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Colossal Magnetoresistance in Potassium Doped Lanthanum Manganite: A Comparative Study of Polycrystalline Solid and Thin Film

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Electrical and magnetic properties of $La_{0.82}K_{0.08}MnO_{3-\delta}$, both in polycrystalline and thin film forms, have been examined in the temperature range 1.2 to 300 K. Near the insulator-to-metal transition temperature of 260 K, the magnetoresistance values were higher for the thin film ($\sim$70%) compared to the polycrystalline sample ($\sim$35%). No magnetoresistance was observed in the thin film at low temperature. A low field magnetoresistance of 30% was observed in the temperature range 1.2–10 K in the polycrystalline sample which can be attributed to the spin dependent scattering of conduction electrons at the grain boundaries.

1. INTRODUCTION

Jonker and van Santen (1) first reported the magnetic and electrical properties of mixed valent lanthanum manganites. They found that pure $LaMnO_3$ is an antiferromagnetic insulator, but $La_{1-x}A_xMnO_3$ ($A = Ca^{2+}$, Sr^{2+}, Ba^{2+}) shows ferromagnetic and metallic behavior for $0 < x \leq 0.4$. Zener (2) proposed "the double exchange" mechanism of magnetic interaction to account for this correlation between ferromagnetic and metallic character. A large decrease in resistance near the insulator-to-metal transition temperature on the application of a magnetic field, now known as colossal magnetoresistance (CMR), was observed in $La_{(1-x)}Pb_xMnO_3$ ($0.25 \leq x \leq 0.4$) (3) and $Nd_{0.5}Pb_{0.5}MnO_3$ single crystals (4). Interest in this subject was revived after the observation of CMR in $La_{0.67}Ba_{0.33}MnO_3$ thin films (5) and subsequent studies on Ca, Sr, and Pb doped lanthanum manganite thin films and single crystals (6–11). Extensive studies on synthesis, crystal chemistry, and magnetic and CMR properties have been carried out by Rao *et al.* (12, 13) and Raveau *et al.* (14). The effects of nonstoichiometry on the crystal structure, transport, and magnetic properties have been studied in $La_{(1-y)}MnO_3$ and $LaMn_{(1-z)}O_3$ perovskites (15). Relatively less attention has been paid to the monovalent ion substituted lanthanum manganites, such as $La_{(1-x)}A_xMnO_3$ (A = Na, K, or Rb). These materials also show magnetic and electrical properties similar to those shown by divalent ion doped lanthanum manganites (16–19). It has been shown that perovskite superstructures like $ALaMn_2O_{6-y}$ (A = K, Rb) are also ferromagnetic conductors similar to the CMR manganites (20). CMR was observed in $La_{0.82}Na_{0.13}MnO_{3-\delta}$ (21) and $La_{(1-x)}K_xMnO_3$ ($x = 0.14$ and 0.2) (22) thin films deposited by pulsed laser deposition (PLD) and electron-beam/thermal coevaporation techniques, respectively. In this paper, for the first time we report a detailed study on the electrical resistivity, magnetic susceptibility, and magnetoresistance properties of a polycrystalline $La_{0.82}K_{0.08}MnO_{3-\delta}$ sample and compare them with thin film deposited by the PLD technique.

2. EXPERIMENTAL

Polycrystalline $La_{0.82}K_{0.08}MnO_{3-\delta}$ was synthesized by the KCl flux method. La_2O_3, $MnCO_3$, and KCl were taken in a high alumina crucible in the molar ratio 0.7:1:16. The mixture was thoroughly ground and heated at 900°C for 24 h and cooled to room temperature. The flux was washed with hot water until the filtrate was free from K^+ and Cl^- ions. The powder was dried, pelletized, and sintered at 1000°C. The chemical composition of the polycrystalline powder was obtained by quantitative analysis of individual ions by independent analytical methods. The lanthanum

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content was estimated by potentiometric titration using a fluoride electrode. The total manganese was estimated by reducing Mn^{3+} and Mn^{4+} by hydrogen peroxide in sulfuric acid and then titrating it against potassium permanganate potentiometrically. Inductively coupled plasma (ICP) emission spectroscopy was employed to estimate the potassium ion concentration. From the known concentrations of La, K, and Mn by these methods, the oxygen content was obtained by iodometric titration. Details of the chemical analysis, chemical composition, and structure of a series of potassium doped lanthanum manganites have been reported in Ref. (19).

