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Magnetic, electrical and thermal properties of $La_{0.80}Sr_{0.20}(Mn_yCo_{1-y})O_3$

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Abstract

The thermal conductivity κ, thermoelectric power S, electrical resistivity ρ and magnetization M of $La_{0.80}Sr_{0.20}(Mn_yCo_{1-y})O_3$ has been measured. By Mn substitution for Co, the initial ferromagnetic-metal behavior is promptly suppressed and $\rho(T)$ becomes semiconductive. In the semiconductive composition range, S is remarkably enhanced and κ is reduced. As a result, pretty large values of the thermoelectric figure of merit Z are realized.

Keywords: $La_{0.80}Sr_{0.20}(Mn_yCo_{1-y})O_3$; Thermal conductivity; Thermoelectric power; Thermoelectric figure of merit

1. Introduction

$(RE_{1-x}AE_x)MO_3$ (RE: rare-earth, AE: alkaline-earth, M: 3d transition metal) type oxides with perovskite structure have attracted renewed interest. The hole doping into these oxides leads to novel and anomalous transport phenomena. The manganite, $La_{1-x}Sr_xMnO_3$, for example, exhibits the well-known colossal magnetoresistance (CMR) [1], while the cobaltites, $La_{1-x}Sr_xCoO_3$, exhibits complex magnetism and metal-insulator transition depending on the hole doping x [2,3]. Recently, cobaltites such as $NaCo_2O_4$ were proposed to be hopeful candidates for thermoelectric application [4]. The undoped $LaCoO_3$ is a nonmagnetic insulator with the low spin state at low temperatures. The hole-doped compound, $La_{0.80}Sr_{0.20}CoO_3$ (LSCoO), transforms to a ferromagnet showing barely metallic electrical conduction. Because unusual physical phenomena tend to appear near the boundaries of competing phases, we examine Mn substitution effect in $La_{0.80}Sr_{0.20}(Mn_yCo_{1-y})O_3$ (LSCoO(y), $0 \leqslant y \leqslant 0.2$) and also survey the potentiality of the Mn-substituted perovskite cobaltate as a thermoelectric material.

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2. Experimental

The single-phase $La_{0.80}Sr_{0.20}(Mn_yCo_{1-y})O_3$ polycrystals were prepared by a solid-state reaction method. Automatic measurements of the thermal conductivity $\kappa(T)$ and the Seebeck coefficient $S(T)$ were performed by a steady-state heat flow method in a Gifford-McMahon (GM) cycle herium refrigerator. The magnetization $M(T)$ was measured by a SQUID magnetometer.

3. Results and discussion

Fig. 1(a) shows $M(T)$ in the field of 0.5 T as a function of temperature T. In LSCoO(0.01, 0.02), the ferromagnetic (FM) transition temperature T_c decreases with increasing y. In LSCoO(0.05), the maximum of $M(T)$ occurs at about 55 K and its value falls below half of the saturation moment of $La_{0.80}Sr_{0.20}CoO_3$. With further increase of y ($\geqslant$0.10), the FM order is completely quenched out. Fig. 1(b) presents the temperature dependence of $\rho(T)$. The ferromagnetic LSCoO(0.01, 0.02) samples retain the metallic conduction below T_c, though $\rho(T)$ increases at low temperatures due to possibly the localization effect. In

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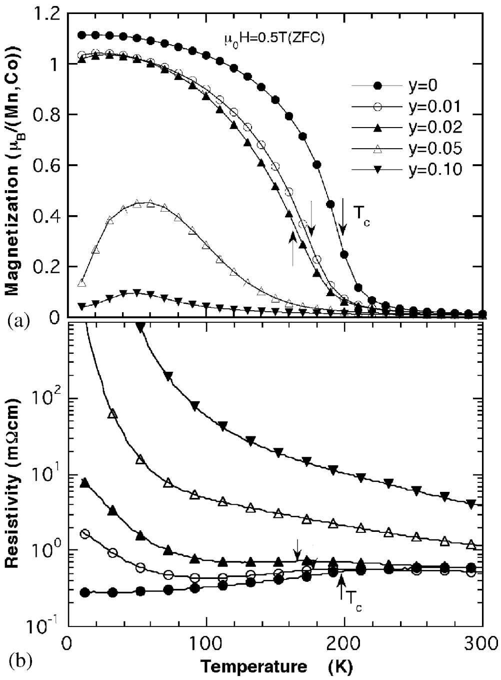

Fig. 1. (a) $M(T)$ and (b) $\rho(T)$ of $La_{0.80}Sr_{0.20}(Mn_yCo_{1-y})O_3$ as a function of T for $y = 0$, 0.01, 0.02, 0.05 and 0.10. The symbols are the same in (a) and (b).

