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Magnetic and magnetoresistance properties in rhombohedral $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ perovskite-type compounds

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Abstract. The effects of monovalent alkali metal substitution into the lanthanide sites in $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ oxides are presented. We report structural features, magnetic and electrical properties of these materials for $0.05 \leq x \leq 0.2$. The lattice symmetry of the samples is found to be rhombohedral. All the phases are ferromagnetic, with Curie temperatures strongly dependent on x , reaching a maximum around 308 K for $\text{La}_{0.8}\text{K}_{0.2}\text{MnO}_3$. A sharp drop of the resistivity is observed just below the Curie temperature. The ferromagnetic–metallic to paramagnetic–semiconducting transition is explained from the suggested distribution of the cations $(\text{La}_{1-x}^{3+}\text{K}_x^+)_{\text{A}}(\text{Mn}_{1-2x}^{3+}\text{Mn}_{2x}^{4+})_{\text{B}}\text{O}_3$ by the double exchange of Mn^{3+} – Mn^{4+} pairs at the B-sublattice. Preliminary magnetoresistance measurements (MR) on bulk ceramic samples display an MR effect of the same amplitude as in the case of the alkaline earth substituted La manganites.

1. Introduction

Perovskite-like compounds derived from LaMnO_3 by partial divalent ion substitution in La^{3+} sites have long been known [1]. Their electrical and magnetic properties has commanded considerable interest lately [2–8]. The study of their magnetotransport behaviour is of significance both for fundamental understanding of correlated electron systems and for potential device applications. Lanthanum ions may be replaced not only by divalent ions but also by others. Compounds substituted by monovalent alkali metals such as K^+ , Rb^+ , Na^+ were synthesized many years ago and tested as oxidation catalysts for exhaust gases for internal combustion engines [9]. Recently these compounds have given rise to some investigations as potential giant MR candidates [10–12]. However, there are only a few data on the magnetic and transport properties of materials with general composition $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ where $\text{A} = \text{K}, \text{Rb}, \text{Na}, \text{Ag}$. Since the valence state of the alkali metal ions is +1, substitution with these ions results in a mixed valence of Mn^{3+} ($t_{2g}^3 e_g^1$; $S = 2$) and Mn^{4+} ($t_{2g}^3 e_g^0$; $S = 3/2$) ions. Their interaction is the origin of the metallic and ferromagnetic properties of these compounds due to the double exchange mechanism effect [13, 14].

In this paper, we present first briefly the synthesis conditions of perovskite-type $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ ($0.05 \leq x \leq 0.2$) by the ceramic route. Then we report some MR observations from the results of both magnetization and resistivity measurements.

2. Experiment

Powder samples of $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ are prepared by the conventional solid state reaction technique. Manganese, potassium and lanthanum sources are respectively MnO_2 , K_2CO_3 and La_2O_3 (dried before use at 700°C). Presintered mixtures (at 1200°C) of stoichiometric MnO_2 and La_2O_3 powders are mixed with a large excess of K_2CO_3 powder and calcinated in air at 900°C for three hours. Cooled powders are frequently ground with ethanol in an agate mortar and pressed into a pellet shape. The pellets are sintered several times at 1000°C for few days. This temperature (1000°C) is high enough that a total evaporation of the excess K_2CO_3 not reacted is achieved. The sintered pellets are then slowly cooled (20°C h^{-1}) in air from 1000 to 700°C , with an additional step of few hours at 700°C .

X-ray powder diffraction data are collected at room temperature with a Siemens D5000 powder diffraction system using $\text{Cu K}\alpha$ radiation. This system is able to detect up to a minimum of 3% of impurities according to our measurements. High-purity silicon powder was used as an internal standard for the lattice parameter determination.

The magnetization was determined in the temperature range $4.2\text{--}320$ K by a vibrating sample magnetometer (VSM) and the electrical measurements have been performed by the standard four probe technique.

3. Results and discussion

3.1. X-ray analysis

Single phases of $\text{La}_{1-x}\text{K}_x\text{MnO}_3$, with no possible unreacted La_2O_3 , MnO_2 or K_2CO_3 materials, are obtained with a sintering temperature of 1000°C for a period of four days. Sample compositions are confirmed by microprobe analysis.

