BRIEF COMMUNICATION

Giant Magnetoresistance in Self-Doped La$_{1-x}$MnO$_{3-\delta}$ Thin Films[1]

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Highly textured La$_{0.7}$MnO$_{3-\delta}$ films were grown on LaAlO$_3$ ⟨100⟩ substrates for the first time. The films showed a metal–insulator transition at 220 K and exhibited giant magnetoresistance with $\Delta R/R_0 = 85\%$ and $\Delta R/R_H > 550\%$. This study demonstrates that the La$_{1-x}$MnO$_{3-\delta}$ films are unique among the other La$_{1-x}$M$_x$MnO$_3$ (M = Ca, Ba, and Pb) thin films showing giant magnetoresistance by virtue of being a self-doped system. © 1995 Academic Press, Inc.

Giant magnetoresistance effects (GMR) in multilayer superlattice thin films containing ferromagnetic layers separated by nonmagnetic layers have generated considerable interest in magnetic layered materials due to their potential use as the sensor element in a magnetoresistive "read" head for information storage systems (1–3). Although magnetoresistance (MR) was observed earlier in Ti$_2$O$_3$ (4) and La$_{1-x}$Pb$_x$MnO$_3$ (5) single crystals, Baibich et al. (1) were the first to report GMR in (Fe/Cr)n multilayer thin films. Subsequently, GMR in oxide systems such as Nd$_{0.5}$Pb$_{0.5}$MnO$_3$ (NPMO) (6) single crystals, in thin films of La$_{0.66}$Ba$_{0.34}$MnO$_3$ (LBMO) (7), La$_{0.72}$Ca$_{0.28}$MnO$_3$ (LCMO) (8), La$_{0.6}$Pb$_{0.4}$MnO$_3$ (LPMO) (9), La$_{1-x}$Sr$_x$MnO$_3$ (10), and in bulk La$_{1-x}$Sr(Ca)$_x$MnO$_3$ systems (11) were reported. A recent report by Jin et al. (12) generated further interest in LCMO films which show a decrease of over 97% in $\Delta R/R_0$. The reason for such colossal GMR is attributed to the ferromagnetic ordering of Mn–O$_2$ layers in the crystallographic a–b planes, separated by nonmagnetic La–(Ca)–O layers, and to antiferro-

magnetic ordering along the c-axis. The presence of mixed valence in Mn (Mn^{3+} and Mn^{4+}) is responsible for the occurrence of both ferromagnetism and metallic conductivity.

Tofield and Scott (13) have compared the oxygen nonstoichiometry of the parent LaMnO$_{3+\delta}$ with that of other perovskite oxides, LaMO$_3$, where M = V, Cr, Fe, and Co. Their study indicated that LaMnO$_{3+\delta}$ is apparently the only system in the lanthanum transition metal perovskites which exhibits a wide range of oxidative nonstoichiometry. The neutron diffraction study of LaMnO$_{3+\delta}$ indicated that any increase in oxygen content over 3.0 results in the oxidation of LaMnO$_3$ to a defect perovskite and in a partial elimination of La$_2$O$_3$, leaving vacancies principally on the lanthanum sites, as per the schematic equation:

$$\text{LaMnO}_{3.12} \rightarrow 0.02\text{La}_2\text{O}_3 + \text{La}_{0.96}\text{MnO}_3. \qquad [1]$$
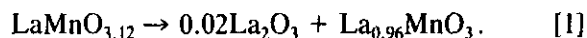
Although studies on the bulk LaMnO$_{3+\delta}$ (14) show magnetic ordering at temperatures as high as 250 K, it is not clear in any of these studies how the extra oxygen is accommodated in the perovskite-related structure. However, LaMnO$_{3+\delta}$ decomposing into La$_{1-x}$MnO$_3$ and La$_2$O$_3$ as in Eq. [1] leads to partial oxidation of Mn^{3+} and Mn^{4+}, which is equivalent to La$_{1-x}$M$_x$MnO$_3$ (M, divalent ion) oxides so far as the idea of doping is concerned. It is noteworthy that Goodenough (15) has reported ferromagnetic ordering and an M–I transition in both La$_{1-x}$MnO$_3$ and La$_{1-x}$M$_x$MnO$_3$, where the Curie temperature, T_c, varies from 166 K for La$_{1-x}$MnO$_3$ to 270 K $< T_c <$ 375 K in the La$_{1-x}$M$_x$MnO$_3$ systems (M, divalent ion).

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It was in this context that we thought it is interesting to study the $La_{1-x}MnO_3$ system in bulk as well as thin film forms. In this report we document a metal–insulator transition in the self-doped $La_{1-x}MnO_{3-\delta}$ system in the bulk solid. We also report, for the first time, thin films of self-doped $La_{1-x}MnO_{3-\delta}$ showing a GMR of 85% for $\Delta R/R_0$ and of over 550% for $\Delta R/R_H$ where R_0 and R_H are the resistances in zero-field and in an applied field.

