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# Enhanced magnetoresistance at room temperature in $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Sc}_x\text{O}_3$ perovskites

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## Abstract

The uncommon Sc ions are employed to partially replace Mn in  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  perovskite. X-ray diffraction patterns indicate a pure single phase with rhombohedral lattice symmetry for  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Sc}_x\text{O}_3$  ( $0 \leq x \leq 0.1$ ). The Curie temperature ( $T_C$ ) is tuned to near room temperature by Sc substitution with  $x = 0.03$ – $0.05$ , and consequently a significant enhancement in magnetoresistance (MR) at room temperature is obtained in the Sc-doped compounds. Magnetic measurement shows no spin coupling between Sc and Mn ions. We suggest that the reduction in  $T_C$  and the enhancement in MR are ascribable to the suppression of ferromagnetic order due to the structural distortion caused by the large  $\text{Sc}^{3+}$  ions.

## 1. Introduction

$\text{ABO}_3$ -type lanthanum manganite perovskites have attracted much attention due to their colossal magnetoresistance in recent years [1, 2]. Since large magnetoresistance (MR) at room temperature and/or low applied field is desired for practical applications, optimizing the operating temperature and reducing the field scale have become the primary goals of the researchers in this area. Some recent progress in low-field magnetoresistance (LFMR) and room temperature magnetoresistance (RTMR) has been obtained for polycrystalline samples with special microstructure and some ferromagnet/insulator-type two-phase manganite-based composites [3–10]. A large number of reports have shown that substitution at the A or B site can significantly modify the MR due to the influence on the double-exchange (DE) interaction of distortion in the  $\text{Mn}^{3+}\text{--O}^{2-}\text{--Mn}^{4+}$  network or through magnetic coupling between the dopant

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and Mn ions [11–16]. In our previous paper [17], we investigated magnetotransport behaviours in  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.9}\text{M}_{0.1}\text{O}_3$  ( $M = \text{Cr, Fe, Ni, Cu}$ ) nanoscaled polycrystals, and found an enhanced LFMR in the B-site-doped manganites. Notably, the B-site doping has a direct impact on the heart of the DE interaction. In general, the substitution of Mn ions suppresses the long-range ferromagnetic (FM) order. It has been well documented that partial substitution at the Mn site of other transition metal ions can greatly reduce the Curie temperature ( $T_C$ ) and enhance the MR. Therefore, replacement of Mn with other metal ions is also an effective approach to achieving LFMR and/or RTMR.

According to the DE mechanism, the  $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{4+}$  network is the key parameter in controlling the magnetic/transport behaviours. The larger the variation in the  $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{4+}$  network, the greater the modification in the MR. Scandium is a special element among 3d transition metal ions because of having the largest ionic radius. A large lattice effect arising from  $\text{Sc}^{3+}$  on magnetic and transport properties was observed in the  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  system [18]. As has been demonstrated,  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (LSMO) has a high  $T_C$  of about 370 K that could be decreased to room temperature by partial replacement of Mn ions. In this paper, we have focused on Sc-doped LSMO ceramic samples in our approach to the problem, and found an evidently enhanced RTMR due to the Sc doping. The mechanism for the observation is also discussed.

## 2. Experimental details

$\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Sc}_x\text{O}_3$  (LSMSO,  $0 \leq x \leq 0.1$ ) samples were prepared by thermal decomposition of precursor complexes, as described elsewhere [6]. The target products were pressed into pellets with a diameter of 6 mm and calcined at 1200 °C for 18 h. The phase was examined by means of x-ray powder diffraction (XRD,  $D_{max}$ -2000, Cu  $K\alpha$ , Rigaku, Japan). Magnetization and MR measurements were performed on a MagLab System 2000 (Oxford, UK). Resistance was measured using a standard four-probe technique. The MR is defined as  $(\rho_H - \rho_0)/\rho_H$ , where  $\rho_0$  and  $\rho_H$  are the resistivity under zero and an applied magnetic field, respectively.

