Structural, magnetic and magnetoresistive properties of $La_{0.7}Sr_{0.3-x}Na_xMnO_3$ manganites

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Abstract
We present the monovalent alkali metal substitution effects upon structural, magnetic and electrical properties in $La_{0.7}Sr_{0.3-x}Na_xMnO_3$ for $0 \leqslant x \leqslant 0.2$. X-ray diffraction patterns show that our powder samples crystallize in a rhombohedral distorted perovskite structure with $R\bar{3}c$ space group. All the samples exhibit a ferromagnetic–paramagnetic transition and metallic–semi-conductor one with increasing temperature. The Curie temperature T_C decreases from 365 to 305 K; however the resistivity transition temperature T_ρ decreases from 340 to 270 K as Na content increases. A magnetoresistance ratio of about 46% at 300 K and in an applied field of 10 T has been observed in the bulk ceramic $La_{0.7}Sr_{0.1}Na_{0.2}MnO_3$ sample.

1. Introduction

The perovskite manganese oxides of general formula $La_{1-x}A_xMnO_3$ where A is a divalent alkali earth element (A = Ba, Sr, Ca), have been intensively studied during the last few years, instigated by their observed colossal magnetoresistance (CMR) effects near the ferromagnetic–paramagnetic transition temperature, T_C [1–3]. The typical composition where this effect is most prominent is around $x \approx 0.3$ [4–6]. It was believed that the spin structure and magneto-transport properties were correlated via the double exchange interaction, controlled by the motion of the e_g electrons from Mn^{3+} to Mn^{4+} ions [7]. However, recent investigations have shown that the double exchange cannot alone explain the observed behaviour in these systems, suggesting that the strong electron–phonon coupling (e.g. via Jahn–Teller effects [8], the average size of the A [9–11] and B site cations [12, 13], the mismatch effect [14], the vacancy in A and B sites [15] and the oxygen deficiency [16, 17]), plays a crucial role. Recently, giant magnetoresistance effects have been also observed in manganites doped with monovalent alkali-metal ions [18, 19]. These compounds were synthesized many years ago and tested as

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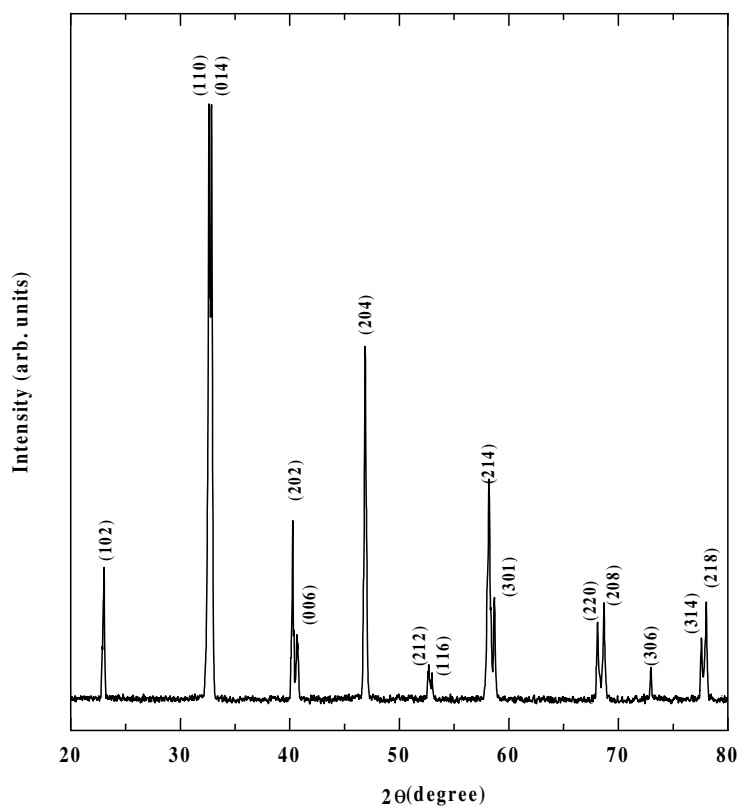
Figure 1. X-ray diffraction patterns at room temperature for $La_{0.7}Sr_{0.1}Na_{0.2}MnO_3$.

oxidation catalysts for exhaust gases for internal combustion engines [20]. Single perovskite phases $La_{1-x}A_xMnO_3$ (A = Na, K) have been observed up to $x = 0.2$, corresponding to 40% of Mn^{4+} content, a result of the larger difference in valence between the La^{3+} and the alkali-metal ions [19, 21]. These compounds crystallize in a rhombohedral distorted perovskite structure with space group $R\bar{3}c$ [21, 22] and exhibit both paramagnetic– ferromagnetic and semiconductor–metallic transitions with decreasing temperature.

