

Influence of Co-site Substitution on Thermoelectric Properties in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$

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Abstract

The effect of the Co-site substitution by the various elements M on the thermoelectric properties has been investigated for the $\text{La}_{0.80}\text{Sr}_{0.20}(\text{Co}_{0.95}\text{M}_{0.05})\text{O}_3$ system. The figure of merit Z and the power factor P depend on the species of the substituted elements through the difference of the ionic radius, the ionic valency, the electronic configuration of 3d-electrons and their spin states. Among these factors, the ionic valency of the substituted elements most strongly influences the thermoelectricity; the 5% substitution by the +2 ions (Mg^{2+} , Ni^{2+}) makes the average Co valency (AV) increase to 3.26 from pristine 3.20 and that by the +4 ions (Sn^{4+} , Cr^{4+}) makes the AV value decrease to 3.16. The substitution by the +4 ions makes the Co valency approach to the optimum AV value (=3.10), enhancing the thermoelectric properties.

1. Introduction

The layered Co-based oxides such as NaCo_2O_4 [1], $\text{Ca}_3\text{Co}_4\text{O}_9$ [2] and $\text{Bi}_{2-x}\text{Pb}_x\text{Co}_2\text{O}_y$ [3] have recently attracted much attention as thermoelectric materials with the high figure of merit Z ($=S^2/\kappa\rho$; the Seebeck coefficient S , thermal conductivity κ , electrical resistivity ρ) and the power factor P ($=S^2/\rho$). High degeneracy of the Co spin state has been pointed out as a possible origin of the large S values [4]. $\text{La}_{1-x}\text{AE}_x\text{CoO}_3$ (AE=Ba, Sr, Ca) has a simple perovskite structure, which consists of three-dimensional network with corner-shared CoO_6 octahedra. Although these systems have been investigated for a long time, there is no systematic report as for the thermoelectric properties. We have investigated the X dependence of the thermoelectric properties for these systems [5,6]. It has been found that the Z and P values take the maxima at $X=0.10$ and the maximum values of Z and P exceeds those for the polycrystals of the layered cobaltites. In NaCo_2O_4 , the Co-site substitution by Cu enhanced the thermoelectric properties through the enhancement of the effective mass of the carrier [7]. We have studied the effect of the Co-site substitution by the 5% Cu ions in $\text{La}_{0.80}\text{Sr}_{0.20}\text{CoO}_3$ system and have concluded that the thermoelectric properties cannot be enhanced by the Cu substitution [8].

In this paper, we systematically investigate the influence of the 5% Co-site substitution with the various elements on the thermoelectric properties of $\text{La}_{0.80}\text{Sr}_{0.20}\text{CoO}_3$. In the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ system, $X=0.10$ has been confirmed to be the optimum hole concentration for the thermoelectric properties, where the average valency of the Co ion, hereafter we abbreviate as AV, is nominally 3.10. Accordingly, $X=0.20$ samples investigated in this study are in the over-doped region. The Co-site substitution may simultaneously introduce the crystal disorder and the changes of AV value and the magnetic entropy. Then the substitution should affect the

electrical resistivity $\rho(T)$, the thermal conductivity $\kappa(T)$ and the Seebeck coefficient $S(T)$ which decide the Z and P values. We try to elucidate the substitution effect on these factors.

2. Experimental

Polycrystalline samples of $\text{La}_{0.80}\text{Sr}_{0.20}\text{CoO}_3$ and $\text{La}_{0.80}\text{Sr}_{0.20}(\text{Co}_{0.95}\text{M}_{0.05})\text{O}_3$ were prepared by a solid-state reaction method. $\text{M}=\text{Mg}^{2+}$ ($3d^0$), Al^{3+} ($3d^0$), Sn^{4+} ($4d^{10}$) ions were adopted as the non-magnetic ions and $\text{M}=\text{Ni}^{2+}$ ($3d^8$), Fe^{3+} ($3d^5$), Cr^{4+} ($3d^2$) as the magnetic ions. The non-magnetic composite $1\%\text{Ti}^{4+}+4\%\text{Ga}^{3+}$, which does not affect the AV value, was also substituted in order to clarify the disorder effect solely. The AV value for $\text{La}_{0.80}\text{Sr}_{0.20}\text{CoO}_3$ is 3.20 and varies depending on the species of M element. The mixtures of raw powders were calcined 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 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 Seebeck coefficient S were measured by a steady-state heat flow method. The magnetization M_0 was measured using a SQUID magnetometer under the magnetic field of 0.5 T after

