ELSEVIER

Journal of Alloys and Compounds 424 (2006) 21–26

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Small polaron transport and glassy ferromagnetism in $(LaSr)Co_{1-x}Fe_xO_4$

Akira Tabuchi [a], Hirofumi Kawanaka [b,*], Hiroshi Bando [b], Toku Sasaki [a], Yoshikazu Nishihara [a]

[a] *Faculty of Science, Ibaraki University, Mito 310-8512, Japan*
[b] *National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8568, Japan*

Received 8 December 2005; accepted 12 December 2005
Available online 10 February 2006

Abstract

We have studied transport and magnetic properties of $(LaSr)Co_{1-x}Fe_xO_4$ system. The conduction of $(LaSr)CoO_4$ is three-dimensional variable range hopping at low temperatures below ~300 K and is expected to be thermally activated hopping above ~900 K. With increasing x the electronic conduction changes from a variable range hopping type to a band-gap type between $x = 0.2$ and 0.6. Substitution of Co by Fe induces ferromagnetism with large hysteresis in the temperature dependence of magnetization below the transition temperature. This glassy ferromagnetism appears in the concentration region where the variable range hopping of small polaron is dominant. In the samples with $x \geq 0.6$ the temperature dependence of magnetization shows an antiferromagnetic behavior. The lattice parameters a and c increase with increasing x. However, the increasing rate of c-axis is small in the variable hopping region below $x \sim 0.2$. The values of resistivity and ferromagnetic moment become maximum around $x = 0.2$. The transport and magnetic properties have a close correlation in this system.

Keywords: Small polaron; Glassy ferromagnetism; $(LaSr)Co_{1-x}Fe_xO_4$

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. In the review by Imada et al. [1] the physical properties of cubic perovskite oxides (ABO_3 type) have been discussed and a complete map of these compounds for 3d electron numbers from 1 to 9 and for electron and hole doping has been presented. The compounds of Co, Fe, and Mn have been now known to be charge-transfer insulators [2–4]. The charge transfer gap becomes large with decreasing d electron number. The results can be applied also to K_2NiF_4 type compounds. In the system of $(La_{2-x}Sr_x)NiO_4$, Wu and Neumeier reported [5] the analysis of resistivity measurements and strong evidence for small polaron transport. They found that $(LaSr)NiO_4$ shows a semiconductor–metal transition around 250 K. On the other hand, Matsuura et al. [6] reported the electrical conductivity and Seebeck coefficient of $(LaSr)CoO_4$ system. From the similarities of the temperature dependence of conductivity and Seebeck coefficient between $(LaSr)CoO_4$ and $La_{1-x}Sr_xCoO_3$ they suggested that the conduction mechanism of $LaSrCoO_4$ is small polaron hopping as in the case of $La_{1-x}Sr_xCoO_3$.

To investigate a correlation between the charge transfer gap and the transport properties, we have studied the transport properties of $(LaSr)Co_{1-x}Fe_xO_4$ system which has the smaller d electron number and the larger charge transfer gap than those in the nickelate. We have reported [7] that the resistivity of $(LaSr)CoO_4$ is also explained by conduction of small polaron which have a more localized character than in the nickelate. However, there is no report on details of transport properties of $(LaSr)Co_{1-x}Fe_xO_4$ system.

Another unusual property of ABO_3-type doped cobaltites is the existence of glassy ferromagnetism in $La_{1-x}Sr_xCoO_3$ [8,9]. The system changes from a glass phase at low Sr doping to a ferromagnetic phase at higher doping. As far as we know, there is

* Corresponding author. Tel.: +81 298615132; fax: +81 298615387.
E-mail address: kawanaka.h@aist.go.jp (H. Kawanaka).

0925-8388/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2005.12.085

few systematic studies of magnetic properties for doped systems of 3d elements with smaller d electron numbers, corresponding to the hole doping. In (LaSr)CoO_4 system it is difficult to make Sr rich samples [10]. Therefore, it might be interesting to study details of magnetic properties of (LaSr)$Co_{1-x}Fe_xO_4$ which is a hole doping system by 3d element.

From the study of transport and magnetic properties of (LaSr)$Co_{1-x}Fe_xO_4$ system, we have found that in the Co rich region the small polaron conduction is dominant and Fe doping induces glassy ferromagnetism. With increasing Fe concentration the conduction changes from a small polaron type to a band-gap type and the magnetic state from a glassy ferromagnetic to an antiferromagnetic one. In this report, discussions on the small polaron transport in (LaSr)CoO_4 and a magnetic phase diagram in (LaSr)$Co_{1-x}Fe_xO_4$ system are given.

2. Experiment

We synthesized polycrystalline materials of (LaSr)$Co_{1-x}Fe_xO_4$ by solid-state reaction from stoichiometric mixtures 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 and then they were re-grounded, 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 (LaSr)CoO_4 were obtained to be $a = 3.802 \pm 0.002$ Å and $c = 12.482 \pm 0.002$ Å. These values are in good agreement with reported values [10,11]. Fig. 1 shows the Fe concentration dependence of lattice parameters. The *a*-axis linearly increases with increasing Fe concentration x in the whole concentration region. On the other hand, the *c*-axis changes little up to $x \sim 0.2$ and above $x \sim 0.2$ it increases linearly.

We made post-annealing of (LaSr)CoO_4 at 500 and 800 °C for 24 h in air. The cooling rate was ∼100 °C/h down to 600 °C and after that it was ∼20 °C/h down to room temperature.

