Enhanced Thermoelectric Properties at X~0.1 in La$_{1-x}$Sr$_x$CoO$_3$ and La$_{1-x}$Sr$_x$(Co$_{1-y}$M$_y$)O$_3$ (M=Cr, Cu)

H. Fujishiro$^*$, Y. Fujime$^1$, Y. Kashiwada$^1$, M. Ikebe$^1$ and J. Hejmanek$^2$

$^1$ Faculty of Engineering, Iwate University, 4-3-5 Ueda, Morioka 020-8551, Japan
$^2$ Institute of Physics of ASCR, Cukrovarnicka 10, 16200 Praha 6, Czech Republic

*email: fujishiro@iwate-u.ac.jp, fax: +81-19-621-6373

Abstract

The thermoelectric properties of the La$_{1-x}$Sr$_x$CoO$_3$ system have been investigated from 10 K to 300 K. The figure of merit Z and power factor $P$ increase with increasing Sr concentration $X$ and show a maximum for $X=0.10$~0.15, where the ferromagnetic (FM) order starts to appear. The maximum Z value ($Z=150 \times 10^{-6}$ K$^{-1}$ at 230 K for $X=0.10$) is larger than those of layered cobaltites. The $Z$ and $P$ values are enhanced by the 5% Co site substitution by Cr for the over-doped concentration ($X=0.20$), but are depressed for the nearly optimum doped one ($X=0.15$). The results are discussed in conjunction with the carrier density $n$ of this system.

1. Introduction

The layered Co-based oxides such as NaCo$_2$O$_4$ [1], Ca$_3$Co$_4$O$_9$ [2] and Bi$_2$Pb$_2$Co$_2$O$_7$ [3] with edge-shared CoO$_6$ octahedra have recently attracted much attention as thermoelectric materials with a high figure of merit Z ($=S^2/k\rho; S$ the thermoelectric power, $k$ the thermal conductivity, $\rho$ the electrical resistivity) and power factor $P$ ($=S^2/\rho$). The high degeneracy of Co spin state has been pointed out as a possible origin of the large $S$ values [4]. La$_{1-x}$Sr$_x$CoO$_3$ (AE=Ba, Sr, Ca) system has a simple perovskite structure, which consists of three-dimensional network with corner-shared CoO$_6$ octahedra. Although this system has been investigated for a long time, there is no systematic report as for the thermoelectric potential as far as we know. In the parent material LaCoO$_3$, the spin state of Co$^{3+}$ shows the low-spin (LS; $S=0$) and/or intermediate-spin (IS; $S=1$) configuration and the ferromagnetic metallic (FM-M) state appears for $X\geq 0.2$ by the introduction of Co$^{5+}$ spins (IS, $S=3/2$). In this paper, we present the thermoelectric properties and the magnetism of the La$_{1-x}$Sr$_x$CoO$_3$ system from 10 K to 300 K. The substitution effect for the Co ion site by the 3d-transition metal ions such as Ti, Cr, Mn, and Cu is also studied and the relation between the thermoelectric properties and the carrier (hole) concentration $n$ is discussed.

2. Experimental

Polycrystalline samples of La$_{1-x}$Sr$_x$CoO$_3$ (0$\leq X \leq 0.50$) and La$_{1-x}$Sr$_x$(Co$_{1-y}$M$_y$)O$_3$ ($X=0.15$~0.30; $Y=0.05, 0.10; M=Cr, Cu$ etc.) were prepared by a solid-state reaction method. The mixtures of raw powders were calcined twice at 1000°C for 24 h in air, pressed into pellets and then sintered at 1450°C for 8 h in air. The samples were heat-treated in flowing oxygen at 900°C for 24 h in order to achieve the oxygen stoichiometry. The oxygen content was measured by the iodometric titration. The measured densities of samples were about 85~90% of the ideal ones. The X-ray diffraction analyses at room temperature confirmed that all the samples were in a single rhombohedral phase. The electrical resistivity $\rho$ was measured by a standard four terminal method. The thermal conductivity $k$ and thermoelectric power $S$ were measured by a steady-state heat flow method [5]. The magnetization $M$ was measured using a SQUID magnetometer under the magnetic field of 0.5 T (zero field cooling). The Hall coefficient was measured at room temperature using the 5 T cryo-cooled superconducting magnet to estimate the carrier concentration $n$.