Table I. The summary of the substituted element M for $\text{La}_{0.80}\text{Sr}_{0.20}(\text{Co}_{0.95}\text{M}_{0.05})\text{O}_3$ investigated in this study.

| Substituted element M | Ionic radius (Å) | 3d electron configuration | Spin configuration | Average valency of Co ion (AV) |
|---|------------------|---------------------------|--------------------|--------------------------------|
| non | - | - | - | 3.20 |
| 1% Ti^{4+} +4% Ga^{3+} | 0.62 | $3d^0$ + $3d^{10}$ | 0 | 3.20 |
| 5% Mg^{2+} | 0.72 | $3d^0$ | 0 | 3.26 |
| 5% Al^{3+} | 0.535 | $3d^0$ | 0 | 3.21 |
| 5% Sn^{4+} | 0.69 | $4d^{10}$ | 0 | 3.16 |
| 5% Ni^{2+} | 0.69 | $3d^8$ | 1 | 3.26 |
| 5% Fe^{3+} | 0.645 | $3d^5$ | 5/2 | 3.21 |
| 5% Cr^{4+} | 0.55 | $3d^2$ | 1 | 3.16 |

zero field cooling (ZFC). All the measurements were performed from 10 K to 300 K. The valencies of the substituted cations were synthetically estimated by the change of the unit cell volume and $\kappa(T)$, $S(T)$ and $M_0(T)$ behaviors [9]. Table I summarizes the ionic parameters of the studied elements.

3. Results and Discussion

Fig. 1 shows the temperature dependence of the magnetization $M_0(T)$ of $\text{La}_{0.80}\text{Sr}_{0.20}(\text{Co}_{0.95}\text{M}_{0.05})\text{O}_3$ for various non-magnetic (upper panel) and magnetic (lower panel) M elements. $\text{La}_{0.80}\text{Sr}_{0.20}\text{CoO}_3$ (LSCO(0.20); $AV=3.20$) shows a ferromagnetic (FM) transition at $T_c=210$ K. T_c of the $M=1\%\text{Ti}^{4+}+4\%\text{Ga}^{3+}$ sample ($AV=3.20$), in which only the crystal disorder should be introduced, decreases down to 150 K. This large depression of T_c may suggest the importance of the double exchange interaction in $\text{La}_{0.80}\text{Sr}_{0.20}\text{CoO}_3$. The M_0 and T_c values for the Mg^{2+} and Ni^{2+} substituted samples ($AV=3.26$) are larger and those for the Sn^{4+} and Cr^{4+} substituted samples ($AV=3.16$) are smaller, compared with those for the $1\%\text{Ti}^{4+}+4\%\text{Ga}^{3+}$ substituted sample. The M_0 and T_c values for the Al^{3+} and Fe^{3+} ions ($AV=3.21$) are slightly larger than those for the $1\%\text{Ti}^{4+}+4\%\text{Ga}^{3+}$ substituted sample and show the intermediate behavior between +2 and +4 substituted ions regardless of the magnetic nature of the elements. Thus the $M_0(T)$ behavior is more directly correlated with the valency of the substituted elements, that is, the AV value.

Fig. 2 shows the temperature dependence of $\rho(T)$. The resistivity $\rho(T)$ of the LSCO(0.20) shows lower values (<1 m Ωcm) with a metallic behavior even at low temperatures. On the other hand, $\rho(T)$ of the $1\%\text{Ti}^{4+}+4\%\text{Ga}^{3+}$ sample is larger (>1 m Ωcm at 300 K) and increases with decreasing temperature T . The $\rho(T)$ values progressively increase for the +2, +3, +4 ion doped samples in this order irrespective of the magnetic nature of the substituted ions. Thus $\rho(T)$ is also closely correlated with the AV value of Co. It is worthwhile to note that $\rho(T)$ increase in the Mg^{2+} , Ni^{2+} and Fe^{3+} substituted samples is not so large compared with that for other samples. Particularly, the small $\rho(T)$ values of the Fe^{3+} substituted sample in comparison to the Al^{3+} substituted one demonstrates the importance of the existence of available $3d$ orbitals for the carrier hopping in the system.