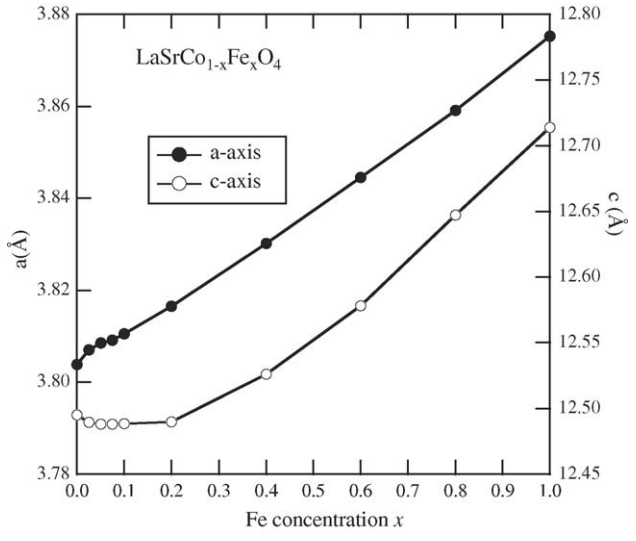

Fig. 1. Fe concentration dependence of lattice parameters.

The lattice parameters of the sample annealed at 800 °C are $a = 3.802 \pm 0.002$ Å and $c = 12.479 \pm 0.002$ Å, which coincide with the as-grown ones within experimental accuracy. To investigate the annealing effect, the thermal gravitational analysis was carried out up to 800 °C in air. The observed weight loss shows that the loss of oxygen is less than 0.5%.

Magnetization measurements were carried out using a SQUID magnetometer between 5 and 350 K. For resistivity measurements a four-probe configuration was used with vacuum evaporation coated gold contacts on the sample. The measurements were made in the range of 77–1200 K.

Mössbauer spectroscopic studies were made in transmission geometry using a constant acceleration mode. The radioactive source was 10 mCi ^{57}Co embedded in a Rh matrix.

3. Experimental results

3.1. Magnetic properties

The inset in Fig. 2(a) shows the temperature dependence of magnetic susceptibility of (LaSr)CoO_4 measured at magnetic field of 5 T. The result is consistent with the report [10] that the (LaSr)CoO_4 is a paramagnet. The effective paramagnetic moment was estimated to be $\sim 2.8\mu_B$. Substitution of Co by Fe induces ferromagnetism. Magnetizations of (LaSr)$Co_{1-x}Fe_xO_4$ measured at 0.1 T vary with temperature as shown in Fig. 2. The magnetization shows a maximum for the sample with $x = 0.2$. The discrepancy between the zero-field-cooled (ZFC) magnetization and the field-cooled (FC) magnetization appears below ∼100 K in all the magnetization curves of the ferromagnetic samples. As shown in Fig. 2(b), the magnetization shows an antiferromagnetic-like peak for the samples with $x = 0.6$ and 0.8. From the above results we find that in the (LaSr)$Co_{1-x}Fe_xO_4$ system a ferromagnetic state is induced by the substitution of Co by Fe and the ferromagnetic state changes into an antiferromagnetic one with increasing Fe.

Fig. 3 shows the magnetic field dependence of magnetization at 5 K. The ferromagnetic behavior is observed for the samples with $x = 0.1$, 0.2, and 0.4. However, the magnetization does not saturate up to 5 T. The ferromagnetic moment extrapolated to zero-magnetic field below 1 T is $\sim 0.15\mu_B$/molecule for the sample with $x = 0.2$, which is far smaller than the value estimated from the localized moment of high-spin Co^{3+} or Fe^{3+} ion. The field dependence of magnetization at 5 K suggests the ferromagnetic state in these samples is a glassy one. To show the glassy behavior of this magnetic state more clearly in weak magnetic fields, we measured the temperature dependences of magnetization at the magnetic fields of 0.01 and 0.001 T for the sample with $x = 0.1$. The results are shown in Fig. 4. The discrepancy between the ZFC and FC curve appears from higher temperatures than the magnetization curve of 0.1 T. The inset in the figure shows the magnetic susceptibility derived from the ZFC magnetization. We find that the sharp peak appeared at 205 K in low-field susceptibility collapses with increasing magnetic field. Since the temperature dependence of magnetization has large hysteresis below T_C and the susceptibility peak derived from the zero-field-cooled magnetization rapidly decreases with increasing magnetic field strength, this ferromagnetic state seems to be a cluster-glass state.

The magnetic transition temperatures T_C and T_N estimated from the temperature dependence of magnetization are plotted in Fig. 5. From the Mössbauer effect of ^{57}Fe in (LaSr)FeO_4 we confirmed that (LaSr)FeO_4 is an antiferromagnet with $T_N = 380$ K [12]. The ferromagnetic transition temperature T_C is nearly constant (220–230 K) in the concentration region of $x \geq 0.05$. On the other hand, the antiferromagnetic transition temperature T_N estimated from the peak of magnetization increases rapidly from 80 to 380 K above $x = 0.6$.

Since the ferromagnetism with $T_C \sim 200$ K is observed above $x \sim 0.2$ in $La_{1-x}Sr_xCoO_3$ [7,8], existence of ABO_3 impurity phase is a serious problem for discussion of magnetism of (LaSr)$Co_{1-x}Fe_xO_4$ system. Fig. 6 shows the X-ray pattern for the sample with $x = 0.1$. The pattern for the sample with the ABO_3 impurity phase is also plotted in the figure. In this study we used the samples with no appreciable ABO_3 impurity phase.