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Magnetism and thermoelectricity in $La_{0.8}Sr_{0.2}Co_{1-z}M_zO_3$ (M:3d transition metal)

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Abstract

Magnetic and thermoelectric properties of $La_{0.8}Sr_{0.2}Co_{1-z}M_zO_3$ system ($z = 0.05$; M: Ti, Cr, Mn, Fe, Ni, Cu, Zn) have been investigated in search of a new thermoelectric material. Co-site substitution by 3d transition metal brought about the large Seebeck coefficient S. As a result, the figure of merit Z increased. The Seebeck coefficient was found to be strongly correlated with the behavior of magnetization.

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1. Introduction

Recently, Co-based oxides have attracted much attention as a possible thermoelectric material with a high figure of merit value ($Z = S^2/\rho\kappa$; S the Seebeck coefficient, ρ the electrical resistivity, κ the thermal conductivity). The high degeneracy of Co-spin configuration related to the low-, intermediate- and high-spin state has been pointed out as an origin of the large S value [1]. Terasaki et al. [2,3] discovered $NaCo_2O_4$ to have the large S value and the low ρ value. They also found that the Co-site substitution by Cu brought about even higher S value, resulting in larger Z. In this paper, we report the effect of Co-site substitution on the magnetic and the thermoelectric properties of $La_{1-x}Sr_xCo_{0.95}M_{0.05}O_3$ and also discuss the correlation of the Seebeck coefficient with the electrical resistivity and the magnetization. We concentrate our attention on the carrier concentration $x = 0.2$, around which the S value and other physical properties are very sensitive to the Co-site substitution.

2. Experimental

Polycrystalline samples of $La_{1-x}Sr_xCo_{1-z}M_zO_3$ were prepared by a solid-state reaction method. The electrical resistivity was measured by a standard four probe method. The Seebeck coefficient and the thermal conductivity were measured by a steady heat flow method. The magnetization was measured using a SQUID magnetometer.

3. Results and discussion

Fig. 1(a) shows the temperature dependence of the electrical resistivity $\rho(T)$. $\rho(T)$ of the pristine sample exhibits a metallic behavior, while substituted samples exhibit semiconducting or metallic-semiconducting behavior. It is interesting to note that $\rho(T)$ of this system depends on the species of the substituting 3d-transition

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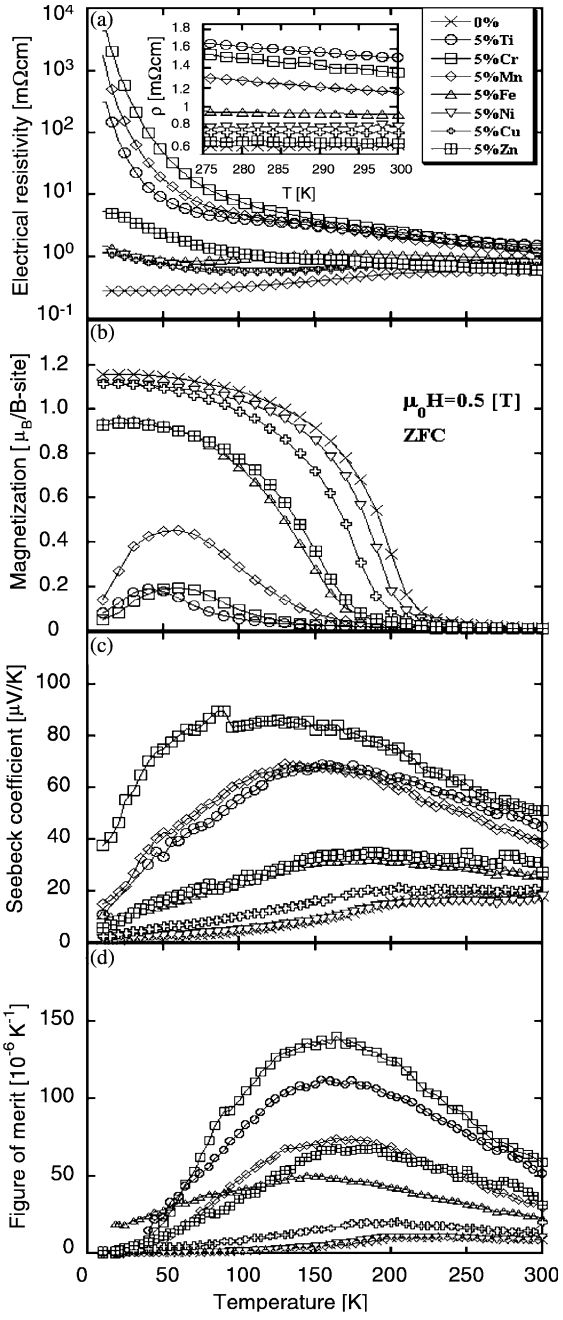