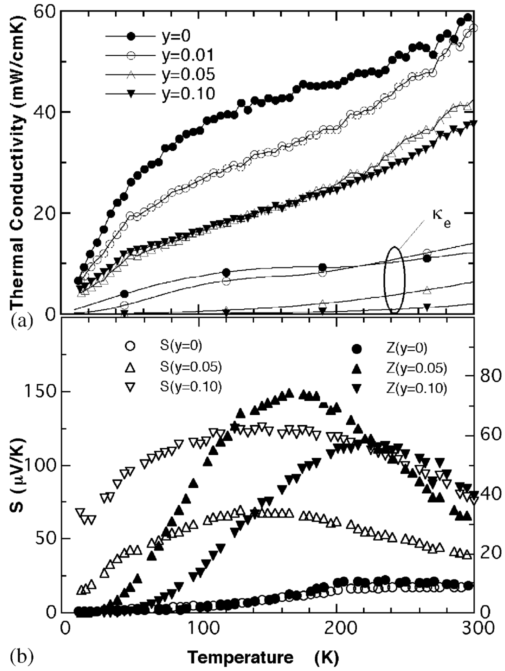

Fig. 2. (a) The temperature dependence of thermal conductivity $\kappa(T)$. The estimated electronic contribution $\kappa_e(T)$ is also shown. (b) The Seebeck coefficient $S(T)$ and the figure of merit Z $(= S^2/\kappa\rho)$ of $La_{0.80}Sr_{0.20}(Mn_yCo_{1-y})O_3$ for $y = 0$, 0.05 and 0.10.

LSCoO(0.05, 0.10), the quench of FM order results in a semiconductive behavior of $\rho(T)$ and $\rho(T)$ values sharply increase with increasing y.

Fig. 2(a) gives $\kappa(T)$ vs. T. The electronic component κ_e estimated on the basis of the Wiedemann–Franz law is also contained in the figure. $\kappa(T)$ is remarkably reduced by only 1% Mn substitution, which originates from the heavy reduction in the phonon component κ_{ph}. The $\kappa(T)$ reduction seems to saturate for $y \geqslant 0.05$. It may be worthwhile to note that $\kappa(T)$ of LSCoO(0.05, 0.10) has a shoulder-like kink at around 50 K, where $M(T)$ takes the maximum in these samples. Fig. 2(b) presents the coefficient S as a function of T. $S(T)$ increases with increasing y and LSCoO(0.10) shows the largest value of $\sim 120\ \mu V/K$ at around 160 K. For applicational purpose, a large value of the thermoelectric figure of merit Z $(= S^2/\kappa\rho)$ is of intrinsic importance. The calculated Z values are also given in Fig. 2(b). Pretty large Z values are realized in LSCoO(0.10). These Z values are, however, more than an order smaller than those of typical semiconductive thermoelectric materials now on practical use. We found that the Z values of LSCoO(0.20) were greatly deteriorated because of too large ρ values.

In summary, $M(T)$, $\rho(T)$, $\kappa(T)$ and $S(T)$ were measured for Mn substituted $La_{0.80}Sr_{0.20}(Mn_yCo_{1-y})O_3$. The FM-metal phase was preserved in initial narrow y region ($y \leqslant 0.02$). For $y \geqslant 0.05$, the FM order was greatly damaged or destroyed and the $\rho(T)$ behavior became semiconductive. The phonon component of $\kappa(T)$ sharply reduced by Mn substitution for Co and the reduction saturated for $y \geqslant 0.05$. The Seebeck coefficient was noticeably enhanced by Mn substitution, especially in the semiconductive composition region. However, the values of the figure of merit Z remained an order of magnitude smaller compared to the level of the possible practical use. The other 3d transition metal substitution effect on $S(T)$ adopting other RE ions are under way.

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