All diffraction lines are indexed in a hexagonal cell derived from a face centred cubic double cell $2a_p \times 2a_p \times 2a_p$ through a slight rhombohedral distortion (space group $R\bar{3}c$). Sample x-ray diffraction patterns showed a strong resemblance to the oxidized rhombohedral LaMnO_3 phase [11, 15, 16] and the $\text{La}_{0.74}\text{Pb}_{0.26}\text{MnO}_3$ phase [17].

A representative x-ray pattern of an $\text{La}_{0.8}\text{K}_{0.2}\text{MnO}_3$ sample with rhombohedral symmetry is displayed in figure 1.

The samples containing a large amount of potassium, corresponding to high $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio, required a rather long annealing period (up to 3 days) in air at 700°C . It is to be signaled that the exact amount of potassium entering the structure depends on the final annealing temperature ($<1000^\circ\text{C}$): the lower the annealing temperature, the higher the amount of potassium and the lower the amount of lanthanum in the dodecahedral sites of the perovskite phase. The lattice parameters (table 1), refined by the Rietveld method [18], do not change monotonically with potassium substitution. These parameters are expected to be dependent on the concentration of Mn^{4+} present in the compounds.

3.2. Magnetic characterizations

Magnetic measurements are carried out on powder samples which compositions have been confirmed by microprobe analysis.

$\text{La}_{1-x}\text{K}_x\text{MnO}_3$ phases ($x = 0.05; 0.10; 0.15$ and 0.20) present strong spontaneous magnetization at room temperature with a Curie point around $285\text{--}310$ K. Figure 2 shows the magnetization field dependence of an $\text{La}_{0.8}\text{K}_{0.2}\text{MnO}_3$ sample at different temperatures in a magnetic field up to 0.65 MA m^{-1} . For each temperature, M increases with increasing H .

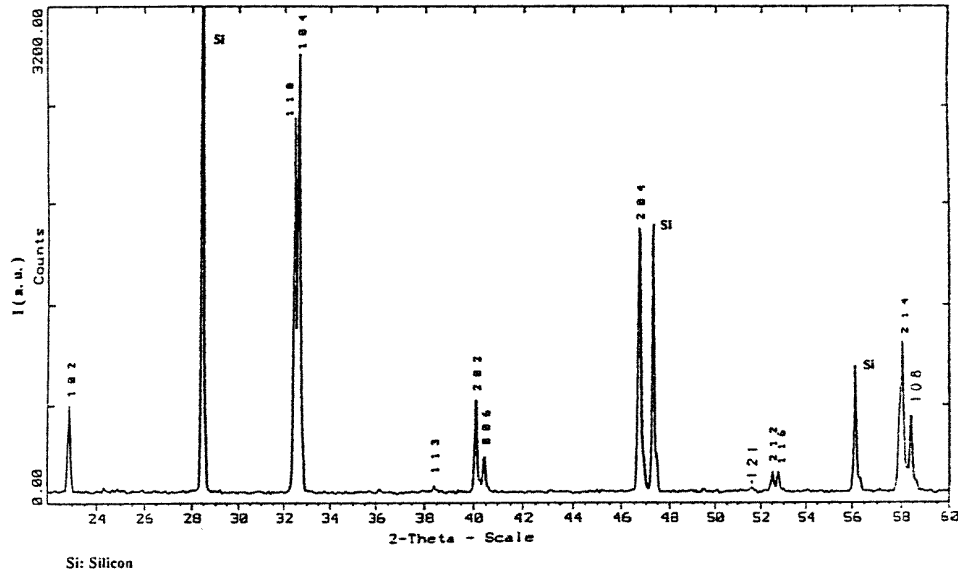


Figure 1. X-ray diffraction patterns of representative $La_{0.8}K_{0.2}MnO_3$ sample.

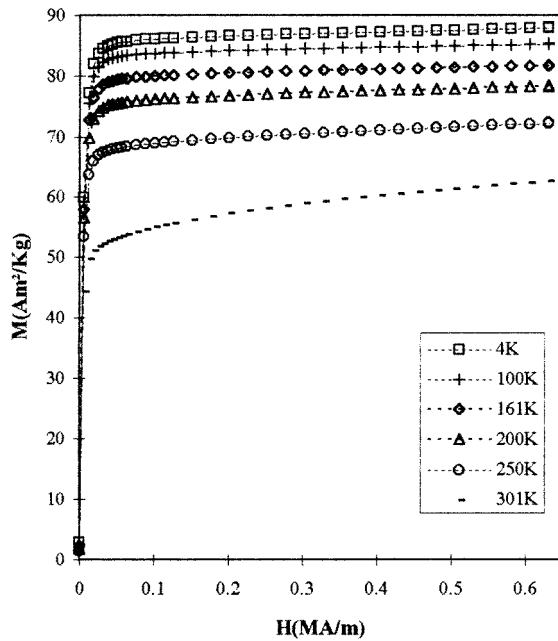


Figure 2. Magnetization curves versus the applied field for a sample of composition $La_{0.8}K_{0.2}MnO_3$.