Fig. 3 shows the temperature dependence of the Seebeck coefficient $S(T)$. In the conventional theory, the Seebeck coefficient increases with increasing ρ value. However, in the present case, the $S(T)$ behavior may be more directly correlated with the magnetization M_0 than the resistivity ρ . Upon cooling, $S(T)$ decreases with increasing magnitude of $M_0(T)$, i.e., the S value decreases at the onset of the ferromagnetism as the freedom of spin directions is quenched and the magnetic entropy is reduced. This result reflects the fact that the Seebeck coefficient represents “entropy per carrier”. We can see in Fig. 3 that $S(T)$ begins to decrease near the FM transition temperature T_c , while $\rho(T)$ continues to increase with decreasing temperatures.

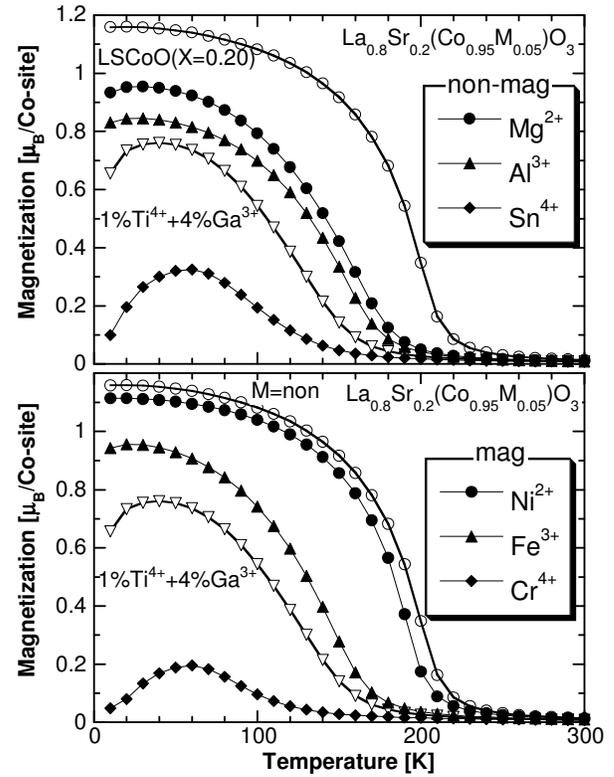


Figure 1: The temperature dependence of the magnetization $M_0(T)$ of $\text{La}_{0.80}\text{Sr}_{0.20}(\text{Co}_{0.95}\text{M}_{0.05})\text{O}_3$ for non-magnetic (upper panel) and magnetic (lower panel) M elements.

