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Phase competition driven temperature broadening of colossal magnetoresistance in $La_{0.815}Sr_{0.185}MnO_3$

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Abstract

It is shown that the temperature dependence of the magnetoresistance (MR) in manganites can be appreciably broadened by enhancing phase competition. By substituting Mn^{4+} with small amounts of Ti^{4+}, the ferromagnetic metallic $La_{0.815}Sr_{0.185}MnO_3$ is pushed closer to the ferromagnetic metallic (FMM)/ferromagnetic insulating (FMI) phase boundary. Ti^{4+} substitution significantly reduces the ferromagnetic and insulator–metal transition temperatures and broadens their evolution. This results in weak temperature dependence of the MR across the M–I transition with a variation of only about 0.5%. Thus, the route adopted is well suited for overcoming one of the major limitations of using colossal magnetoresistive manganites as magnetosensitive devices.

Keywords: Manganites; Collosal magnetoresistance

1. Introduction

The phenomenon of colossal magnetoresistance (CMR) when it was discovered in doped manganites $A_{1-x}B_xMnO_3$ ($A = La^{3+}$, Nd^{3+}, Pr^{3+} and $B = Ca^{2+}$, Ba^{2+}, Sr^{2+}) in 1993 [1] held great promise for making sensitive magnetic devices and enhanced magnetic storage. However, the intense research activity that followed has led to widespread agreement that the CMR arises as a result of competing phases and the ensuing intrinsic nano-microscale inhomogeneity [2]. While this has unearthed a fertile area of basic research, it seems to have dissuaded applied researchers. The present report is an account of our ongoing efforts to manipulate the competing phases and inhomogeneity to extract desirable device-worthy features.

An important criterion for making a magnetosensitive device is that the observed MR should not vary appreciably with temperature over the range of 'room temperatures' observed around the globe. Since the MR in manganites exhibits a peak across the concomitant paramagnetic–ferromagnetic and insulator–metal transitions, it is a strong function of temperature. To the best of our knowledge, there is only one report that has addressed the problem of broadening the temperature dependence of MR by using a heterostructure of fused polycrystalline samples of $(La_{1-y}Pr_y)_{0.7}Ca_{0.3}MnO_3$ [3].

We report preliminary results of magnetotransport and magnetic susceptibility studies on TiO_2: $La_{0.875}Sr_{0.185}MnO_3$ mixtures in an attempt to address this issue. $La_{0.815}Sr_{0.185}MnO_3$ was chosen because of its proximity to the ferromagnetic metal (FMM)–ferromagnetic insulator (FMI) phase boundary (making it susceptible to disorder induced phase competition) in the phase diagram but with a high Curie temperature (294 K).

2. Experiment

Polycrystalline $La_{0.815}Sr_{0.185}MnO_3$ (LSMO185) samples were prepared by conventional solid-state reaction route. The powder obtained was mixed with TiO_2 in the mole ratio of 1: x where $x = 0$, 0.01, 0.03 and pressed into pellets and sintered again in air at 1100 °C for 3–4 h. AC susceptibility measurements were performed using a Sumitomo AC susceptometer (Sumitomo Heavy Electric Co., Japan). Magnetotransport measurements using the four probe method in a 1 T electromagnet.

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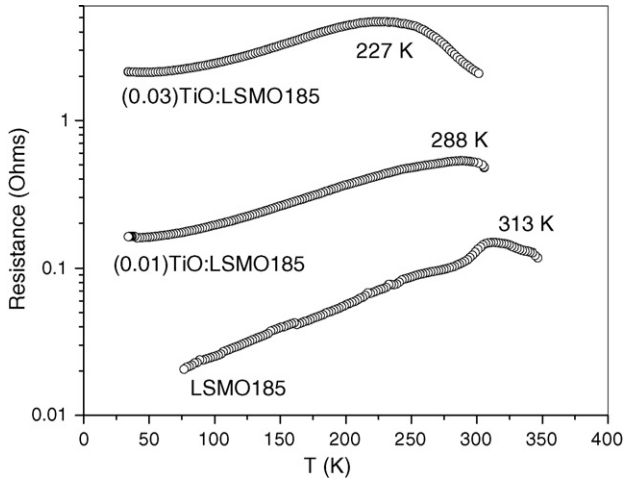

Fig. 1. Temperature variation of resistance for TiO:LSMO185 mixtures. The temperature at which $dR/dT = 0$ is taken as the metal–insulator transition temperature.

