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Small polaron transport in $LaSrCoO_4$

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Abstract

We have studied transport properties of $LaSrCoO_4$ system, which has a much larger charge-transfer gap than the nickelate and compared the results with those of the nickelate. The temperature dependence of the resistivity $\rho(T)$ below ~400 K follows the three-dimensional variable range hopping formula. Above 900 K, $\rho(T)$ is describable in terms of the formula for the conductivity contributed from the thermally activated hopping of small polarons. The hopping energy is found to be much larger than that in the case of nickelate. From these results, it is concluded that the resistivity of $LaSrCoO_4$ is explained by conduction of small polarons which have a more localized character than in the nickelate.

Keywords: 71.30.+h

Keywords: Semiconductors; Powder metallurgy; X-ray diffraction; Electronic transport

1. Introduction

The physical properties of 3d transition metal oxides having a single layered perovskite structure (K_2NiF_4 type) have been studied with interest not only because of the similarity of these oxides with the superconducting Cu oxide, but because there is much to be learnt about mechanisms of metal–insulator transitions of these systems. Some attention has been paid to cubic perovskite oxides (ABO_3 type) with 3d transition metals of Co [1], Fe [2], and Mn [3], which have been now known to be charge-transfer insulators. The charge transfer gap becomes large with increasing d electron number also in K_2NiF_4 type compounds. In the K_2NiF_4 series compounds, $LaSrFeO_4$ is an antiferromagnetic insulator with $T_N = 380$ K [4]. On the other hand, $LaSrCoO_4$ is a paramagnet with semiconducting conduction [5]. $LaSrNiO_4$ shows a semiconductor–metal transition around room temperature [6]. Magnetism and resistivity of $LaSrFe_{1-x}Co_xO_4$ will be published [7].

The semiconducting behavior in $LaSrNiO_4$ is explained by small polaron transport. There is no detailed analysis for $LaSrCoO_4$. We measured resistivity of $LaSrCoO_4$ upto 1200 K and compared the results with those of $LaSrNiO_4$.

2. Experiment

We synthesised polycrystalline material of $LaSrCoO_4$ by solid state reaction from stoichiometric mixtutres of La_2O_3, $SrCO_3$ and Co_3O_4 with 3N purity. They were sintered in air atmosphere at 750 °C for 3 h. After that they were regrounded, pressed into pellet and sintered at 1300 °C for 24 h.

From the analysis with X-ray diffraction, we confirmed that all the samples were single-phase ones with a tetragonal crystal structure. The lattice parameters of a and c were estimated to be 3.802 ± 0.002 Å and 12.482 ± 0.002 Å, respectively.

We performed measurements of resistivity by four-probe method in the range of 77–1200 K and of susceptibility by SQUID magnetometer between 5 K and 350 K. Fig. 1 shows the temperature dependence of magnetic susceptibility

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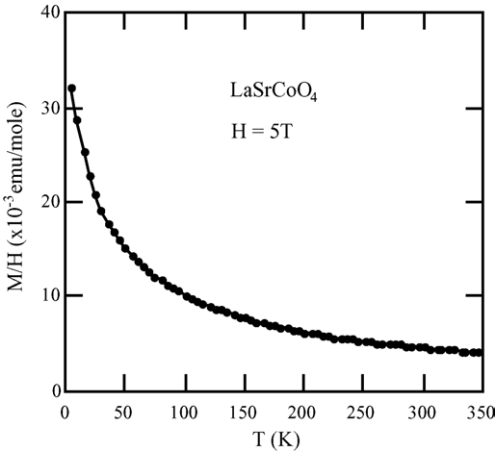

Fig. 1. Temperature dependence of magnetic susceptibility.

measured at magnetic field of 5 *T*. The result is consistent with the result that the $LaSrCoO_4$ is a paramagnet [5].

3. Results and discussion

Fig. 2 shows the natural logarithmic resistivity of $LaSrCoO_4$ as a function of *T*. The upper curve shows the resistivity of as-grown sample and the lower one that of annealed sample at 800 °C for 24 h. The value of resistivity below ∼500 K drastically decreases by annealing. Here we discuss the results of the sample with the lowest resistivity. The lattice constant changes little after the annealing.

Fig. 3 shows the natural logarithmic resistivity plotted against $T^{-1/4}$. This logarithmic resistivity is proportional to $T^{-1/4}$ below ∼200 K. That is, at low temperature below ∼200 K the resistivity follows three-dimensional variable range hopping formula:

$$\rho(T) = \rho_0 \exp\left(\frac{U}{T^{1/4}}\right), \quad (1)$$

where ρ_0 and *U* are fitting parameters.