At temperatures below 250 K, the $La_{0.8}K_{0.2}MnO_3$ sample is rapidly saturated at an applied field of about 40 kA m^{-1} ; while at 300 K the sample does not saturate totally even at an applied field up to 0.3 MA m^{-1} . The saturation magnetization increased when temperature

decreased. A maximum of $88 \text{ Am}^2 \text{ kg}^{-1}$ is observed at 4 K corresponding to an average value of $3.5 \mu_B/\text{Mn atom}$. Assuming fixed valences for La (3^+), K (1^+) and stoichiometric O (2^-), the calculated spin-only saturation magnetization for full alignment of the spins is $M_{stb} = 0.4 \times 3\mu_B + 0.6 \times 4\mu_B = 3.6\mu_B$ (using Mn^{3+} : $S = 4/2$ and Mn^{4+} : $S = 3/2$).

Figure 3 represents the variation of the spontaneous magnetization in the temperature range (5 K–320 K) under a magnetic field of 40 kA m^{-1} . At 5 K, the magnitude of magnetization is $3.5 \mu_B$, i.e. essentially identical to the saturation magnetization found above. The shape of the magnetization curve shows a homogenous granulometry composition. The temperature dependence of the magnetic moment per mole $M(T)$ may be described by the Brillouin–Weiss molecular field theory modelling the degree of spin collinearity.

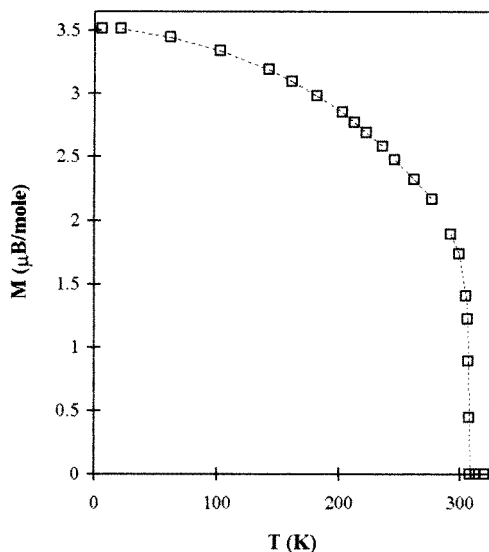


Figure 3. Variation of the spontaneous magnetization with temperature for a sample of composition $\text{La}_{0.8}\text{K}_{0.2}\text{MnO}_3$.

Compositional dependence of Curie temperatures (determined from the maximum slope of dM/dT in $M(T)$ curves) for $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ series is given in table 1. It is clear that substitution of monovalent alkali metal K at the La sites, leading to a mixed valency of Mn ions, gives rise to ferromagnetism. Curie temperature increases monotonically with increasing potassium content without appreciable change in the saturation magnetization.

Complete magnetic characterization including FMR high frequency experiments are in progress.

Table 1. Cell parameters (triple hexagonal cell) and Curie temperature for rhombohedral $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ ($x = 0.2, 0.15, 0.1, 0.05$).

Composition x	a (Å)	c (Å)	T_C (K)
0.2	5.512(3)	13.382(2)	308
0.15	5.510(5)	13.376(0)	303
0.1	5.520(1)	13.372(4)	294
0.05	5.524(6)	13.375(9)	286

3.3. Resistivity and MR characterizations

Resistivity measurements performed on an La_{0.8}K_{0.2}MnO₃ ceramic bar are given in figure 4. The temperature dependence of the zero-field resistivity shows a metallic-like behaviour (i.e. $d\rho/dT > 0$) in the low temperatures regime and a transition to a semiconducting state, characterized by a peak, at $T_\rho \approx 297$ K which is slightly lower than the magnetic transition ($T_C = 308$ K). Above 297 K, the resistivity scales with thermally activated nearest neighbour hopping ($\rho \propto \exp(U/K_B T)$; $U \approx 60$ meV) which can be attributed to magnetic polaron. Although we are limited by the experimental measurements of the resistivity versus temperature up to 345 K, the correspondence of the exponential variation with the data is excellent and superior to fit functions based on power-law behaviour.

