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Tuning colossal magnetoresistance response at room temperature by $La_{2/3+y}Sr_{1/3-y}Mn_{1-y}Cr_yO_3$

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Abstract

The special formula of $La_{2/3+y}Sr_{1/3-y}Mn_{1-y}Cr_yO_3$ with $[Mn^{3+}]/([Mn^{4+}]+[Cr^{3+}])$ ratio fixed at optimal proportion 2:1 was designed to tune colossal magnetoresistance (CMR) response around room temperature and test the possibility of ferromagnetic (FM) interaction of hetero-ionic coupling between Mn^{3+} and Cr^{3+}. The polycrystalline bulk samples were fabricated by the traditional solid-state reaction method. The structural, magnetic, electrical transports and magnetoresistance (MR) properties were investigated. An enhancement of CMR at room temperature with appropriate content y has been observed, meanwhile, substituting Cr for Mn in manganites shows inefficiency in lowering ferromagnetic–paramagnetic (FM–PM) transition temperature T_c and metal–insulator (M–I) transition temperature T_p. Experimental results indicate that there might exist a FM coupling between Mn^{3+} and Cr^{3+}.

Keywords: Perovskite manganites; Ferromagnetic interaction; Colossal magnetoresistance

1. Introduction

Mixed-valence manganites with perovskite structure of formula $La_{1-x}A_xMnO_3$ (where A = Ca, Sr in the range $0.2<x<0.5$) have been the subject of scientific and technological interests, owing to negative CMR [1–3] effect and potential application to magnetic devices. The CMR has been basically understood in terms of the double exchange (DE) interaction [4], which correlates the electrical transport to magnetic configuration by considering the FM coupling between Mn^{3+} and Mn^{4+} ions through charge carriers hopping.

From the application point of view, it is important to improve MR at room temperature. Usually, many groups have attempted to substitute other elements for Mn ions in pure $La_{2/3}Sr_{1/3}MnO_3$ (LSMO), such as Al [5], Fe [6], Co [6], Ti [7], Ni [8] and Cr [9–12], but comparably high fields of several teslas are required to obtain a higher sensitivity of resistivity to magnetic field at room temperature, which is not very appealing for applications. Accordingly, other groups focused on the investigation of extrinsic MR such as intergrain MR (IMR) [13–15]. Although the IMR shows a larger response to low field, a higher value is observed only at low temperature, this makes it difficult to apply to electronic devices.

In order to obtain large CMR around room temperature, we think it is a possible way to substitute Cr for Mn with special formula $La_{2/3+y}Sr_{1/3-y}Mn_{1-y}Cr_yO_3$. Among these doping elements, Cr^{3+} has the same electronic configuration t_{2g}^3 as Mn^{4+} and a similar ionic radius to that of Mn^{3+}. For this special formula, the $[Mn^{3+}]/([Mn^{4+}]+[Cr^{3+}])$ ratio is fixed at 2:1 by assuming that Cr^{3+} plays the role of Mn^{4+} in the Mn^{3+}–O–Cr^{3+} interaction. As we know, the $[Mn^{3+}]/[Mn^{4+}]$ ratio is in optimal proportion 2:1 in pure LSMO, so there exists a strong DE interaction which corresponds to a higher T_p and small resistivity. Meanwhile, it is worth noting that doped Cr^{3+} induces a rather slow decreasing effect on T_c and T_p [9–12], these features make Cr^{3+} an interesting ion to study the possible existence of FM interaction between Cr^{3+} and Mn^{3+}. Moreover, compared

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with the reported Cr doping manganites $La_{2/3}Sr_{1/3}Mn_{1-y}Cr_yO_3$ [9–12], the substituting Cr for Mn in $La_{2/3+y}Sr_{1/3-y}Mn_{1-y}Cr_yO_3$ is a distinct technique to study the interaction between Cr^{3+} and Mn^{3+}.

In this paper, we report electrical transport and magnetic properties of polycrystalline bulk samples $La_{2/3+y}Sr_{1/3-y}Mn_{1-y}Cr_yO_3$ ($0 \le y \le 0.12$). An enhancement of CMR around room temperature was observed from the experimental results, and the possibility of FM interaction between Cr^{3+} and Mn^{3+} was discussed.

2. Experimental procedure

Polycrystalline samples $La_{2/3+y}Sr_{1/3-y}Mn_{1-y}Cr_yO_3$ ($0 \le y \le 0.12$) were synthesized by the traditional solid-state reaction method. Mixed powders of stoichiometric amounts of high purity La_2O_3, $SrCO_3$, MnO_2 and Cr_2O_3 (with purities higher than 99%) were thoroughly ground and first fired in air at 1000 °C for 24 h to achieve decarbonation. Then, the powders were heated at the temperature of 1150 °C for 24 h with intermediate grinding. Following cooling to room temperature, the materials were reground and again calcined at 1300 °C for another 24 h. After the third heat treatment, the samples were ground to a fine powder and pressed into pellet forms. Finally, these pellets were sintered in air at 1450 °C for 30 h followed by slow cooling to room temperature.

The structural characterization of samples was examined using X-ray diffraction (XRD) (X'Pert PRO, PANalytical B.V. company) at room temperature. All electrical transport and magnetic properties were performed by a commercial physical property measurement system (PPMS, Quantum Design).