In the $LaSrNiO_4$, the temperature region of variable range hopping is below 20 K [6]. In the small polaron system, the conductivity changes from variable range hopping to the thermally activated hopping of small polarons, with increasing temperature [8]. This change is observed in nickelates [6] above 100 K.

Fig. 4 shows the plot of the natural logarithmic of ρ/T as a function of $1/T$. Above ∼1000 K, the resistivity follows the formula:

$$\rho(T) = \rho_0 T \exp\left(\frac{E_A}{k_B T}\right), \quad (2)$$

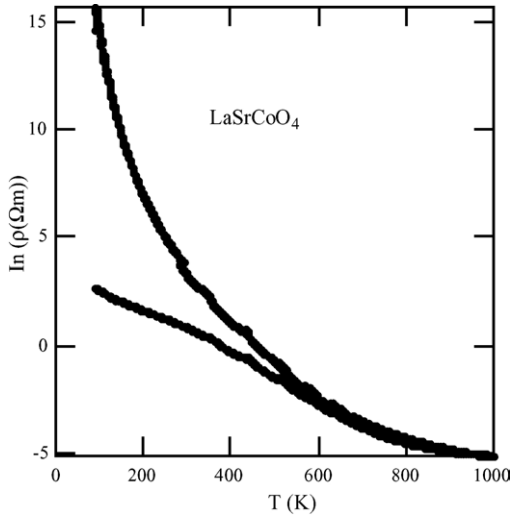

Fig. 2. Natural logarithmic resistivity as a function of *T*. The upper curve shows the resistivity of as-grown sample and the lower one that of annealed sample at 800 °C for 24 h.

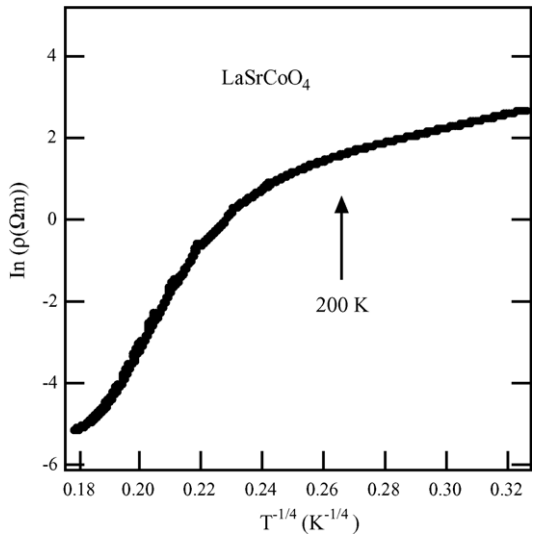

Fig. 3. Natural logarithmic resistivity as a function of $T^{-1/4}$.

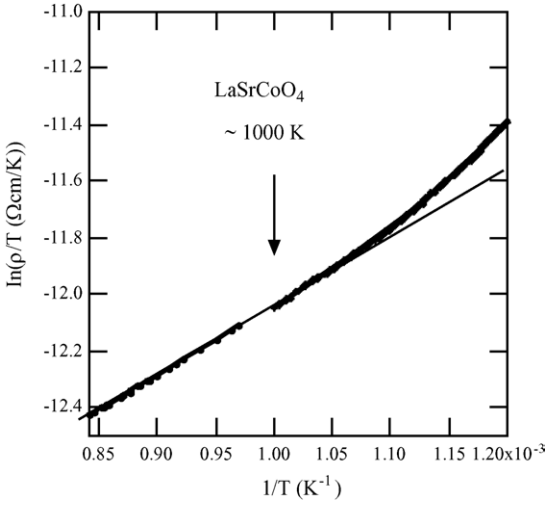

Fig. 4. Natural logarithmic of ρ/T as a function of $1/T$.

where E_A is the hopping energy. The results indicate that the contribution to the conductivity comes from the thermally activated hopping of small polarons above 900 K. The hopping energy E_A of small polarons is about 200 meV. The value is as large as ten times of the nickelate. Therefore, it is estimated that the delocalization of carriers occurs at around 2000 K. On the other hand, in the nickelate the carrier delocalization is observed around 300 K [6].

4. Conclusion

We have studied transport properties of $LaSrCoO_4$ system, which has a much larger charge-transfer gap than the nickelate and compared the results with those of the nickelate. The resistivity follows three-dimensional variable range hopping formula below ~400 K which is given by $\rho(T) = \rho_0 \exp(U/T^{\beta})$. The value of β is 1/4 for 800 °C annealed samples. Above 900 K, the resistivity follows the formula $\rho(T) = \rho_0 T \exp(E_A/k_B T)$ with the thermally activated polaron hopping energy E_A ~200 meV. From these results, it is concluded that the resistivity of $LaSrCoO_4$ is explained by conduction of small polarons which have a more localized character than in the nickelate.

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