The thin films (≈ 2000 Å) of $La_{0.82}K_{0.08}MnO_{3-\delta}$ (LKMO) were grown on 8×4 mm $LaAlO_3$ (100) (LAO) substrates using a KrF excimer laser ($\lambda = 248$ nm, energy density = 1.8 J/cm^2, and pulse rate 5 Hz). During the deposition, the substrate temperature and oxygen partial pressure was maintained at 725°C and 450 mtorr, respectively. The films were *in-situ* annealed at 700°C for 2 h in oxygen (~ 700 mtorr) and then cooled down to room temperature. The presence of potassium ions in the thin film was confirmed by energy dispersive X-ray (EDX) analysis. However, the exact chemical composition of the film could not be obtained from EDX due to the presence of lanthanum ions in the $LaAlO_3$ substrate. However, the potassium to manganese intensity ratio in the film was about the same as that of the polycrystalline sample. The polycrystalline powder as well as the thin film were characterized by an X-ray diffraction technique using Cu$K\alpha$ radiation. Magnetic susceptibility measurements were carried out with a Lewis coil force magnetometer. The magnetoresistance measurements down to 1.2 K were carried out with a dc four-point probe technique.

3. RESULTS AND DISCUSSION

The composition of the polycrystalline powder estimated by the chemical analysis was $La_{0.82}K_{0.08}MnO_{2.89}$ with 24% of Mn in +4 oxidation state. The X-ray diffraction pattern of polycrystalline $La_{0.82}K_{0.08}MnO_{2.89}$ powder is shown in Fig. 1 (curve a). No impurity peaks were observed in the powder diffraction pattern. The compound crystallizes in a rhombohedral structure with the lattice parameter $a = 5.46(5)$ Å and $\alpha = 60^\circ\ 61(4)'$. Figure 1 (curve b) shows an X-ray diffraction pattern of a LKMO thin film. The sharp (100), (200), and (300) peaks observed here indicated that the film is highly oriented in the (100) direction. In films, the crystal structure is usually referred to as psuedocubic, characterized by a single lattice parameter a'. The lattice parameter a' of the LKMO film is 3.866(6) Å. However, a small rotation of the MnO_6 octahedra may lead to orthorhombic or rhombohedral distortions in the thin film, which cannot be detected by a θ–2θ scan due to the oriented nature of the film.

Magnetization plotted as a function of temperature for both the polycrystalline and the thin film $La_{0.82}K_{0.08}MnO_{3-\delta}$ is shown in Fig. 2. The polycrystalline sample shows a paramagnetic to ferromagnetic transition (T_C) around 300 K, whereas the thin film shows the transition at a lower temperature (~ 275 K). The *as-deposited* films showed the transition at a much lower temperature (around 200 K). This indicates that the film is oxygen deficient