3. Results and discussion

The temperature dependence of resistance for the three samples ($x = 0$, 0.01 and 0.03) is shown in Fig. 1. It is seen that the resistivity peak observed at 313 K for LSMO185 decreases to 288 K for ($x = 0.01$)TiO:LSMO185 sample and to 227 K for the (0.03)TiO:LSMO185 sample. The temperature dependence of the AC susceptibility for the three samples is shown in Fig. 2. The paramagnetic–ferromagnetic transition temperature (T_C) decreases from 294 K for LSMO185 to 263 and 234 K for (0.01)TiO:LSMO185 and (0.03)TiO:LSMO185 samples, respectively. The decrease in both the paramagnetic–ferromagnetic and insulator–metal transitions with increase in TiO_2 content suggest that Ti^{4+} ions with a $3d^0$ configuration replaces Mn^{4+} ions diminishing the strength of the double exchange interaction between Mn^{3+} and Mn^{4+} in LSMO widely accepted to be responsible for coexistence of ferromagnetism and metallicity in manganites [4]. A significant

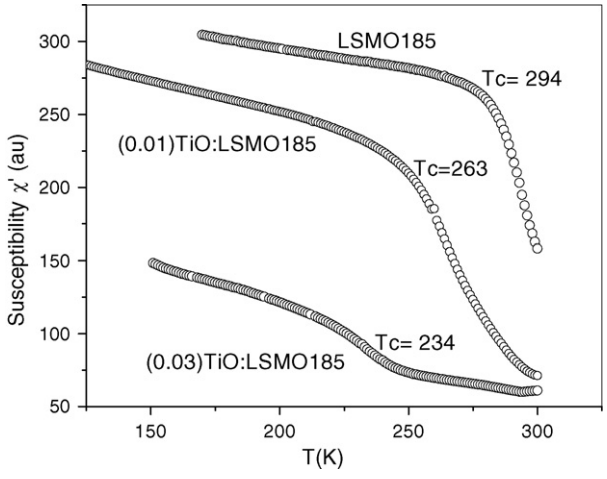

Fig. 2. Temperature dependence of AC susceptibility for the TiO:LSMO185 mixtures. The temperature corresponding to the minimum of $d\chi/dT$ is taken as the Curie temperature.

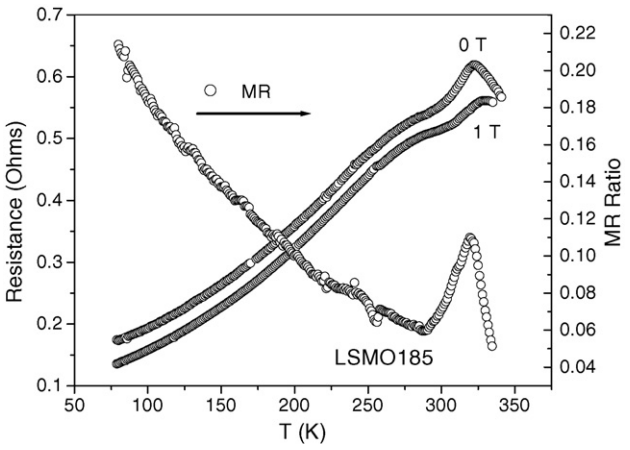

Fig. 3. Temperature dependence of resistance in applied fields of zero and 1 T and magnetoresistance for LSMO185.

decrease in transition temperatures is observed only for a small addition of TiO_2. In order to understand this, we consider the fascinating phase diagram of $La_xSr_{1-x}MnO_3$ [5]. The phase diagram is especially complex for $x < 0.2$ where ferromagnetic metallic, ferromagnetic insulating (FMI) and antiferromagnetic insulating phases are observed. Ti^{4+} substitution in LSMO185 results in an effective decrease of 'x' (equivalent to the Mn^{4+} concentration) pushing it closer to the FMM/FMI phase boundary of $x \sim 0.17$. The sensitivity of phase transitions towards Ti^{4+} substitution is attributed to the resulting competition between FMM and FMI. This can be inferred from broadening of the magnetic and metal–insulator transition in the Ti-substituted samples (Figs. 1 and 2).

