends to increase with $x$, which means that Ca acts as a scattering center. $S$ is also increased with $x$ as shown in Fig. 3(b). Considering that both $\rho$ and $S$ increase with Ca, we conclude that the substitution of Ca$^{2+}$ for Na$^+$ decreases the carriers. Namely the majority carrier of NaCo$_2$O$_4$ is a hole, which is consistent with the transport properties of Na$_{0.7}$Co$_{2.3}$O$_4$. As expected, the TE properties are (slightly) improved by decreasing $n$, and $S^2/\rho$ is maximized at $x=0.15$.

One may notice that Na$_{1.1}$Co$_2$O$_4$ shows different $\rho$ between Figs. 2 and 3. The magnitude of $\rho$ was scattered from batch to batch, possibly because the control of the grain growth is difficult. (Thermopower is a quantity less affected by grain boundaries, and the measured $S$ was independent of batches within experimental errors.) To see the reproducibility we made Na$_{1.1}$Co$_2$O$_4$ as a reference at every preparation run. Figure 4 shows $\rho$ for Na$_{1.1}$Co$_2$O$_4$ prepared in different runs, where the magnitude of $\rho$ is scattered beyond experimental errors ($\sim 10\%$). We note that the relative change of $\rho$ among the same batch is reproducible, and the $T$ dependence is essentially identical from batch to batch. All the $\rho - T$ data in Fig. 4 normalized at 295 K fall into a single curve, as shown in the inset of Fig. 4.

Figure 5 shows $\rho$ of Na$_{1.1}$Co$_2$O$_4$ in Fig. 2(a) is plotted in a log-log scale. Since $\rho$ is linear below 50 K and above 80 K, $\rho$ is proportional to $T^p$ in the two regions. From fitting $\rho$ by $T^p$, we estimated $p$ to be 0.67 below 50 K and 1.2 above 80 K (see the solid and dashed lines in Fig. 5). We will remark three points on the $T$ dependence of $\rho$. First, it is a piece of evidence for strong correlation that $\rho$ continues to decrease with decreasing $T$ down to 4.2 K where no phonons are thermally excited. At least we can say that the conduction in this system is not dominated by the conventional electron-phonon scattering. Secondly the $T$ dependence of $\rho$ of this system is not typical for strongly correlated systems. In usual strongly correlated systems, resistivity and electron-electron scattering are proportional to $(k_B T/E_F)^2$. Most of heavy fermions, $t$-orbital metals, transition-metal oxides [2], and high-$T_c$ superconductors [3] show $\rho \propto T^2$. As shown in the inset of Fig. 5, $\rho$ for Na$_{1.1}$Co$_2$O$_4$ is not proportional to $T^2$ at any temperatures. A prime exception is the $T$-linear resistivity in high-$T_c$ superconductors [3]. Actually, $\rho$ and $S$ of Na$_2$Co$_2$O$_4$ are qualitatively consistent with some theories for high-$T_c$ superconductors [3]. In particular, $\rho$ of Na$_{1.1-x}$Ca$_x$Co$_2$O$_4$ can be explained by adjusting the parameters in Ref. 13. Thirdly all the samples show no indication of localization. This means that the mean free path (MFP) of the carriers is much longer than the lattice parameters [3] and that the carriers do not feel the disorder in the Na layer. On the other hand, phonons will be affected by the disorder in the Na layer, since the disordered Na$^+$ ions make ionic bonding with adjacent O$^{2-}$ ions. In fact, a preliminary measurement has revealed that $\kappa$ for Na$_{1.1}$Co$_2$O$_4$ is as low as 10 mW/cmK [4] suggesting that MFP of the phonons is of the order of the lattice spacing. Thus MFP of the carriers is much longer than MFP of the phonons in Na$_2$Co$_2$O$_4$. We therefore propose that this material is a new class of “electron crystals and phonon glasses”.

Finally let us comment on strong correlation. Since the diffusive part of $S$ corresponds to the transport entropy, as mentioned above, larger electronic specific heat can give larger $S$. Thus $S$ would be enhanced if the carriers could couple with some outside entropy such as optical phonon, spin fluctuation, or orbital fluctuation. Recently a similar scenario is independently proposed by Palsson and Kotliar [4]. Heavy fermions and valence-fluctuation systems are indeed the case, some of which show large $S$.

Very recently Ando et al. [5] have measured the specific heat of Na$_{1.1-x}$Ca$_x$Co$_2$O$_4$ at low temperatures, and have found a large electronic specific heat of 48 mJ/mol K$^2$, which is one order of magnitude larger than conventional metals.

In summary, we have prepared polycrystals of Na$_{1+x}$Co$_2$O$_4$ and Na$_{1.1-x}$Ca$_x$Co$_2$O$_4$, and measured the resistivity and thermopower from 4.2 to 300 K. The excess Na and the substituted Ca affect the transport properties of NaCo$_2$O$_4$ differently. The former seems to de-
crease the effective conducting region, and the latter decreases the carrier density. The temperature dependence of the resistivity is drastically changed by substituting Ca, which strongly suggests that the scattering mechanism depends on the carrier density. Combining this with the peculiar temperature dependence of the resistivity, we conclude that strong electron-electron correlation plays an important role in this compound.

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Fig. 3. (a) Resistivity and (b) Thermopower of Na$_{1.1-x}$Ca$_x$Co$_2$O$_4$ plotted as a function of temperature.

Fig. 4. Resistivity of Na$_{1.1}$Co$_2$O$_4$ prepared in different batches. The solid curves represent samples sintered at 860°C, and the dashed curve represents a sample sintered at 920°C. The magnitude of resistivity is scattered beyond experimental errors (~10%). The resistivity normalized at 295 K is shown in the inset.

Fig. 5. Log-log plot of the resistivity of Na$_{1.1}$Co$_2$O$_4$. The data are the same as in Fig. 2(a). The solid and dashed lines represent $\rho \propto T^{0.67}$ and $\rho \propto T^{1.2}$, respectively. The inset shows $\rho$ plotted as a function of $T^2$. 

FIG. 3 Kawata et al.

FIG. 4. Kawata et al.

FIG. 5 Kawata et al.