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Magnetic and transport properties of samples of the approximate composition $La_{0.9}Ba_{0.1}MnO_3$ with different cation deficiencies

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Abstract

Different cation deficiency doped $La_{0.85}Ba_{0.1}MnO_3$ and $La_{0.9}Ba_{0.05}MnO_3$ and $La_{0.9}Ba_{0.1}Mn_{0.95}O_3$ and stoichiometric $La_{0.9}Ba_{0.1}MnO_3$ polycrystalline bulk samples were synthesized at 1500 °C, the ac magnetic susceptibility, resistivity and magnetic resistance (MR) of the samples were tested, and it is found that stoichiometric phase $La_{0.9}Ba_{0.1}MnO_3$ sample have the highest ferromagnetic transition temperature T_c, and $La_{0.9}Ba_{0.05}MnO_3$ sample have the lowest ferromagnetic transition temperature T_c. $La_{0.85}Ba_{0.1}MnO_3$ sample have the largest magnetic resistance (MR), except $La_{0.9}Ba_{0.05}MnO_3$ sample, the other samples have the same MR peak temperature.

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Keywords: Manganites; ac susceptibility; Resitivity, Magnetic resistance

1. Introduction

Since the observation of colossal magnetoresistance (CMR) effect in doped manganese oxides $La_{1-x}A_xMnO_3$ (where A is divalent ions, such as Ca, Sr, and Ba), they have been extensively investigated because of their theoretical interests and potential application [1–5]. Although the double exchange interaction between pairs of Mn^{3+} and Mn^{4+} ions is responsible for the ferromagnetic and metallic properties in these manganese oxides and pairs of Mn^{3+} and Mn^{4+} can be controlled by changing the doping level [5–7] or oxygen stoichiometry [8], over and above, these properties are also known to strongly depend on the following: average A site ionic size (influencing bond distance d between Mn and O, and bond angle between Mn and oxygen O) [9], the electronegativity [10] and variance [11] of substituted ions, etc. For the cation deficiency doped manganese oxides $La_{1-x}MnO_3$, significant differences in the magnetic and electric properties have been reported in literatures [12–16]. In this paper, we will report the electrical transport and magnetic properties of $La_{0.9}Ba_{0.1}MnO_3$ with different cation deficiency.

2. Experimental

The different deficiency doped bulk ceramic samples of $La_{0.9}Ba_{0.1}MnO_3$ were synthesized using a conventional solid state reaction method. The stoichiometric amounts of La_2O_3, $BaCO_3$ and MnO_2 were mixed, ground and fired at 1300–1400 °C repeatedly. Finally the obtained powders were pelletized into disc samples, and fired at 1500 °C in air for 20 h followed by furnace cooling, respectively. All the samples were characterized by X-ray diffraction (XRD) with Cu Kα radiation. The testing samples were taken from the as-prepared disc samples, respectively, the resistivity was measured by the standard four-probe method. AC magnetic susceptibility was measured at 1 kHz by a lock-in technique. The MR was measured using square-probe array method in the magnetic field of 0–1 T. We defined MR ratio as MR ratio (%) = $(R_0 - R_H)/R_0$; where R_0 is the zero-field resistivity and R_H is the resistivity when the magnetic field was applied.

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of the four different $La_{0.9}Ba_{0.1}MnO_3$, $La_{0.85}Ba_{0.1}MnO_3$, $La_{0.9}Ba_{0.05}MnO_3$ and $La_{0.9}Ba_{0.1}Mn_{0.85}O_3$ samples. The XRD patters indicate that the as-prepared samples have the same perovskite structure with almost the same lattice parameter. Within the XRD sensitivity, no obvious difference is detected.

The temperature-dependent ac susceptibility χ is shown in Fig. 2. The ferromagnetic transition for all the samples starts at

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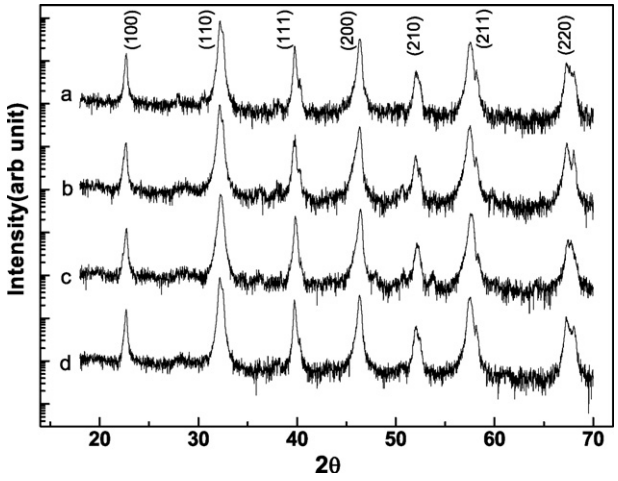