3. Results and Discussion

3.1 La$_{1-x}$Sr$_x$CoO$_3$ (0$\leq X \leq 0.50$) system

Figs. 1(a)~1(d) show the temperature dependence of the (a) electrical resistivity $\rho(T)$, (b) thermoelectric power $S(T)$, (c) thermal conductivity $k(T)$ and (d) magnetization $M(T)$ of La$_{1-x}$Sr$_x$CoO$_3$, respectively. These figures also contain the results of La$_{1-x}$Sr$_x$(Co$_{0.95}$Cr$_{0.05}$)O$_3$ ($X=0.15$, 0.20), which are to be discussed in the following subsection. $\rho(T)$ and $S(T)$ decrease with increasing Sr concentration $X$. The positive $S(T)$ value reduces suddenly for $X>0.20$, where the system shows the FM-M order. The decrease of $S(T)$ comes from the increase of $n$ and/or the decrease of the degeneracy in the Co spin state due to the FM transition. $\kappa(T)$ increases with increasing $X$ and a slight enhancement in $\kappa(T)$ for $X=0.20$ can be observed below the FM transition temperature $T_c$ ($=220$ K). The larger $\kappa(T)$ value and the $\kappa(T)$ anomaly below $T_c$ are attributable to the electronic contribution, $\kappa_e(T)$, as estimated by the Wiedemann-Franz law.

Fig. 2 shows the temperature dependence of the (a) figure of merit $Z(T)$ and (b) power factor $P(T)$ of La$_{1-x}$Sr$_x$CoO$_3$, which was calculated using the data shown in Figs. 1(a)~1(c). The $Z(T)$ and $P(T)$ show the peak below the room temperature, decreasing with the further decrease of $T$. The $Z(T)$ and $P(T)$ values increase with increasing $X$, show a maximum at $X=0.10$ and decrease with the further increase of $X$. The characteristic temperatures, $T(Z_{\text{max}})$ and $T(P_{\text{max}})$, at which the $Z$ and $P$ values reach the maximum, decrease with increasing $X$ up to $X=0.15$.

Fig. 3 presents the $X$ dependence of $Z$ for La$_{1-x}$Sr$_x$CoO$_3$ at 300 K. A clear peak can be seen at $X=0.10$ and then the $Z$ value decreases with increasing $X$. It is to be noticed that the maximum $Z$ value at 300 K is higher than those of layered misfit cobaltites such as poly-crystalline (p)-Ca$_3$Co$_4$O$_9$ [2], single-crystalline (s)-Bi$_2$Sr$_2$Pb$_2$Sr$_2$Co$_2$O$_{9+}$ ($X=0.44$) [3], p-NaCo$_2$O$_4$ [6], and p-NaCo$_2$Cr$_3$O$_7$ [7], which have recently
been investigated vigorously. Although the $P$ values obtained by this work are about one order of magnitude smaller than that for the NaCo$_2$O$_4$ single crystal (~5 mW/K²m; [1]), the present $P$ values are larger than those of the other layered cobaltites at 300 K. The large $P(T)$ and $Z(T)$ values originate from the larger $S$ and relatively small $\rho$ values of this system around $X \sim 0.1$, where the FM moment starts to appear.

### 3.2 La$_{1-X}$Sr$_X$(Co$_{1-Y}$M$_Y$)O$_3$ (M=Cr, Cu) system

In a previous paper [8], we investigated the Co site substitution effect by the 3$d$-transition metal elements (M=Ti, Cr, Mn, Fe, Ni, Cu and Zn) on the thermoelectric properties and the magnetism in the La$_{1-X}$Sr$_X$(Co$_{1-Y}$M$_Y$)O$_3$ system ($X=0.15$–$0.30$, $Y=0.05$ and 0.10). These properties depend on the 3$d$-transition metal element substituted for the Co ions. We show the typical results for M=Cr, which results in the
best thermoelectric property improvement, and M=Cu, which was reported to enhance the P and Z values in NaCo$_2$YCu$_4$O$_4$ [9]. The temperature dependences of $\rho(T)$, $S(T)$, $\kappa(T)$ and $M(T)$ of La$_{1-x}$Sr$_x$(Co$_{0.95}$Cr$_{0.05}$)O$_3$ (X=0.15 and 0.20) are shown in Figs. 1(a)-1(d). $\rho(T)$ and $S(T)$ increase and $\kappa(T)$ decreases with the substitution of 5% Co by Cr for both $X=0.15$ and 0.20. The $M(T)$ value and the FM transition temperature $T_c$ decrease with the substitution by Cr. The $\rho(T)$ and $M(T)$ behaviors of La$_{0.80}$Sr$_{0.12}$(Co$_{0.95}$Cr$_{0.05}$)O$_3$ are nearly identical to those of La$_{0.80}$Sr$_{0.10}$CoO$_3$, and those of La$_{0.80}$Sr$_{0.20}$(Co$_{0.95}$Cr$_{0.05}$)O$_3$ are also nearly identical to La$_{0.80}$Sr$_{0.12}$CoO$_3$. These results suggest that the main effect of the small amount Co-site substitution by Cr is merely to make the hole concentration $n$ lower. As a result, the $\rho(T)$ and $S(T)$ values increase and $\kappa(T)$ decreases because the substituting element acts as scattering centers at the same time. $Z(T)$ and $\Pi(T)$ of the La$_{0.80}$Sr$_{0.12}$(Co$_{0.95}$Cr$_{0.05}$)O$_3$ and La$_{0.80}$Sr$_{0.20}$(Co$_{0.95}$Cr$_{0.05}$)O$_3$ samples are contained in Figs. 2(a) and 2(b).