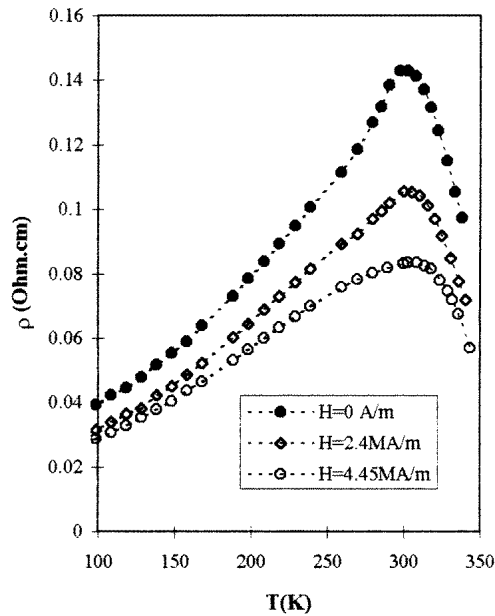


Figure 4. Resistivity curves versus temperature registered in different magnetic fields for La_{0.8}K_{0.2}MnO₃ sample.

For samples with different composition ($x = 0.05, 0.10, 0.15, 0.20$) the same resistivity characteristics are obtained. The maximum of resistivity (ρ_{max}) falls and shifts to higher temperatures with increasing potassium content.

The application of a magnetic field results in several changes including a large reduction in resistance values over the entire studied temperature range and a resistivity maximum shift to a higher temperature leading to an MR effect (figure 5).

The resistivity curves versus temperature registered for $x = 0.2$ in magnetic fields of 0, 2.4 and 4.45 MA m⁻¹ are shown in the same figure. By applying a magnetic field the metal to semiconducting transition temperature T_ρ increases significantly from $T_\rho = 297$ K (for $H = 0$ A m⁻¹) to $T_\rho = 305$ K (for $H = 4.45$ MA m⁻¹).

The largest change in resistivity takes place around the resistivity peak, and thus gives rise to a prominent giant magnetoresistance effect. A net maximum value of the resistivity is observed around 300 K corresponding to an elevated MR coefficient, as can be deduced from

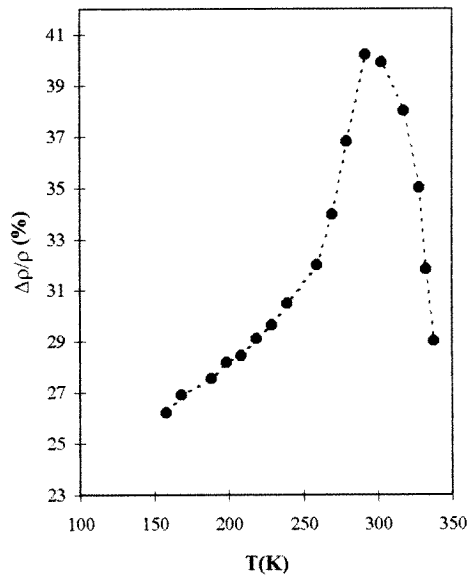


Figure 5. Temperature dependence of the magnetoresistance showing a maximum ratio of 40% under 4.45 MA m^{-1} at 300 K.

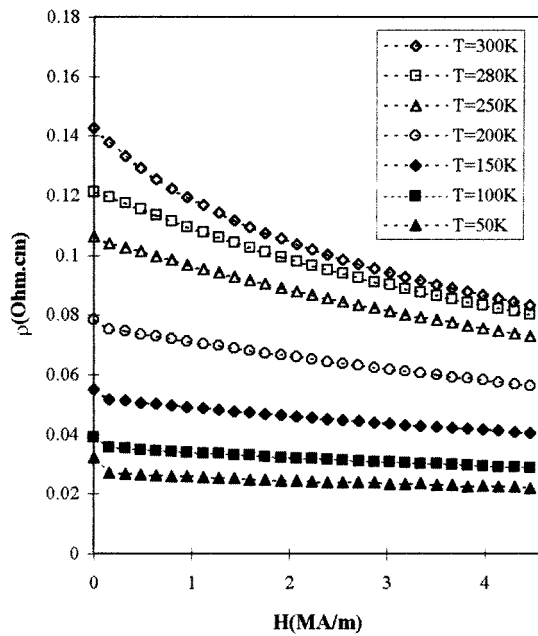


Figure 6. Field dependencies of the resistivity for rhombohedral $\text{La}_{0.8}\text{K}_{0.2}\text{MnO}_3$.