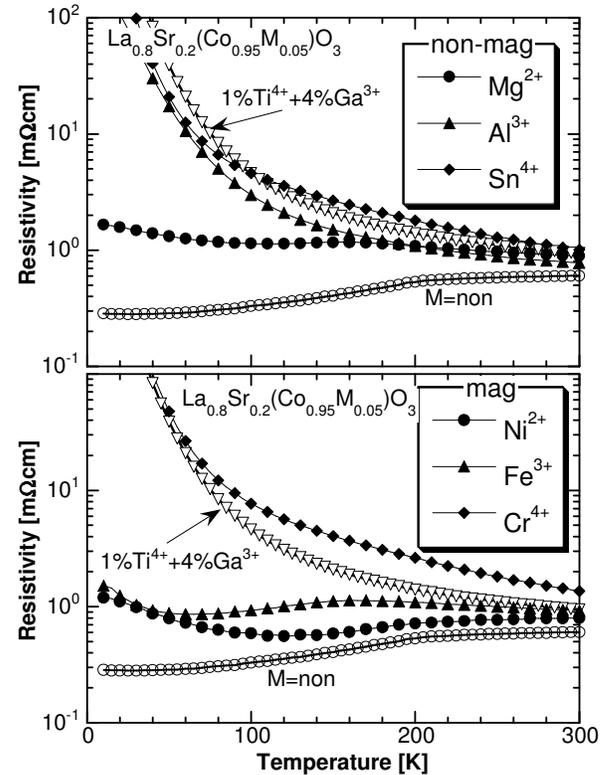


Figure 2: The temperature dependence of the resistivity $\rho(T)$ of $\text{La}_{0.80}\text{Sr}_{0.20}(\text{Co}_{0.95}\text{M}_{0.05})\text{O}_3$ for non-magnetic (upper panel) and magnetic (lower panel) M elements.

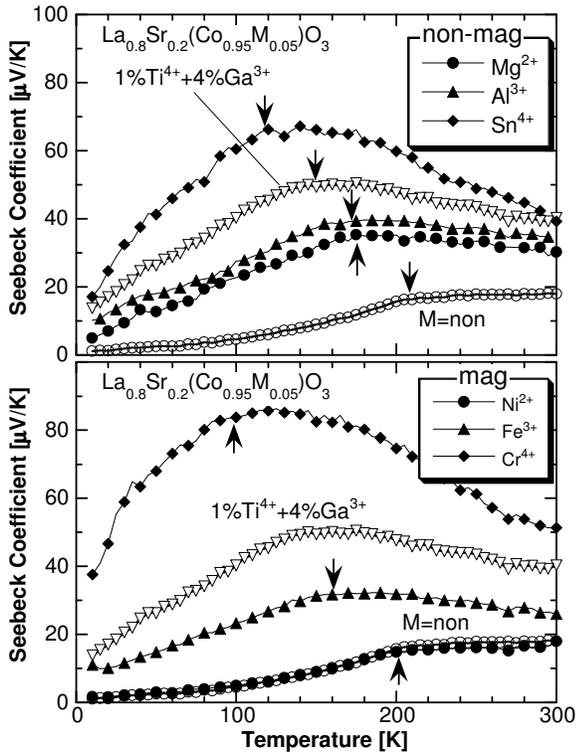


Figure 3: The Seebeck coefficient $S(T)$ of $\text{La}_{0.80}\text{Sr}_{0.20}(\text{Co}_{0.95}\text{M}_{0.05})\text{O}_3$ for non-magnetic (upper panel) and magnetic (lower panel) M elements. The arrows show the FM transition temperature T_c determined by $M_0(T)$.

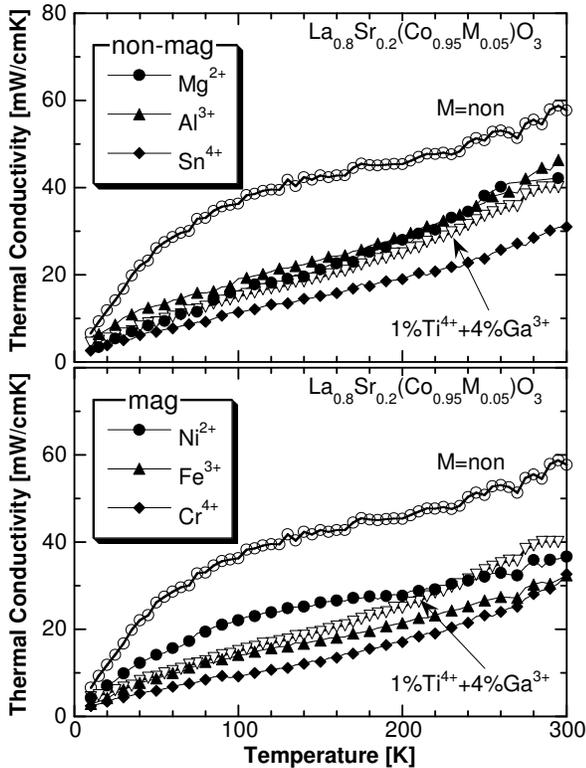


Figure 4: The thermal conductivity $\kappa(T)$ of $\text{La}_{0.80}\text{Sr}_{0.20}(\text{Co}_{0.95}\text{M}_{0.05})\text{O}_3$ for non-magnetic (upper panel) and magnetic (lower panel) M elements.

