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[1*], Y. Fujine[1], Y. Kashiwada[1], M. Ikebe[1] and J. Hejtmanek[2]

[1] Faculty of Engineering, Iwate University, 4-3-5 Ueda, Morioka 020-8551, Japan

[2] Institute of Physics of ASCR, Cukrovarnivka 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 x 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 $NaCo_2O_4$ [1], $Ca_3Co_4O_9$ [2] and $Bi_{2-X}Pb_{X}Co_2O_y$ [3] with edge-shared CoO_6 octahedra have recently attracted much attention as thermoelectric materials with a high figure of merit Z ($=S^2/\kappa\rho$; S the thermoelectric power, κ the thermal conductivity, ρ 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]. $La_{1-X}AE_{X}CoO_{3}$ (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 $X\geq0.2$ by the introduction of Co^{4+} 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≤X≤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 ρ was measured by a standard four terminal method. The thermal conductivity κ 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≤X≤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 $\kappa(T)$ 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, $T(Z_{max})$ and $T(P_{max})$, 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)- $Ca_3Co_4O_9$ [2], single-crystalline (s)-$Bi_{2.3-X}Pb_{X}Sr_{2.6}Co_2O_y$ (X=0.44) [3], p-$NaCo_2O_4$ [6], and p-$NaCo_{2-X}Cu_XO_4$ [7], which have recently

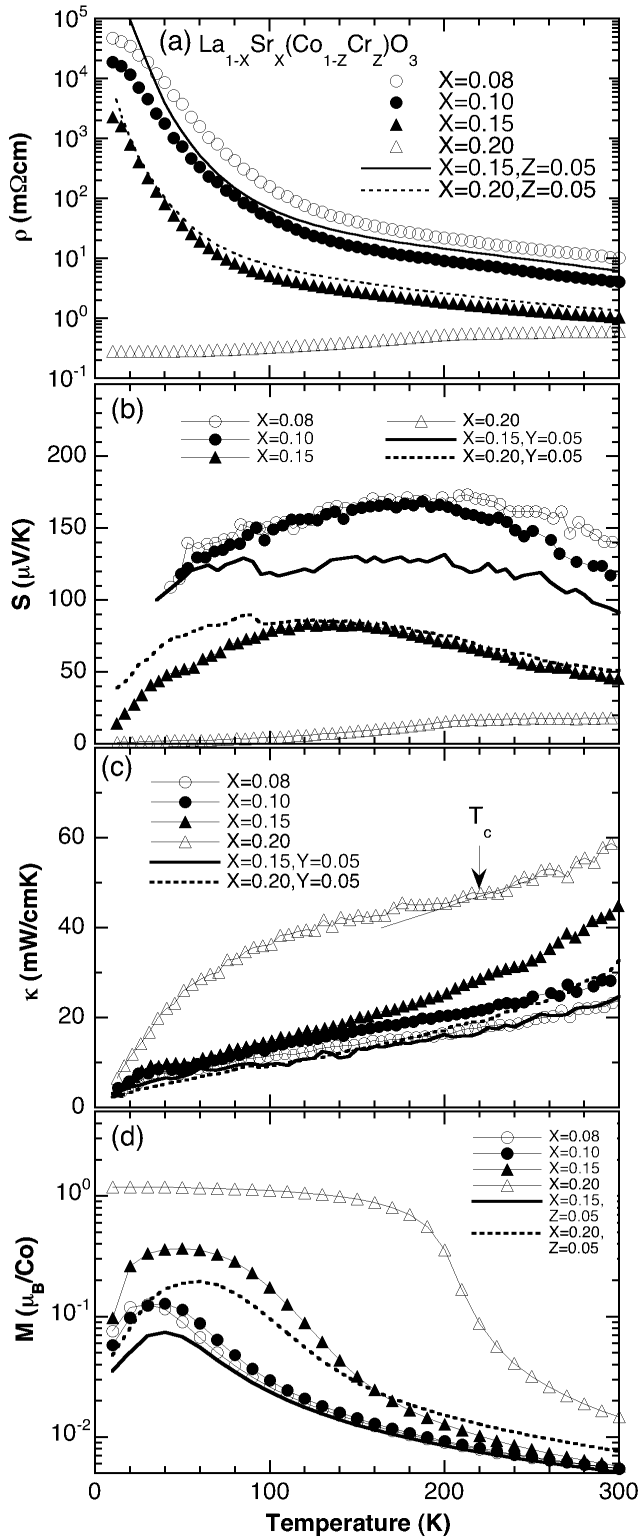**Figure 1:** The temperature dependence of (a) $\rho(T)$, (b) $S(T)$, (c) $\kappa(T)$ and (d) $M(T)$ of the La$_{1-X}$Sr$_X$CoO$_3$ (0.08≤X≤0.20) and La$_{1-X}$Sr$_X$(Co$_{0.95}$Cr$_{0.05}$)O$_3$ (X=0.15, 0.20) systems.