Fig. 1. X-ray diffraction patterns of the four different samples: (a) $La_{0.9}Ba_{0.1}MnO_3$, (b) $La_{0.85}Ba_{0.1}MnO_3$, (c) $La_{0.9}Ba_{0.05}MnO_3$ and (d) $La_{0.9}Ba_{0.1}Mn_{0.95}O_3$.

almost the same temperature (about 230 K), but the transition width sensitively depends on the different ion deficiency. For the stoichiometric $La_{0.9}Ba_{0.1}MnO_3$ sample, the transition is the sharpest and the susceptibility amplitude is the largest. And for the $La_{0.9}Ba_{0.05}MnO_3$ sample, the transition peak temperature is the lowest and the susceptibility amplitude is greatly decreased. The $La_{0.85}Ba_{0.1}MnO_3$ sample and $La_{0.9}Ba_{0.1}Mn_{0.95}O_3$ sample have almost the same susceptibility, only below 210 K, the former is larger than the latter. At low temperature, susceptibility reduced and spin-glass-like behaviour happened for all samples, which may be explained by spin-cluster model.

Fig. 3 shows the change in resistivity of different samples with temperature. Every sample exhibits semiconductor resistivity and a inflexion nearly at its respective temperature T_C. Within the whole range of temperature we investigated, the resistivity is sensitively depends on the different ion deficiency. For the stoichiometric $La_{0.9}Ba_{0.1}MnO_3$ sample, the resistivity is

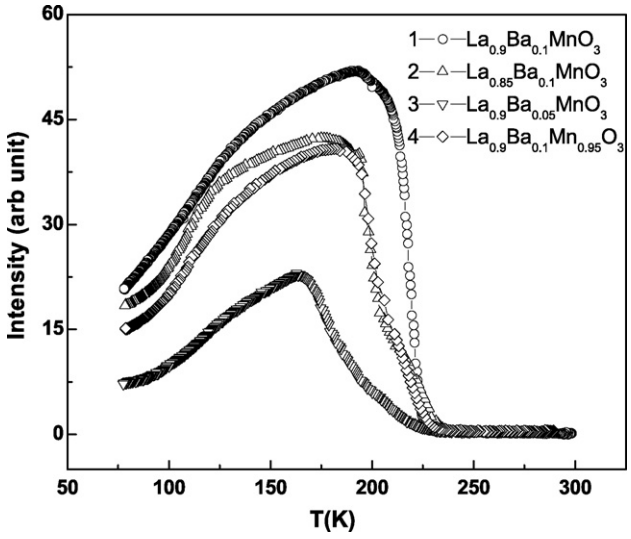

Fig. 2. The temperature-dependent ac susceptibility χ of the four different samples.

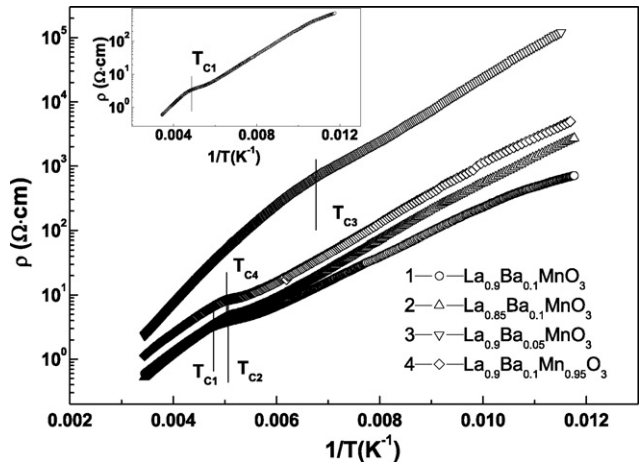

Fig. 3. The temperature-dependent resistivity of the four different samples.

the least. The resistivity of $La_{0.9}Ba_{0.1}Mn_{0.95}O_3$ sample is slight larger than that of $La_{0.85}Ba_{0.1}MnO_3$ sample. Corresponding to the susceptibility, the resistivity of the $La_{0.9}Ba_{0.05}MnO_3$ sample is obvious larger than that of the other samples, especially at low temperature, from $La_{0.9}Ba_{0.1}MnO_3$ sample to $La_{0.9}Ba_{0.05}MnO_3$ Sample, the resistivity increased by more than two orders.

The magnetoresistance ratio (MR), defined as $\nabla R/R_0 = (R_0 - R_H)/R_0$, where R_0 and R_H are the resistivity of the zero field and an applied field H, respectively, is plotted in Fig. 4. Every sample exhibits a MR peak nearly at its respective temperature T_C. Calculation show the MR ratios for 1 T applied field are more than 20% for the $La_{0.85}Ba_{0.1}MnO_3$ sample and 19% for the stoichiometric $La_{0.9}Ba_{0.1}MnO_3$ sample, and almost the same 16% for the other two samples.