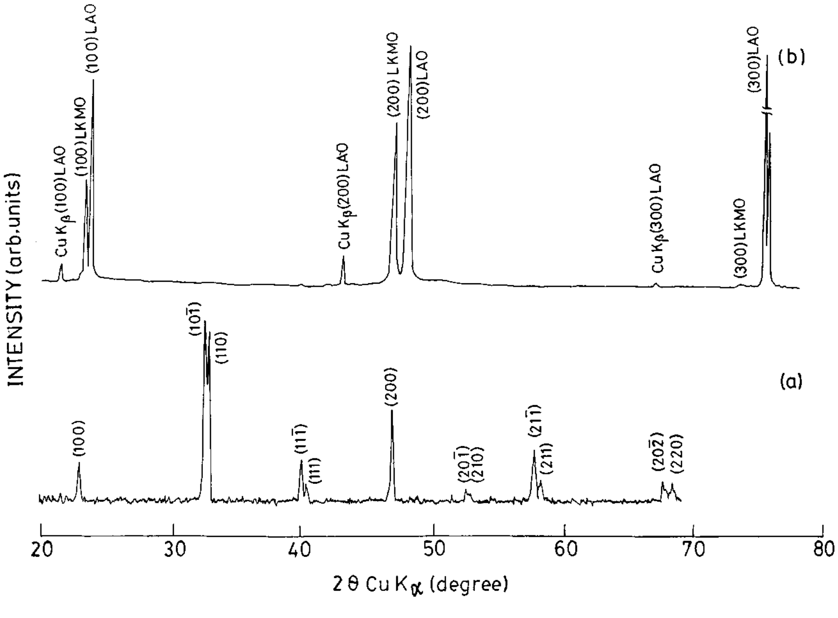

FIG. 1. The X-ray diffraction pattern of $La_{0.82}K_{0.08}MnO_{3-\delta}$ (a) polycrystalline powder and (b) thin film.

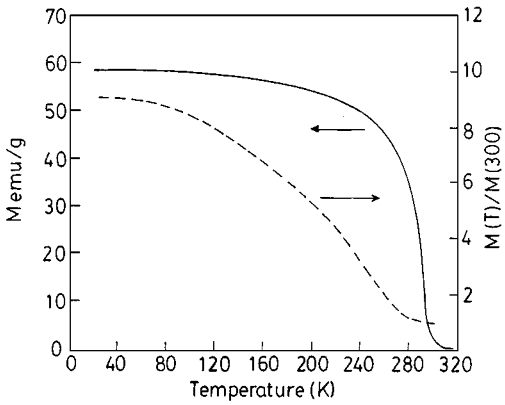

FIG. 2. Magnetization as a function of temperature for $La_{0.82}K_{0.08}MnO_{3-\delta}$ polycrystalline powder (continuous line) and thin film (hatched line) measured in an excitation field of 1 kOe and 600 Oe, respectively.

compared to the polycrystalline sample. On *in-situ* oxygen annealing, the T_C was enhanced from 200 to 275 K. Further oxygen annealing of the thin film sample did not increase the T_C.

Resistivity of the polycrystalline $La_{0.82}K_{0.08}MnO_{3-\delta}$ sample as a function of temperature with and without an applied magnetic field is shown in Fig. 3. There is an insulator-to-metal transition at around 260 K. A large decrease in resistance and a shift in peak resistance toward the higher temperature have been observed on application of 6 T magnetic field. The magnetoresistance here is defined as $\Delta R/R(0) = 100[(R(H) - R(0))/R(0)]$, where $R(0)$ is the resistance at zero field and $R(H)$ is the resistance at an applied magnetic field H. The magnetoresistance as a function of temperature is also shown in Fig. 3. A negative magnetoresistance of 40 and 45% is observed near the insulator-to-metal transition temperature (260 K) and at low temperatures ($T \leq 10$ K), respectively. In Fig. 4, the magnetoresistance as a function of the magnetic field at different temperatures is given for the polycrystalline $La_{0.82}K_{0.08}MnO_{3-\delta}$ sample. It is clear from Fig. 4 that at low temperature resistance drops sharply as a function of the magnetic field. The drop is highest at lowest temperature (1.2–10 K) and decreases with increasing temperature. The magnetoresistances in the polycrystalline sample at high and low temperature are of different origin. Intrinsic negative MR at the insulator-to-metal transition temperature is due to the suppression of spin fluctuations under a large magnetic field. Extrinsic negative MR at low temperatures (< 100 K) is due to the spin dependent scattering of the electrons at the grain boundaries. The conduction electrons are almost completely polarized inside a single magnetic domain; electrons are easily transferred between Mn^{3+} and Mn^{4+} through O^{2-} ions. When these electrons move across the grains, strong spin dependent scattering at the boundaries leads to a higher zero-field resistivity (23). Application of moderately low fields (~ 0.5 T) enhances the spin polarized tunneling between the grains, thereby decreasing the resistivity of the material. The extrinsic giant magnetoresistance has also been observed in CrO_2, a half-metallic ferromagnet at absolute zero (24).