## 3. Results and discussion

Figure 1 presents XRD patterns for typical LSMSO with  $x = 0, 0.03, 0.05$  and 0.1. All of the samples exhibit a single phase indexed by rhombohedral lattice symmetry with a space group of  $R\bar{3}c$ . Using the Cohen method [19], we can establish that the lattice constant increases monotonically from 5.4607 to 5.4710 Å while  $x$  varies from 0 to 0.1. This is consistent with the fact that the radius of  $\text{Sc}^{3+}$  (0.745 Å) is much larger than that of  $\text{Mn}^{3+}$  (0.645 Å).

Figure 2 shows the temperature dependence of the magnetization ( $M$ ) for LSMSO at 200 Oe. All of the samples undergo a sharp transition from a FM to a paramagnetic (PM) state.  $T_C$  is obtained by finding the minimum of  $dM/dT$ . As shown in the inset of figure 2,  $T_C$  drops linearly from 368 to 228 K at an average rate of 14 K for 1%  $\text{Sc}^{3+}$  substitution while  $x$  varies from 0 to 0.1. The values of  $T_C$  are 318, 311 and 290 K for  $x = 0.03, 0.04$  and 0.05 respectively, which are close to room temperature. Figure 3 shows the field dependence of  $M$  for LSMSO at 5 K. The magnetization tends to be saturated at a low field for all of the samples, indicating a long-range FM order. The magnetic moment per B-site ion ( $\mu_{exp}$ ) obtained at 5 T decreases linearly with increasing  $x$ , as shown in the inset of figure 3. Considering the dilution of nonmagnetic  $\text{Sc}^{3+}$ , the moment per Mn ion is expected to be  $(1 - x)\mu_{exp}$ , which is close to a constant. This demonstrates that the magnetic coupling between Sc and Mn ions in the

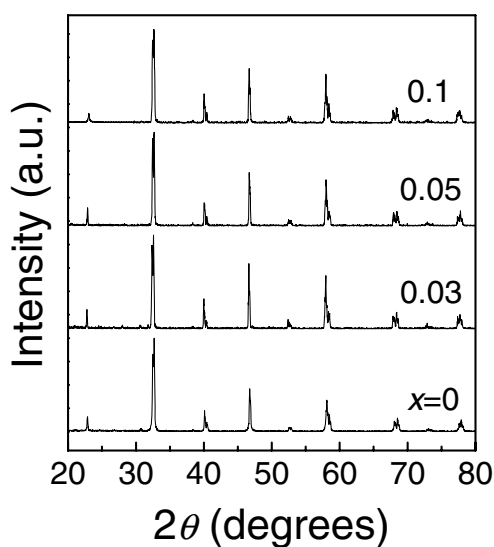


Figure 1. XRD patterns for typical LSMSO samples with  $x = 0, 0.03, 0.05$  and  $0.1$ .

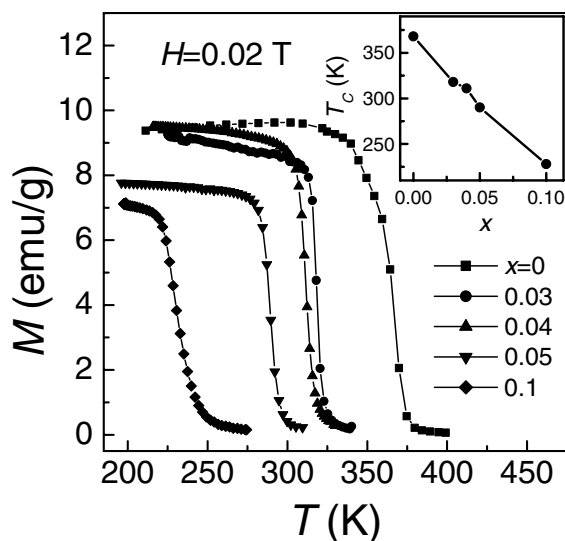
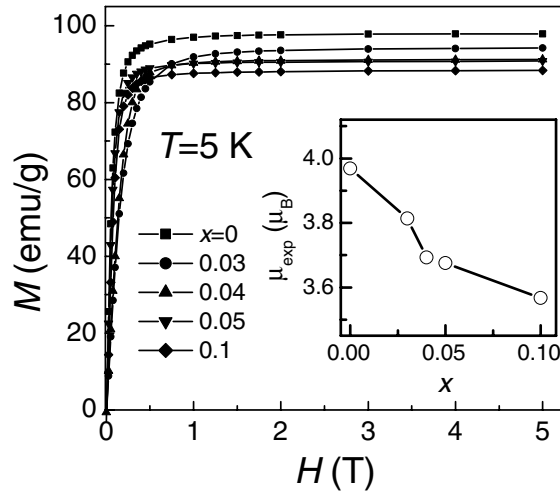