Those phenomenon has been traditionally understood on the basis of the double-exchange (DE) model and Jahn-Teller effects [17–20]. When La ions in the $LaMnO_3$ were replaced by a divalent element Ba, proportional amount of Mn^{3+}, with electronic configuration $t_{2g}^3 e_g^1$, is substituted with Mn^{4+} (t_{2g}^3) and form a mixed-valence state of Mn^{3+}–Mn^{4+}. The hopping magnitude of e_g electron between spin aligned Mn^{3+} and Mn^{4+} ions via

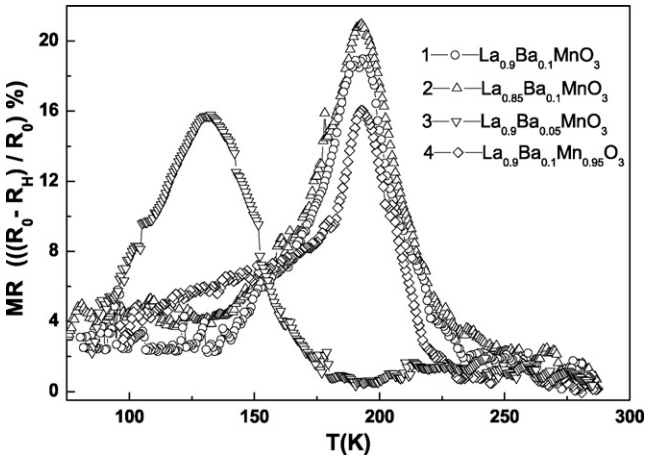

Fig. 4. The temperature-dependent of the magnetoresistance ratio (MR) of the four different samples.

O^{2-} rests on the angle (θ_{ij}) between the neighboring spins, and relates to the applied magnetic field. In a hole doped CMR system, the mixed valence state of Mn^{3+}–Mn^{4+} is a key component for understanding CMR effect and the transition from a ferromagnetic metal to a paramagnetic semiconductor. At low doped concentration ($x \leq 0.2$, x is the doped concentration of divalent cation), Alonso et al. [21] propose that Mn^{4+} holes are localized around bivalent cations forming ferromagnetic clusters, and the undistorted clusters around the bivalent ions are also locally conducting although the spatial localization imposed by the bivalent ions dopants results in clusters that are electrically isolated from each other.

The concentration of Mn^{4+} holes in $La_{0.9}Ba_{0.1}MnO_3$ is 10%. For $La_{0.85}Ba_{0.1}MnO_3$ and $La_{0.9}Ba_{0.1}Mn_{0.95}O_3$, the cation deficiency ratios are only 5%, respectively, and the concentrations of Mn^{4+} holes are 25%. But for $La_{0.9}Ba_{0.05}MnO_3$, the Ba cation deficiency ratios are almost 50%, and the concentration of Mn^{4+} holes is about 20%, less than that of the two deficiency samples. The deficiencies may exist on defect or small separation of cation oxides which may cause some disorder. Although the Mn^{4+} holes of the three deficiency samples are higher than that of the $La_{0.9}Ba_{0.1}MnO_3$ sample, the disorder due to vacancies decreases the Curie temperature. At the same time, compare with the stoichiometric $La_{0.9}Ba_{0.1}MnO_3$, the change of bond angle between Mn and oxygen O in $La_{0.9}Ba_{0.05}MnO_3$ is larger than those in $La_{0.85}Ba_{0.1}MnO_3$ and $La_{0.9}Ba_{0.1}Mn_{0.95}O_3$, so the double change of Mn^{3+} and Mn^{4+} in $La_{0.9}Ba_{0.05}MnO_3$ sample is greatly reduced, and the change of susceptibility, resistivity and MR for $La_{0.9}Ba_{0.05}MnO_3$ sample is more remarkable than those of the other two cation deficient samples. As for $La_{0.85}Ba_{0.1}MnO_3$ sample, have more Mn cation than the other samples, which may improve the MR, but due to the disorder, the resistivity is still larger than that of the stoichiometric sample.

4. Conclusion

In summary, we have investigated the ac magnetic and electric and MR properties of different deficiency doped $La_{0.9}Ba_{0.1}MnO_3$, the T_C and amplitude of ferromagnetic transitions for all cation deficiency samples are lower than that of the stoichiometric sample, at the same time the resistivity for all cation deficiency samples are larger than that of the stoichiometric sample. Especially for the Ba cation deficiency sample, the change of double exchange is largest, the changes of susceptibility and resistivity are largest correspondingly. In all, the disorder due to the vacancies decreases the Curie temperature although the number of Mn^{4+} ions increases in the all cation deficiency samples.

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