The magnetoresistance (MR) for LSMO185, the (0.01)TiO:LSMO185 and (0.03)TiO:LSMO185 samples are shown in Figs. 3–5. The striking feature of these plots is that while MR for LSMO185 exhibits a prominent peak across the M–I transition, the MR for the Ti-substituted samples is significantly broad over an extended temperature region about the resistivity peak. At low temperatures, the MR increases upon cooling for all samples. This is a typical feature of

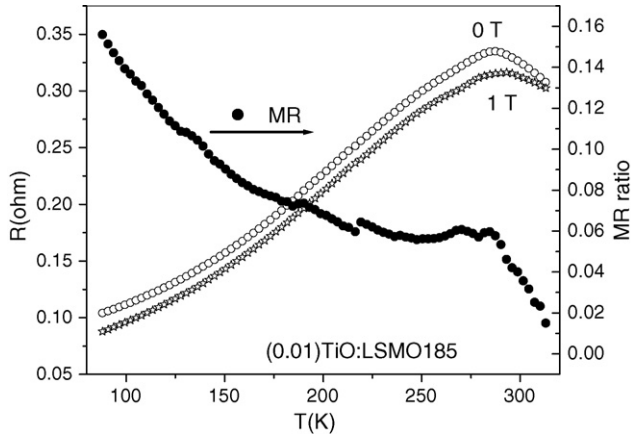

Fig. 4. Temperature dependence of resistance in applied fields of zero and 1 T and magnetoresistance for (0.01)TiO:LSMO185.

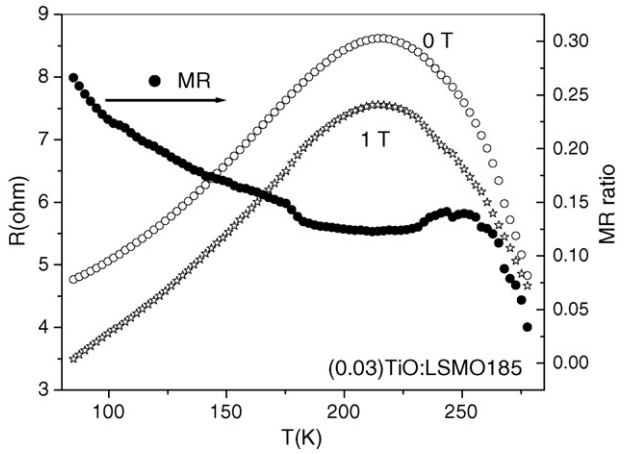

Fig. 5. Temperature dependence of resistance in applied fields of zero and 1 T and magnetoresistance for (0.03)TiO:LSMO185.

polycrystalline samples and arises as a result of spin-polarized tunneling across grain boundaries [6].

The (0.01)TiO:LSMO185 sample exhibits an average MR (defined as $[R(0) - R(H)]/R(0)$) of 5.7% (in a field of 1 T) over a temperature range 239–277 K with only a variation of less than 0.5 %. The corresponding values for the (0.03)TiO:LSMO185 sample are 12.6% (in a field of 1 T; 185–233 K) with a variation of less than 0.5%.

A previous attempt to broaden the MR [3] resulted in an average MR of about 46% (or 85% using $MR = [R(0) - R(H)]/R(H)$ as in Ref. [3]) in a field of 3 T between 230 and 280 K with a variation of about 7%. Thus, the present work is a significant improvement in broadening the temperature dependence of the magnetoresistance.