Fig. 4 shows the temperature dependence of the thermal conductivity $\kappa(T)$. $\kappa(T)$ of the $\text{LSCoO}(0.20)$ shows the largest value among the samples studied. $\kappa(T)$ of all the substituted samples decreases owing to the introduction of the crystal disorder. It is worthwhile to note that, in Fig. 4(b), the $\kappa(T)$ enhancement similar to that of the pristine $\text{LSCoO}(0.20)$ can be seen below T_c for the Ni^{2+} substituted sample. The $\kappa(T)$ enhancement below T_c is attributable to the electronic contribution $\kappa_e(T)$ as estimated by the Wiedemann-Franz law.

The thermoelectric figure of merit $Z(T)$ can be estimated using the results in Figs. 2 to 4. Fig. 5 shows $Z(T)$ for the respective samples. The $Z(T)$ takes the peak below the room temperature and decreases with the further decrease of T . All the Z values of the substituted samples increase in comparison to that of $\text{LSCoO}(0.20)$. The Z value of the 4+ ion substituted sample ($AV=3.16$) is the largest and decreases with increasing AV value for both magnetic and non-magnetic cation substitutions. As mentioned before, the Z value takes a maximum at $X=0.10$ ($AV=3.10$) in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$. The substitution by the +2 ions makes the AV value increase to 3.26 and AV further deviate from the optimum value. The substitution by the +4 ions makes AV decrease to 3.16, approaching to the optimum value. Although the substitution by the +3 ions (Al^{3+} , Fe^{3+}) does hardly influence to the AV value, the increase of $S(T)$ and $\rho(T)$ and the decrease of $\kappa(T)$ take place due to the introduced crystal disorder and resultant change of T_c .

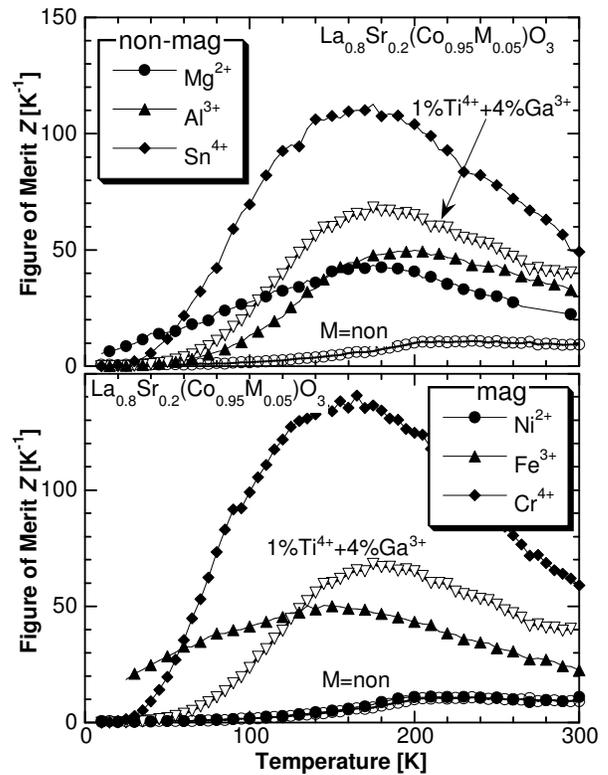


Figure 5: The temperature dependence of the Figure of merit $Z(T)$ of $\text{La}_{0.80}\text{Sr}_{0.20}(\text{Co}_{0.95}\text{M}_{0.05})\text{O}_3$ for non-magnetic (upper panel) and magnetic (lower panel) M elements.