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/K^{2}m; [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
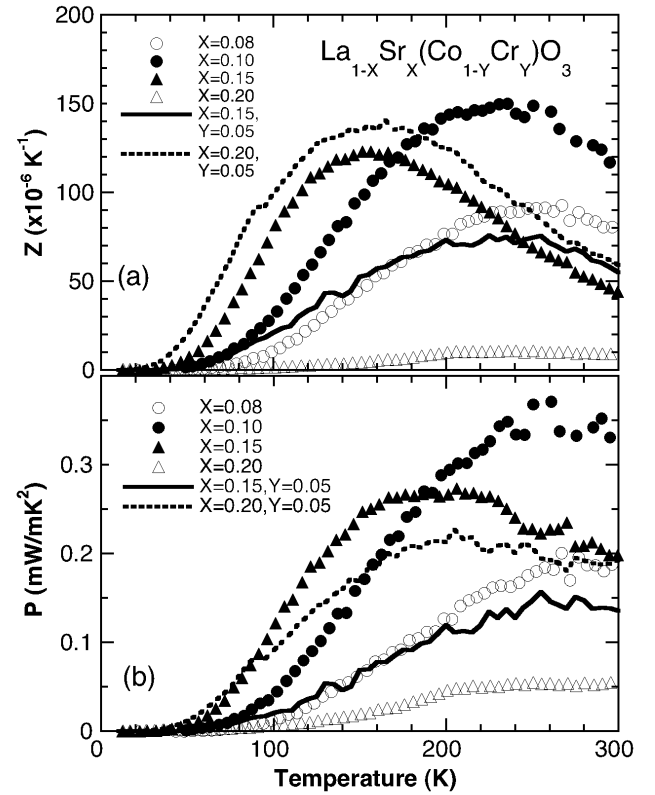

Figure 2: The temperature dependence of the (a) $Z(T)$ and (b) $P(T)$ of the La$_{1-X}$Sr$_X$CoO$_3$ (0.08≤X≤0.20) and La$_{1-X}$Sr$_X$(Co$_{0.95}$Cr$_{0.05}$)O$_3$ (X=0.15, 0.20) systems.
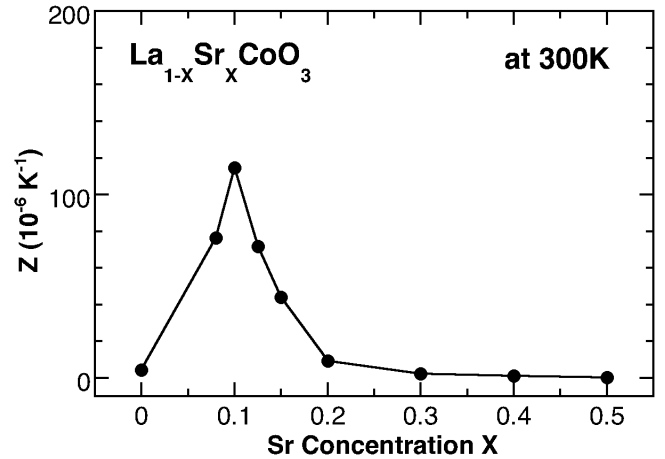

Figure 3: The X dependence of Z for La$_{1-X}$Sr$_X$CoO$_3$ at 300 K.

from the larger S and relatively small ρ values of this system around X~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 3d-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 3d-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 $NaCo_{2-Y}Cu_YO_4$ [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 $La_{0.85}Sr_{0.15}(Co_{0.95}Cr_{0.05})O_3$ are nearly identical to those of $La_{0.90}Sr_{0.10}CoO_3$, and those of $La_{0.80}Sr_{0.20}(Co_{0.95}Cr_{0.05})O_3$ are also nearly identical to $La_{0.85}Sr_{0.15}CoO_3$. 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 $P(T)$ of the $La_{0.85}Sr_{0.15}(Co_{0.95}Cr_{0.05})O_3$ 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 $NaCo_{2-Y}Cu_YO_4$ 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 $La_{1-x}Sr_xCoO_3$ at 300 K as a function of n. With increasing n, the P value increases, shows a maximum at $n\sim3\times10^{21}$ 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_2Te_3, the Z or P values show a maximum at n in the order $\sim10^{19}$ 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 ρ value and the larger n (or X) gives the smaller ρ 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 3d-transition metal element has not been confirmed
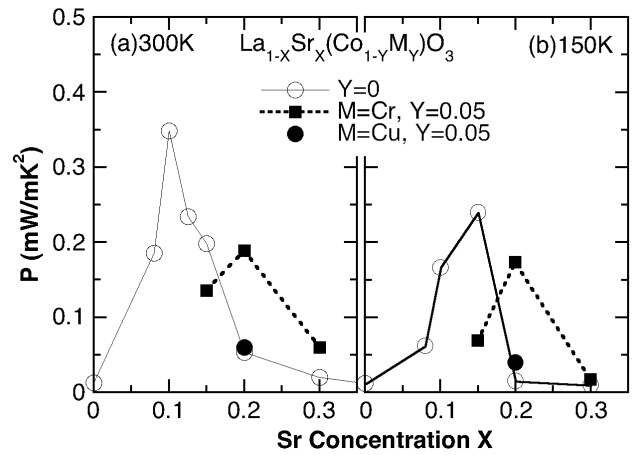