the resistivity curves versus the applied field, registered at different temperatures (figure 6). At 300 K, a magnetoresistance ratio (defined as $\Delta\rho/\rho_0 = [\rho(H=0) - \rho(H)]/\rho(H=0)$) as high as 40% is obtained under a magnetic field of 4.45 MA m^{-1} .

3.4. Discussion

We investigated structural, magnetic and electrical properties of alkali metal substituted La_{1-x}K_xMnO₃ oxides. X-ray diffraction patterns with no secondary phases are obtained with an x-ray system capable of 3% impurity detection. Moreover, there is no indication of magnetic impurities in magnetization curves. The possible change in the desired composition of samples is thus to be taken out. To interpret structural and magnetic data, it is necessary to know the cation valency distribution for compositions. The suggested distribution with K⁺ substituting lanthanum perovskite sites is: (La_{1-x}³⁺K_x⁺)_A(Mn_{1-2x}³⁺Mn_{2x}⁴⁺)_BO₃.

The parent compound LaMnO₃ is an antiferromagnetic insulator. Compounds of the series La_{1-x}K_xMnO₃ ($x = 0.05; 0.10; 0.15$ and 0.20) exhibit magnetization and resistance curves characteristic of a transition from a ferromagnetic–metallic to a paramagnetic–semiconducting state, as temperature increases. These results are of great interest since they show that a small doping by monovalent potassium element changes dramatically the magnetic and transport properties of these phases.

In the same way, as for the other manganites, the Curie temperature increases as the dopant content x increases. The increase of T_C , corresponding to the extension of the metallic state, can be easily explained by the arising of Mn⁴⁺ ions among the regular Mn³⁺ ions due to monovalent potassium doping. The ferromagnetic interaction between Mn³⁺/Mn⁴⁺ pairs is enhanced via the double exchange mechanism and consequently the ferromagnetic–metallic state is favoured.

The zero field resistivity presents a maximum which decreases and shifts to higher temperatures when increasing potassium content. The origin of this reduction in resistivity should be attributed to the systematic increase of charge carriers with alkali substitution.

An important observation deals with the fact that the conductivity in this series is related to the ferromagnetic transition temperature. The higher the T_C , the lower the resistivity. This means that the metallic and ferromagnetic properties originate from the same physical mechanism.

In this paper we focused on an La_{0.8}K_{0.2}MnO₃ sample with high spontaneous magnetization and a sharp transition at the Curie temperature characteristic of a good ferromagnet. At low temperatures the substantial drop in resistivity is clearly correlated with the ferromagnetic state and indicates, furthermore, that the composition of the sample is homogeneous. For temperature above T_p , the resistivity data reveal a thermally activated behaviour. Once the ferromagnetic state is established, the resistivity drops precipitously. Such a behaviour is not inconsistent with the ‘spin-polaron’ model [19] proposed to explain the colossal magnetoresistance effect. Below T_C a local ordering of Mn-spin moments occurs and impedes the formation of a spin polaron, which liberates the motion of free carriers and causes the reduction of resistivity.

The temperature dependence of the magnetoresistance shows a substantial effect of the magnetic field on resistivity over the entire range studied (5–320 K). A magnetoresistance ratio of 40% is calculated at 300 K in a magnetic field of 4.45 MA m⁻¹. Such a value is of the same magnitude as in the case of some alkaline earth substituted La manganites. Meanwhile, our experimental measurements are limited to an applied field up to 4.45 MA m⁻¹. A possible important magnetoresistance ratio can be reached at room temperature by applying higher magnetic field.

3.5. Conclusion

Potassium substituted oxides are ferromagnetic conductors at temperatures close to room temperature. They constitute very promising candidates as potential giant magnetoresistance

materials. Other substituted monovalent alkali metal manganites would be good materials exhibiting GMR effect and their studies could be of considerable interest.

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