3. Results and discussion

Fig. 1 shows the XRD patterns of $La_{2/3+y}Sr_{1/3-y}Mn_{1-y}Cr_yO_3$ polycrystalline samples with $y=0$, 0.08, 0.1 and 0.12, respectively. The XRD patterns prove that all samples are single phase in rhombohedral perovskite structure. Meanwhile, no impurity phases are observed, which suggest that the doped Cr substitutes mainly for Mn. The similarity between the crystal structures of pure and Cr doping samples implies that doped Cr^{3+} ion does not obviously change the crystal structure of pure LSMO, which may mainly result from the similar ionic size of Mn^{3+} and Cr^{3+}. Moreover, one can see that there is a variation in the XRD patterns with increasing y content, such as the intensities of diffraction peaks (104), (006), (018) and (208). The variation was also observed in other elements doping LSMO [7,12,16], which indicates that the variation results from the substituting foreign elements for Mn.

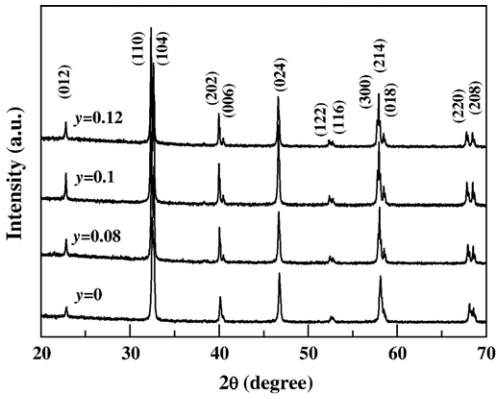

Fig. 1. XRD patterns of samples $La_{2/3+y}Sr_{1/3-y}Mn_{1-y}Cr_yO_3$ with $y=0$, 0.08, 0.1 and 0.12.

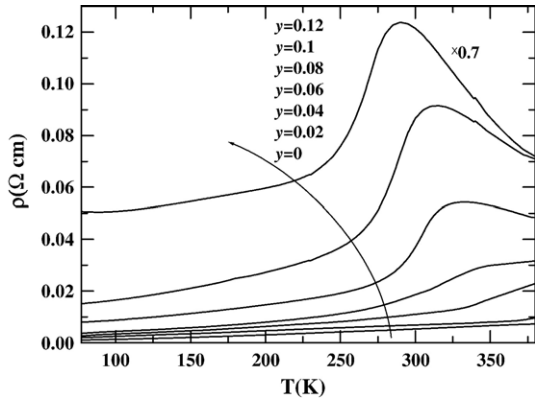

Fig. 2. Resistivity versus temperature in zero field of $La_{2/3+y}Sr_{1/3-y}Mn_{1-y}Cr_yO_3$ ($0 \le y \le 0.12$).

Fig. 2 depicts the resistivity (ρ) as a function of temperature (T) measured without magnetic field for $La_{2/3+y}Sr_{1/3-y}Mn_{1-y}Cr_yO_3$ samples. It is found that the ρ–T curves are different from those of $La_{2/3}Sr_{1/3}Mn_{1-y}Cr_yO_3$ reported by other groups [10,11]. The double-peaked feature of ρ–T curves was observed in $La_{2/3}Sr_{1/3}Mn_{1-y}Cr_yO_3$, which can be regarded as an intrinsic characteristic and ascribed to the crucial role of Cr^{3+}. However, as seen in Fig. 2, there appears a single M–I transition peak in the ρ–T curves of $La_{2/3+y}Sr_{1/3-y}Mn_{1-y}Cr_yO_3$, which may be interpreted in terms of the $[Mn^{3+}]/([Mn^{4+}]+[Cr^{3+}])$ ratio fixed in optimal values 2:1. The resistivity peaks become obviously sharper and its values increase with the increase of y, simultaneously, the M–I transition characterized by a peak occurs at T_p that shifts to lower temperature, which can be attributable to the weakening of the DE interaction. Whereas, the downward shift of T_p caused by Cr doping is much less than that by other elements [5–8,16]. One can see that the T_p is around room temperature for samples with $y=0.08$, 0.1 and 0.12, thus, we have investigated magnetization and MR of them thereinafter.

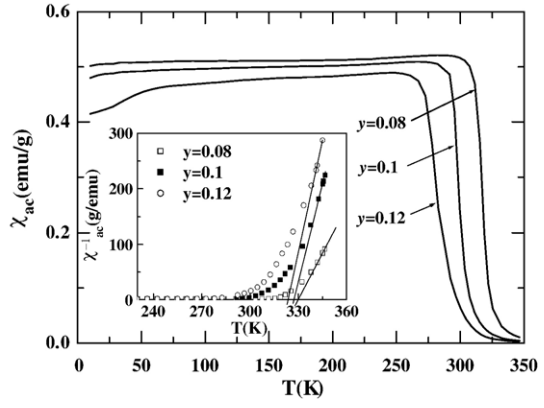

Fig. 3. Temperature dependence of ac susceptibility for $La_{2/3+y}Sr_{1/3-y}Mn_{1-y}Cr_yO_3$ with $y=0.08$, 0.1 and 0.12. Inset: reciprocal ac susceptibility as a function of temperature.