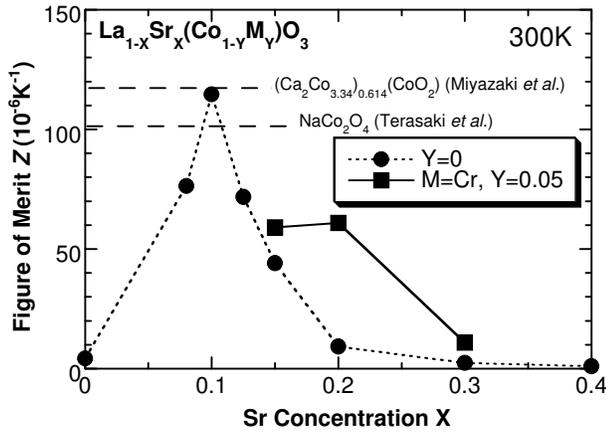


Figure 6: The figure of merit Z of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and $\text{La}_{1-x}\text{Sr}_x(\text{Co}_{0.95}\text{Cr}_{0.05})\text{O}_3$ at 300 K. The Z values of the polycrystals of layered cobaltites are also shown.

Fig. 6 shows the Sr concentration dependence of Z for $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and $\text{La}_{1-x}\text{Sr}_x(\text{Co}_{0.95}\text{Cr}_{0.05})\text{O}_3$. As can be seen, the Z value of $115 \times 10^{-6} \text{ K}^{-1}$ at 300 K is the largest for $\text{La}_{0.90}\text{Sr}_{0.10}\text{CoO}_3$, which is comparable with the reported values of $\text{Ca}_3\text{Co}_4\text{O}_9$ and NaCo_2O_4 polycrystals [10,11], though the Z values obtained by the present work are about an order of magnitude smaller than that for the NaCo_2O_4 single crystal. The Z value of the $\text{La}_{1-x}\text{Sr}_x(\text{Co}_{0.95}\text{Cr}_{0.05})\text{O}_3$ is larger than that of the $\text{LSCoO}(0.20)$ and shows a peak at $X=0.20$. The results in Fig. 6 suggests that the thermoelectric properties are enhanced by the Cr-substitution for over-doped Sr concentration ($X=0.20$) and the optimum X value for the 5% Cr^{4+} substituted system, $X(Z_{\text{max}})$, shifts to higher X compared with the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$.

4. Conclusions

The influence of the Co-site substitution by 5% with the various elements ($M=\text{Mg}^{2+}$, Al^{3+} , Sn^{4+} for the non-magnetic ions and $M=\text{Ni}^{2+}$, Fe^{3+} , Cr^{4+} for the magnetic ions) on the thermoelectric properties has been investigated for the $\text{La}_{0.80}\text{Sr}_{0.20}(\text{Co}_{0.95}\text{M}_{0.05})\text{O}_3$ system. Important experimental results and conclusions obtained in this study are summarized as follows.

- (1) The thermoelectric properties (the figure of merit Z and the power factor P) change depending on the species of the substituted elements.
- (2) The valency of the substituted elements most strongly influences the thermoelectricity; the substitution by the +2 ions (Mg^{2+} , Ni^{2+}) makes the average Co valency (AV) increase to 3.26 and that by the +4 ions makes the AV value decrease to 3.16 from $AV=3.20$ for the pristine $\text{La}_{0.80}\text{Sr}_{0.20}\text{CoO}_3$.
- (3) The lattice disorder introduced by the 5% doping results in the decrease of the thermal conductivity κ and the increase of the resistivity ρ and Seebeck coefficient S . The magnetization M_0 and the ferromagnetic transition temperature T_c also decrease by the disorder effect, suggesting the significant contribution of double exchange mechanism to the ferromagnetic order.

(4) The $S(T)$ behavior is more directly related with the magnetization $M_0(T)$ than the resistivity $\rho(T)$. $S(T)$ begins to decrease near T_c , where the freedom of the magnetic entropy begins to be quenched. In contrast, $\rho(T)$ continues to increase with decreasing temperatures.

(5) The optimum P and Z values for $\text{La}_{0.80}\text{Sr}_{0.20}(\text{Co}_{0.95}\text{Cr}_{0.05})\text{O}_3$ has been realized by the magnetic Cr^{4+} doping, though these values do not exceed the corresponding best values of $\text{La}_{0.90}\text{Sr}_{0.10}\text{CoO}_3$.

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