In order to obtain an insight into the origin of the broadened magnetoresistance, we prepared another sample with higher TiO_2 concentration ($x = 0.16$). The temperature dependence of AC susceptibility and resistance is shown in Fig. 6. It is clear that (0.16)TiO:LSMO185 is a ferromagnetic insulator. The low temperature ferromagnetic state is complex and requires further study to understand the nature of magnetism better.

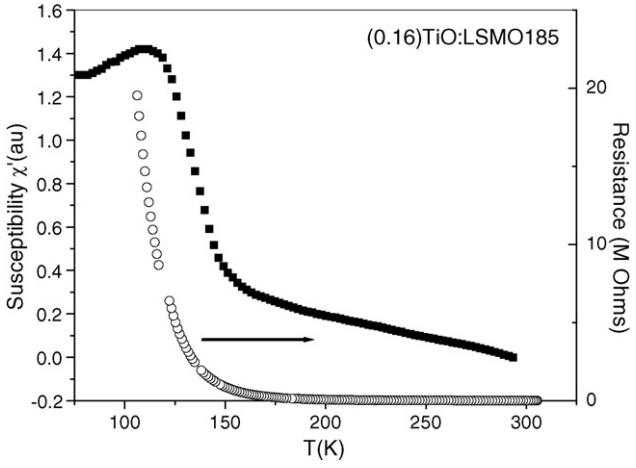

Fig. 6. Temperature dependence of AC susceptibility and resistance for (0.16)TiO:LSMO185.

However, it is clear that Ti^{4+} substitution drives LSMO185 towards the FMI/FMM phase boundary. The presence of random Mn^{3+}, Mn^{4+} and Ti^{4+} charge densities in the lattice may result in the tendency to form FMM and FMI phases. Such a disorder induced phase competition can be intuitively modeled [2] by using a random field Ising model (RFIM) with a Hamiltonian defined as $H = -J\sum_{\langle ij\rangle} S_i^z S_j^z - \sum_i h_i S_i^z$ where $S_i^z = +1$ or -1 is an Ising variable, representative of the competing FMI and FMM phases near a first order transition. Disorder manifests itself as a local tendency to prefer one of the two states and is represented by a random field, viz. h_i, the direction in which the variables S_i^z arrange themselves.

Monte Carlo simulations have shown [7] that in the presence of disorder clusters of both states coexist above and below the M–I transition. With increase in disorder, it is energetically favourable for the competing phases to form smaller clusters and the M–I transition arises as a result of a percolation of metallic clusters. A large low temperature resistivity nearly comparable to that in the insulating state at room temperature and a broad M–I and paramagnetic–ferromagnetic transitions are some typical characteristics of percolative tendencies. From Figs. 1 and 2, it is seen that the ideas of disorder-driven percolative transport within a RFIM model may be applied to the present situation. Simulations using this model [7] show that when an external magnetic field is applied there is a percolation among disconnected clusters and the metallic regions grow in size at the expense of the insulating regions resulting in a decrease in resistivity. In the absence of disorder, the M–I transition is sharp coinciding with the onset of spontaneous magnetization and in the presence of a magnetic field, the resistivity peak exhibits a prominent shift towards higher temperatures due to the suppression of spin fluctuations. This results in a prominent peak in the MR as seen for LSMO185 (Fig. 3). With increase in disorder, the M–I transition is extended over a large temperature region well below the magnetic transition [8]. For such a case, the M–I transition in the presence of magnetic fields is also broad and the resistivity peak may not shift significantly to higher temperatures at least for small fields as seen for (0.03)TiO:LSMO185 (Fig. 5). We suggest that this is the origin of the broadened temperature dependence of magnetoresistance in TiO:LSMO185 arising from competing FMM and FMI clusters.

We have shown that a small amount of Ti substitution in a FMM manganite close to the FMI phase boundary can be used to tune magnetotransport properties and broaden the temperature dependence of MR. In order to realize a device with nearly temperature independent MR, one will have to grow novel FMM/FMI heterostructures that will exploit the phase competition outlined in this study.

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