The bulk sample of nominal composition $La_{0.7}MnO_3$ was prepared by the ceramic method. The component oxides La_2O_3 and $MnCO_3$ were mixed in stoichiometric amounts and ground in alcohol. The powder was dried, reground, and heated at 1050°C for 24 hr. Shown in Fig. 1 (curve a) is the X-ray diffraction pattern of the bulk solid recorded using a JEOL-JDX 8p powder diffractometer with Cu$\kappa\alpha$ radiation. The compound crystallizes in the rhombohedral structure, which can be indexed for a hexagonal unit cell with $a = 5.514(4)$ Å and $c = 13.319(2)$ Å. The lattice parameters agree well with recent powder X-ray and neutron diffraction studies (16) for $La_{1-x}MnO_{3-\delta}$ ($x = 0.15$). All the lines in the X-ray pattern could be indexed to the $La_{1-x}MnO_{3-\delta}$ phase, except for a weak line (at $2\theta = 36.2°$) corresponding to Mn_3O_4, which, from relative intensities, was estimated to be about 4% in abundance. The total oxygen estimation was carried out by iodometric titration. By taking into account the amount of Mn_3O_4 present in the sample the chemical analysis leads to the composition $La_{0.76}MnO_{2.73}$. The corresponding charge distribution of the cations in the oxide
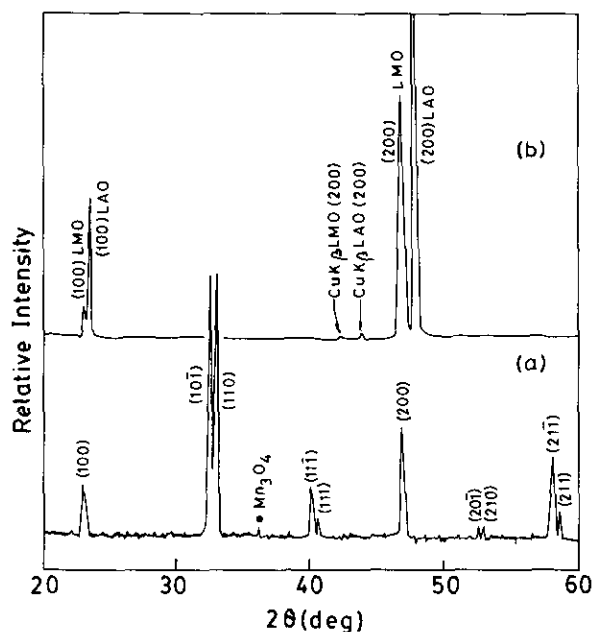

FIG. 1. X-ray diffraction pattern of (a) a polycrystalline sample of $La_{0.76}MnO_{2.73}$ (LMO) without Ag addition and (b) an as-deposited LMO thin film on LaAlO$_3$ substrate without the addition of Ag. XRD pattern of LMO film with Ag addition was identical to curve b.
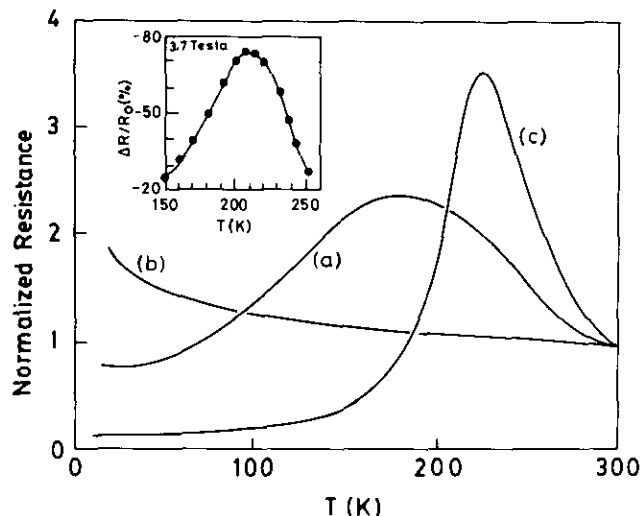

FIG. 2. R versus T plot of the (a) LMO polycrystalline sample without the addition of Ag (b, c) LMO thin film without and with the addition of Ag, respectively. Inset shows the plot of MR ratio versus temperature at 3.7 T.

can be represented by $La_{0.76}^{3+} Mn_{0.82}^{3+} Mn_{0.18}^{4+} O_{2.73}$, which clearly shows 18% of Mn to be in the tetravalent state.

The resistance versus temperature (R vs T) curve of the bulk sample is shown in Fig. 2 (curve a). The room temperature resistivity, ρ, of the bulk sample was 6 mΩ cm. The compound exhibits a clear maximum at 180 K. Magnetic susceptibility measurements confirmed the ferromagnetic ordering at the peak, which is often considered to be indicative of an M–I transition. Such behavior is in line with alkaline-earth-metal-doped LaMnO$_3$ systems (15). This implies that partial conversion of Mn^{3+} to Mn^{4+} is caused by vacancies at the lanthanum and oxygen sites; thus, this compound represents a self-doped system.