The resistivity as a function of temperature for the thin films in the presence and absence of an applied magnetic field is given in Fig. 5. The MR as a function of temperature is also given in the same figure. It can be seen that no significant magnetoresistance is found at low temperature.

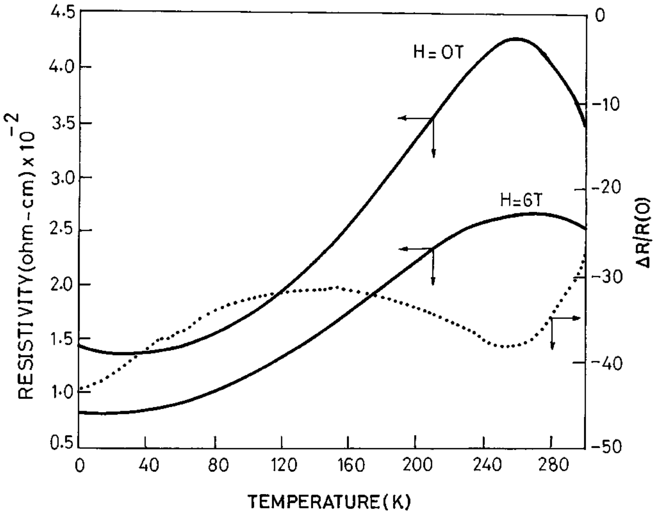

FIG. 3. Resistivity as a function of temperature for the polycrystalline $La_{0.82}K_{0.08}MnO_{3-\delta}$ pellet in the presence and absence of an applied magnetic field. The magnetoresistance (under a magnetic field of 6 T) as a function of temperature of the same sample is shown in dotted lines.

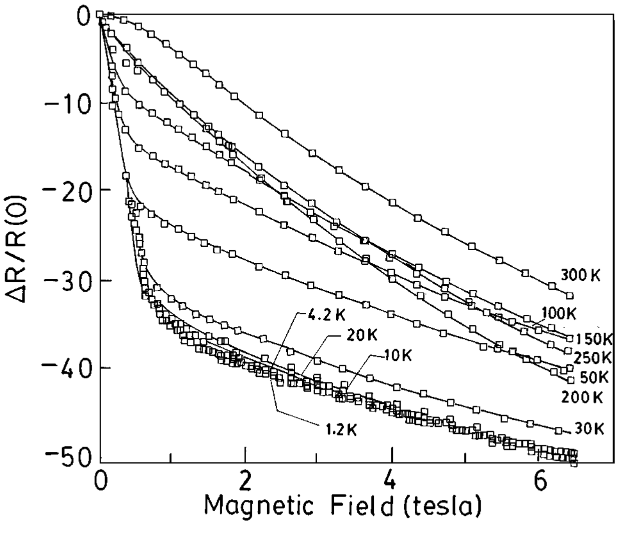

FIG. 4. Magnetoresistance as a function of magnetic field for a polycrystalline $La_{0.82}K_{0.08}MnO_{3-\delta}$ pellet at various temperatures.