Figs. 4(a) and 4(b) show the $P$ value of the Cr- and Cu-substituted samples at (a) 300 K and (b) 150 K as a function of $X$. The $P$ value decreases for $X=0.15$ and increases for $X=0.20$ by the Co-site substitution by Cr, compared with the non-substituting samples. These results can be understood in the following way. The thermoelectric properties are enhanced by the Cr-substitution for over-doped Sr concentration ($X=0.20$), but are depressed by the nearly optimum one ($X=0.15$) because $n$ is decreased by the Cr substitution. $X(P_{\max})$, at which $P$ takes the maximum, shifts to higher $X$ compared with the non-substituted system. On the other hand, for the Co-site substitution by Cu, there is no distinct improvement for the $P$ value, which makes a clear contrast to that for the NaCo$_2$YCu$_4$O$_4$ system [9].

3.3 Carrier concentration

We arrange the experimental results of the thermoelectric properties using the carrier concentration $n$ determined Hall effect measurement to discuss the effect of the substitution for all the La$_{1-x}$Sr$_x$(Co$_{1-Y}$M$_Y$)O$_3$ samples. Fig. 5(a) shows the $P$ value of the non-substituted La$_{1-x}$Sr$_x$CoO$_3$ at 300 K as a function of $n$. With increasing $n$, the $P$ value increases, shows a maximum at $n=3\times 10^{19}$ cm$^{-3}$, and then decreases. Fig. 5(b) shows the $P$ value at 300 K for the La$_{1-x}$Sr$_x$(Co$_{1-Y}$M$_Y$)O$_3$ samples (M=Cr and Cu) as a function of $n$. For the fixed $X$, $n$ decreases with increasing content of the substituted element $Y$. In the $X=0.20$ system, $P$ shows a maximum for $Y=0.05$ and then decreases for $Y=0.10$. On the other hand, in the $X=0.15$ system, $P$ decreases for the 5% Co-site substitution by Cr and Cu. In a conventional theory for thermoelectric semiconductors such as Bi$_2$Te$_3$, the $Z$ or $P$ values show a maximum at $n$ in the order $\sim 10^{19}$ cm$^{-3}$, which is about two orders of magnitude smaller than that for the present system. In general, the smaller $n$ (or $X$) gives the larger $\rho$ value and the larger $n$ (or $X$) gives the smaller $\rho$ and $S$ values. As a result, the maximum $Z$ or $P$ is necessarily realized at the optimum carrier concentration. The clear effect on the thermoelectric properties due to the spin state of the substituted 3$d$-transition metal element has not been confirmed at the present stage. A detailed study, for example, the substitution effect for the Co site by non-magnetic elements (Al and Ga), is in progress.

4. Conclusions

The thermoelectric properties of the La$_{1-x}$Sr$_x$CoO$_3$ ($0\leq X \leq 0.50$) and La$_{1-x}$Sr$_x$(Co$_{1-Y}$M$_Y$)O$_3$ ($X=0.15$, 0.20, 0.30; $Y=0.05$, 0.10; M=Cr, Cu) systems have been investigated
from 10 K to 300 K. Important experimental results and conclusions obtained in this study are summarized as follows.

(1) For the \( \text{La}_{1-x}\text{Sr}_x\text{CoO}_3 \) system, the figure of merit \( Z \) and power factor \( P \) increase with increasing Sr concentration \( x \), showing a maximum at \( x=0.10-0.15 \) (e.g., \( Z=150 \times 10^6 \) \( \text{K}^{-1} \) at 230 K for \( x=0.10 \)), where the carrier concentration \( n \) is \( 3-4 \times 10^{21} \text{cm}^{-3} \) and the ferromagnetic (FM) moment starts to appear. The maximum \( Z \) and \( P \) values are larger than those of promising layered cobaltites such as polycrystalline \( \text{Ca}_3\text{Co}_4\text{O}_9 \) at 300 K.

(2) The substitution for the Co-site by Cr most strongly enhances the \( Z \) and \( P \) values for the over-doped concentration \( (x=0.20) \), but depresses them for the nearly optimum doped one \( (x=0.15) \). However, these values for the substituted system cannot exceed those of the non-substituted system.

(3) These results can be understood on the basis of the carrier concentration \( n \) of this system. The Co-site substitution by Cr seems to merely make the \( n \) value lower.

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