The observation of an M–I transition with ferromagnetic ordering in bulk, $La_{0.76}MnO_{2.73}$ (LMO), prompted our efforts to fabricate thin films by pulsed laser deposition. A bulk LMO sample was used as the target for the deposition of LMO films on LaAlO$_3$ (100) substrates by the laser deposition technique, employing a KrF excimer laser ($\lambda = 248$ nm, reprate = 5 Hz) with a pulse energy density of 1.8 J/cm^2 (of 350 mJ). The substrate temperature was maintained at 720°C, with an O$_2$ pressure of about 550 mTorr during the deposition. The films were cooled under 300 Torr of oxygen after the deposition.

The LMO films were $\approx$2500 Å in thickness. The X-ray diffraction study of the film shows a highly textured growth of the LMO film on the LaAlO$_3$ substrates, as shown in Fig. 1 (curve b). Reflections corresponding to (100) and (200) lines of LMO were observed, along with corresponding LaAlO$_3$ peaks, indicating that the growth is cubic with the lattice parameter $a = 3.86$ Å, close to the pseudo cubic "a" parameter of bulk LMO.

Although the R vs T plot for the bulk LMO target showed a peak at 180 K (Fig. 2, curve a), the as-deposited film of this composition exhibited weak semiconducting behavior (Fig. 2, curve b) down to 15 K. This discrepancy may be associated with the inadequate oxidation of Mn^{3+} to Mn^{4+} ions in the films, due to oxygen deficiency during deposition. The oxygen deficiency in the films, in turn, is caused by the dominance of O_2-outdiffusion over O_2-indiffusion during growth of these films at elevated temperature (720°C). To promote O_2-indiffusion, 5% Ag_2O was added to the bulk LMO target and sintered at 800° for 24 hr. This target was used for the thin film deposition. The powder XRD pattern of the Ag added LMO target was found to be similar to bulk LMO without Ag. Transmission electron microscopy showed the presence of Ag metal in $La_{1-x}MnO_3$. During the ablation of the Ag-metal-containing target, the silver becomes oxidized to AgO; during film growth the AgO dissociates, yielding its oxygen to the LMO film. It is noteworthy that addition of Ag_2O to bulk $YBa_2Cu_3O_{7-x}$ (YBCO) increases the oxygen content in the YBCO film (17).

It was gratifying that the LMO film containing Ag indeed showed the same metal–insulator behavior as that of the bulk sample (curve c in Fig. 2). The inset of Fig. 2 shows the variation of MR ratio with temperature at a magnetic field of 3.7 T. The maximum at 210 K indicates ferromagnetic ordering which lies to the left of the M–I transition temperature, as observed by Jin et al. (12) for the LCMO thin films.

Magnetoresistance measurements were carried out using a superconducting magnet with a maximum applied field of 6 T, in both the parallel and perpendicular directions to the film surface. The GMR values of the LMO film measured in both directions to the applied magnetic field were of the same magnitude, indicating that the system is nearly isotropic. Shown in Fig. 3 are the MR curves with the magnetic field perpendicular to the film. The most striking feature is the magnitude of the $\Delta R/R_0$ ratio, which is 85% of GMR at 210 K, while $\Delta R/R_H = 550\%$, as shown in the inset of Fig. 3. This value for the as-deposited LMO films is quite significant as compared with the recent report on LCMO systems, where $\Delta R/R_0$ is reported to be 97% at 77 K. From our studies, it is clear that the phase giving rise to magnetic ordering both in bulk and in film is $La_{1-x}MnO_{3-\delta}$, with an estimated lanthanum and oxygen defect concentration of $x = 0.24$ and $\delta = 0.27$, respectively. This suggests that it is the vacancies in lanthanum and oxygen sites that cause such a large change in resistance.

In summary, we have presented the first observation of an M–I transition and ferromagnetic ordering in the bulk, and the fabrication of self-doped LMO thin films on $LaAlO_3$ substrate showing GMR $= 85\%$ in the as-deposited films. The observation of such large magnitude of GMR in the self-doped LMO films is attributed to lanthanum and oxygen vacancies.

ACKNOWLEDGMENTS

FIG. 3. Plot of magnetoresistance ratio versus magnetic field at different temperatures. Inset shows a plot of $\Delta R/R_H$ versus magnetic field.

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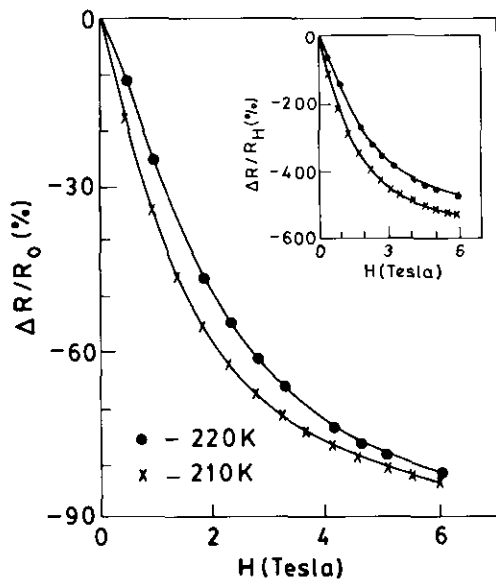13. B. C. Tofield and W. R. Scott, *J. Solid State Chem.* **10**, 183 (1974).

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