Figure 2. The temperature dependence of the magnetization ( $M$ ) for LSMSO with  $x = 0, 0.03, 0.04, 0.05$  and  $0.1$  at  $200$  Oe; the inset shows the Curie temperature ( $T_C$ ) as a function of the Sc doping level  $x$ .

perovskite lattice is rather limited. Indeed,  $\text{Sc}^{3+}$  has empty  $3d$  and  $4s$  shell orbitals, and thus exhibits no inherent magnetic moment. This differs from the outcome of some other B-site doping, such as that with  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$  and  $\text{Ni}^{2+}$ , in which a strong spin coupling exists between the dopant and Mn ions [14–16]. We suggest that the suppression of FM order due to the structural distortion caused by  $\text{Sc}^{3+}$  is responsible for the reduction in  $T_C$ .

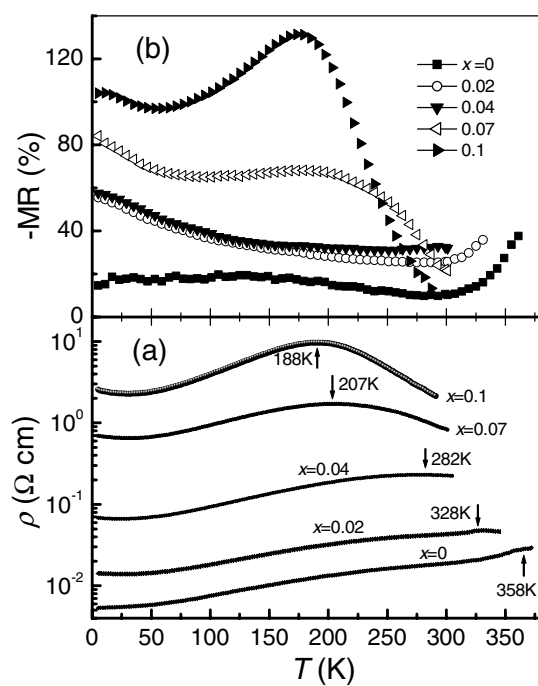
Our chief intention in this paper is to explore a marked MR near room temperature, where the shift of  $T_C$  to room temperature is crucial for achieving the RTMR effect. Figure 4 displays



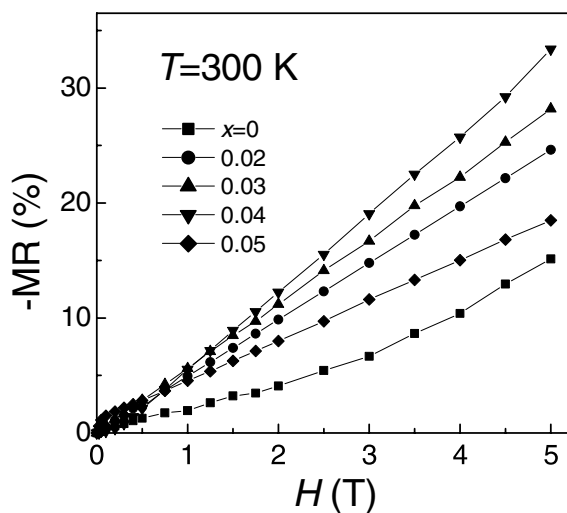
**Figure 3.** Magnetization ( $M$ ) as a function of applied field for LSMO. The magnetic moment per B-site ion ( $\mu_{\text{exp}}$ ) obtained at 5 T is shown in the inset.