Fig. 1. (a) The electrical resistivity, (b) the magnetization, (c) the Seebeck coefficient, and (d) the figure of merit of $La_{0.8}Sr_{0.2}Co_{0.95}M_{0.05}O_3$ as a function of temperature. The symbols are the same in all figures. The inset of (a) represents the electrical resistivity near the room temperature.

element. Near the room temperature, as shown in the inset, the electrical resistivity decreases with increasing atomic number.

Fig. 1(b) shows the temperature dependence of the magnetization $M(T)$. $M(T)$ of this system exhibits the ferromagnetic behavior for the pristine, and for by Fe, Ni, Cu, and Zn substituted samples. In contrast, by Ti, Cr, and Mn substituted samples do not show apparent ferromagnetic behavior. For the substitution by the larger atomic number element than Co, both the magnitude of $M(T)$ and the ferromagnetic transition temperature T_c decrease with increasing atomic number. On the other hand, for the substituting element with atomic number smaller than that of Co, the magnitude of $M(T)$ and T_c decrease with decreasing atomic number.

Fig. 1(c) shows the temperature dependence of the Seebeck coefficient $S(T)$. As can be seen in Fig. 1(b) and (c), the Seebeck coefficient is correlated with the magnetization. $S(T)$ increases with decreasing magnitude of $M(T)$. i.e., the S value decreases with the onset of the ferromagnetism as the freedom of spin direction is quenched and the magnetic entropy is decreased. This result reflects the fact that the Seebeck coefficient represents "entropy per carrier". In the conventional theory, the Seebeck coefficient increases with increasing the ρ value. We can find in Fig. 1(c), that the Seebeck coefficient begins to decrease near the ferromagnetic transition temperature, while $\rho(T)$ continues to increase with decreasing temperature. This result implies that the Seebeck coefficient is more strongly correlated with the magnetization than the electrical resistivity in the present cobaltite.

Fig. 1(d) shows the temperature dependence of the figure of merit. To determine the Z value, the thermal conductivity $\kappa(T)$ was measured for respective samples. By substituting Co-site by 3d-transiton elements, Z value increases and Cr substituted sample marks about $150 \times 10^{-6}\,K^{-1}$ near 150 K, which is about 15 times larger than that of the non-substituted sample.

In summary, we measured the electrical resistivity, the magnetization, the thermal conductivity, and the Seebeck coefficient for $La_{0.8}Sr_{0.2}Co_{0.95}M_{0.05}O_3$. The $\rho(T)$ value near the room temperature decreased with increasing atomic number of substituting 3d elements. S was more strongly correlated with $M(T)$ than $\rho(T)$. The figure of merit increased by 3d-transition metal element substituting at Co-site, and the largest Z was obtained for the substitution by 5% Cr. Z seems to take the optimum value just before the ferromagnetism is established in the $La_{0.8}Sr_{0.2}Co_{0.95}M_{0.05}O_3$ compounds.

References

[1] W. Koshibae, et al., Phys. Rev. B 62 (2000) 6869.
[2] I. Terasaki, et al., Phys. Rev. B 56 (1997) R12685.
[3] I. Terasaki, et al., Jpn. J. Appl. Phys. 40 (2001) L65.