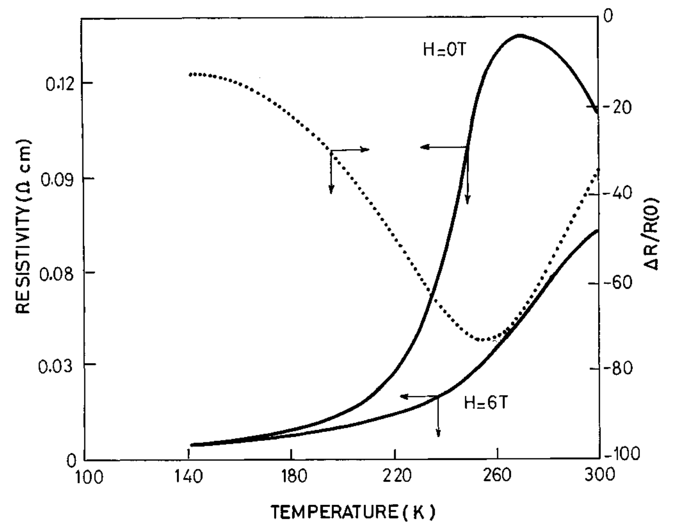

FIG. 5. Resistivity as a function of temperature for the $La_{0.82}K_{0.08}MnO_{3-\delta}$ thin film in the presence and absence of an applied magnetic field. The magnetoresistance (under a magnetic field of 6 T) as a function of temperature of the film is shown in dotted lines.

The extrinsic magnetoresistance originating from the spin dependent scattering of the electrons at the grain boundaries is absent in the thin film. The magnetoresistance as a function of the magnetic field at various temperatures is given in Fig. 6. A maximum negative magnetoresistance of 69% was observed near the insulator-to-metal transition. The MR decreases on either side of the transition temperature.

The results indicate that the transport and magnetic properties of the potassium doped lanthanum manganites are similar to those of the alkaline earth metal doped rare earth manganites. Since the valence state of potassium is $+1$, it oxidizes twice the amount of Mn^{3+} to Mn^{4+}. Therefore, a small amount of potassium doping in $LaMnO_3$ is sufficient for it to show properties such as insulator-to-metal transition, paramagnetic-to-ferromagnetic transition, and colossal magnetoresistance. La-site vacancy and oxygen deficiency also play a major role in the magnetic and transport properties of these materials. The oxygen deficiency is known to decrease T_C and enhance CMR (25, 26). Higher CMR of a LKMO thin film observed here compared to that reported by Chen *et al.* (22) may be due to the La-site vacancy and the oxygen deficiency.

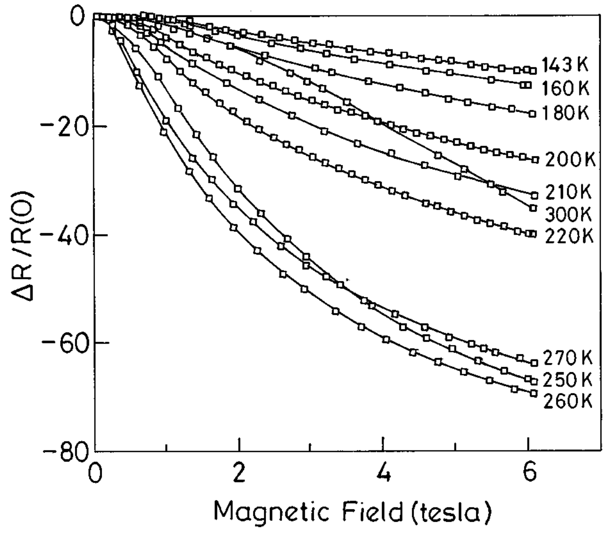

FIG. 6. Magnetoresistance as a function of magnetic field for a LKMO thin film at various temperatures.

4. CONCLUSION

A detailed study of the colossal magnetoresistance has been carried out on a potassium doped polycrystalline lanthanum manganite sample in the temperature range of 1.2 to 300 K for the first time. A large negative magnetoresistance of 30% was observed in the polycrystalline sample in the temperature range 1.2 to 10 K in a relatively low magnetic field of 0.5 T. The LKMO thin films were fabricated by the PLD technique. The magnetic field dependence of the resistance has been studied in detail. A magnetoresistance of ~70% was observed near the insulator-to-metal transition temperature in the film and no significant MR was observed at the low temperatures.

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