Figure 4: The P values of the $La_{1-X}Sr_X(Co_{1-Y}M_Y)O_3$ samples (Y=0, 0.05 and M=Cr, Cu) at (a) 300 K and (b) 150 K as a function of X.
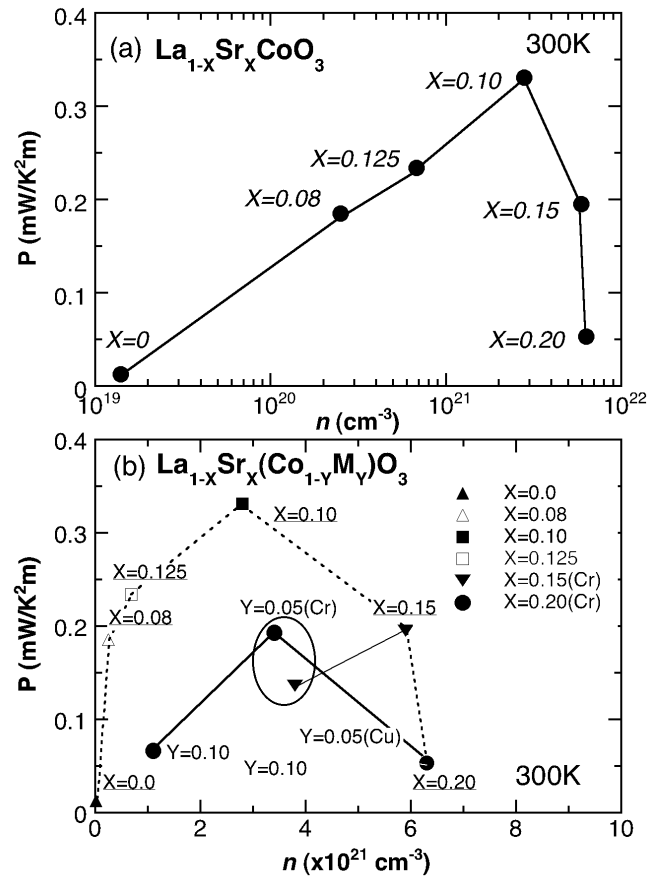

Figure 5: The P values at 300 K of the samples investigated in this study as a function of the carrier concentration n.

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 $La_{1-X}Sr_XCoO_3$ ($0{\leq}X{\leq}0.50$) 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 $La_{1-X}Sr_XCoO_3$ 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 x 10^{-6} K^{-1} at 230 K for X=0.10), where the carrier concentration n is 3~4 x 10^{21} 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 $Ca_3Co_4O_9$ 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.

References

1. Terasaki, I. *et al*, "Large thermoelectric power in $NaCo_2O_4$ single crystals," *Phys. Rev. B*, Vol. 56 (1997), pp. R12685-R12687.
2. Masset, A.C. *et al*, "Misfit-layered cobaltite with an anisotropic giant magnetoresistance," *Phys. Rev. B*, Vol. 62 (2000), pp. 166-175.
3. Ito, T. *et al*, "Thermoelectric properties of $Bi_{2.3-X}Pb_XSr_{2.6}Co_2O_y$ Single Crystals," *Jpn. J. Appl. Phys.*, Vol. 39, No. 12A (2000), pp. 6658-6660.
4. Koshibae, W. *et al*., "Thermopower in cobalt oxides", Phys. Rev. B, vol. 62 (2000), pp. 6869-6872.
5. Fujishiro, H. *et al*., "Low temperature thermal diffusivity and conductivity measurement under an identical experimental setup", *Cryogenic Engineering*, Vol. 28 (1993) pp. 533-539 (in Japanese).
6. Takahata, K. *et al*, "Low thermal conductivity of the layered oxide $(Na,Ca)Co_2O_4$," *Phys. Rev. B*, Vol. 61 (2000), pp. 12551-12555.
7. Terasaki, I. *et al*, "Thermoelcteric Properties of $NaCo_{2-X}Cu_XO_4$ Improved by the Substitution of Cu for Co," *Jpn. J. Appl. Phys.*, Vol. 40 (2001), pp. L65-L67.
8. Fujine, Y. *et al*, "Magnetism and thermoelectricity in $La_{0.80}Sr_{0.20}Co_{1-Z}M_ZO_3$ (M:3*d* transition metal)," *submitted to J. Mag. Mag. Mat.* (2003)
9. Terasaki, I *et al,* "Impurity-induced transition and impurity-enhanced thermopower in the thermoelectric oxide $NaCo_{2-X}Cu_XO_4$," *Phys. Rev. B*, Vol. 65, (2002), pp. 195106.1-7.