the thermal dependence of the zero-field resistivity ( $\rho_0$ ) and the MR ratio for the LSMO series. For  $x = 0-0.1$ , FM metallic and PM insulating regions are distinctly observed in the  $\rho_0-T$  data, and the metal-insulator (M-I) transition occurs around the corresponding  $T_C$ . When  $x$  is around 0.04, the M-I transition appears in the vicinity of room temperature, which favours enhancement of the RTMR effect. Moreover,  $\rho_0$  increases by more than two orders of magnitude on increasing  $x$  from 0 to 0.1. For Sc substitution in the lattice, two scenarios could lead to the elevated resistivity. First, the insertion of larger  $\text{Sc}^{3+}$  ions results in a great distortion of  $\text{MnO}_6$  octahedra and, as a consequence, the carrier mobility is reduced and the forbidden band above the Fermi level is broadened [18]. Secondly, since the outer 4s shell of Sc is of small spatial extent, Sc ions are inaccessible to the conductive electrons and hence become blocking sites for the electron transport in the lattice, which introduces another forbidden path for the conduction by percolation. Generally, larger resistivity and lower  $T_C$  give rise to a higher MR ratio. For LSMO, the optimal MR effect occurs around its M-I transition, which is far above room temperature, but its RTMR is very small. As compared with LSMO, the Sc-doped samples exhibit a remarkable enhanced MR from low temperature up to room temperature. It should be mentioned that the MR at low temperatures slightly increases with Sc doping level, which can be explained by the enhanced spin-polarized electron tunnelling caused by Sc substitution. Because the transport behaviours at low temperatures predominantly reflect the extrinsic features, the doped Sc ions can build in-grain barriers while FM order is forming in the lattices [17]. In order to illustrate the enhancement in the RTMR clearly, we plot the MR as a function of the applied field ( $H$ ) at 300 K in figure 5. It is observable that the MR increases almost linearly with  $H$ , which is attributed to the suppression of intragrain spin fluctuation [3]. The slope of the  $-\text{MR}-H$  curve for all of the Sc-doped samples is larger than that of LSMO, indicating that the introduction of  $\text{Sc}^{3+}$  enhances the intragrain spin fluctuation. The maximal MR enhancement was observed at  $x = 0.04$ .  $-\text{MR}_{H=5\text{ T}}$  at 300 K is 34% for  $x = 0.04$ , double that of 15% for  $x = 0$ .

The magnetic and transport properties of the manganites are traditionally interpreted within the framework of the DE mechanism. Since substitution at the B site has a direct action at the heart of the DE, the possible spin coupling between the dopant and Mn should be taken



**Figure 4.** The temperature dependence of (a) the zero-field resistivity and (b) the MR ratio for typical LSMSO samples. The arrows indicate the M-I transition, and the transition temperatures are labelled.



**Figure 5.** RTMR as a function of the applied field for LSMSO.

into consideration. However, the magnetic results have shown that no spin coupling exists between Sc and Mn ions; therefore, the structural distortion should be the most important reason for the modification in the magnetic/transport properties. It is well known that the coupling between the mobile holes and the localized  $t_{2g}$  electrons is controlled by the  $\text{Mn}^{3+}$ -

$O^{2-}-Mn^{4+}$  ion transfer integral  $t_{ij}$ , which is strongly dependent on the Mn–O–Mn angle. With the substitution of  $Sc^{3+}$ , an additional dopant-size-induced local strain effect [16, 18] together with the size mismatch between A- and B-site ions leads to a great distortion of  $MnO_6$  octahedra and, as a consequence, the average Mn–O bond distance is lengthened and the average Mn–O–Mn angle is compressed. We believe that the reduction of  $T_C$  and MR enhancement are essentially ascribable to the weakening of the DE interaction caused by the larger  $Sc^{3+}$  ions at the Mn site.

#### 4. Conclusions

Magnetic and transport properties of  $La_{0.7}Sr_{0.3}Mn_{1-x}Sc_xO_3$  have been investigated. A large MR at room temperature is obtained around  $x = 0.04$ , which is related to the shift of  $T_C$  to room temperature tuned by Sc substitution. Our results show that the B-site doping of  $Sc^{3+}$  is also a possible route to achieving improved MR at room temperature.

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