In order to understand the effects of substituting a divalent element by a monovalent one on the structural, magnetic and electrical properties, we have prepared a novel manganite series, $La_{0.7}Sr_{0.3-x}Na_xMnO_3$ ($0 \leqslant x \leqslant 0.20$), in which the Sr^{2+} is partially substituted by Na^+.

2. Experiment

$La_{0.7}Sr_{0.3-x}Na_xMnO_3$ bulk samples ($x = 0$–0.20) were prepared using the standard ceramic processing technique by mixing La_2O_3, $SrCO_3$, Na_2CO_3 and MnO_2 in appropriate proportions. The obtained powder was first heated in air at 1173 K for 72 hours with an intermediate regrinding before being pressed into pellets under 4 tons cm^{-2} and sintered at 1473 K for 96 hours in air with several periods of grinding and repelleting. Finally, the samples were cooled to room temperature. The $La_{0.7}Sr_{0.3}MnO_3$ ($x = 0$) sample was fired at 1674 K for 72 hours and air quenched.

Table 1. Crystallographic data for La$_{0.7}$Sr$_{0.3-x}$Na$_x$MnO$_3$ samples with nominal Mn^{4+} content.

Compositions	% Mn^{4+}	a (Å)	α (°)	Unit cell volume V (Å^3)
La$_{0.7}$Sr$_{0.3}$MnO$_3$	30	5.459	60.43	58.11
La$_{0.7}$Sr$_{0.25}$Na$_{0.05}$MnO$_3$	35	5.457	60.44	58.05
La$_{0.7}$Sr$_{0.2}$Na$_{0.1}$MnO$_3$	40	5.451	60.46	57.89
La$_{0.7}$Sr$_{0.15}$Na$_{0.15}$MnO$_3$	45	5.449	60.47	57.83
La$_{0.7}$Sr$_{0.1}$Na$_{0.2}$MnO$_3$	50	5.447	60.49	57.76
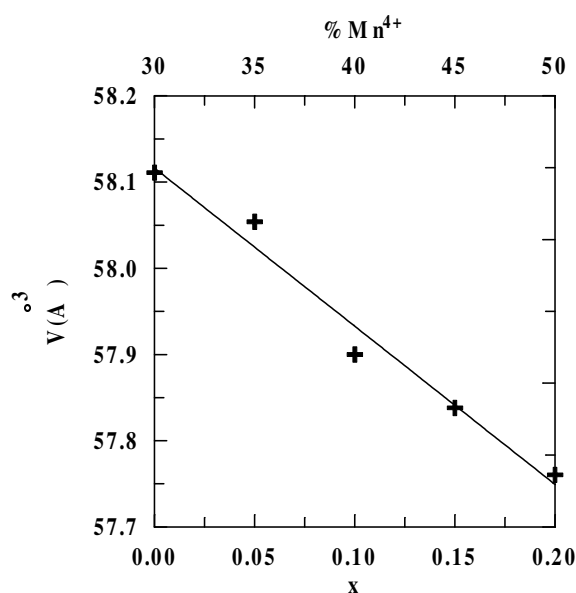
**Figure 2.** Variation of the unit cell volume as a function of x for La$_{0.7}$Sr$_{0.3-x}$Na$_x$MnO$_3$.

The phase purity and crystal structure were examined using a Siemens D5000 x-ray powder diffraction system with Cu Kα radiation. This system is able to detect up to a minimum of 3% of impurities according to our measurements.

Magnetization measurements as a function of temperature under an applied field of 0.05 T were carried out using a home-made Faraday type balance for the parental compound La$_{0.7}$Sr$_{0.3}$MnO$_3$ ($x = 0$) and a SQUID magnetometer for samples with $x \geqslant 0.05$. Electrical resistivity and magnetoresistance were measured as a function of temperature by the standard four probe technique.

3. Results and discussion

3.1. X-ray characterization

In our La$_{0.7}$Sr$_{0.3-x}$Na$_x$MnO$_3$ samples, the substitution of divalent Sr by the monovalent element Na leads to an increase in the Mn^{4+} content from 30% ($x = 0$) to 50% ($x = 0.2$). At room temperature, the structural investigation shows that all of our synthesized samples are in a single phase and crystallize in a perovskite structure. X-ray diffraction patterns have been indexed in the rhombohedral system with space group $R\bar{3}c$. Figure 1 shows the x-ray diffraction patterns for La$_{0.7}$Sr$_{0.1}$Na$_{0.2}$MnO$_3$.
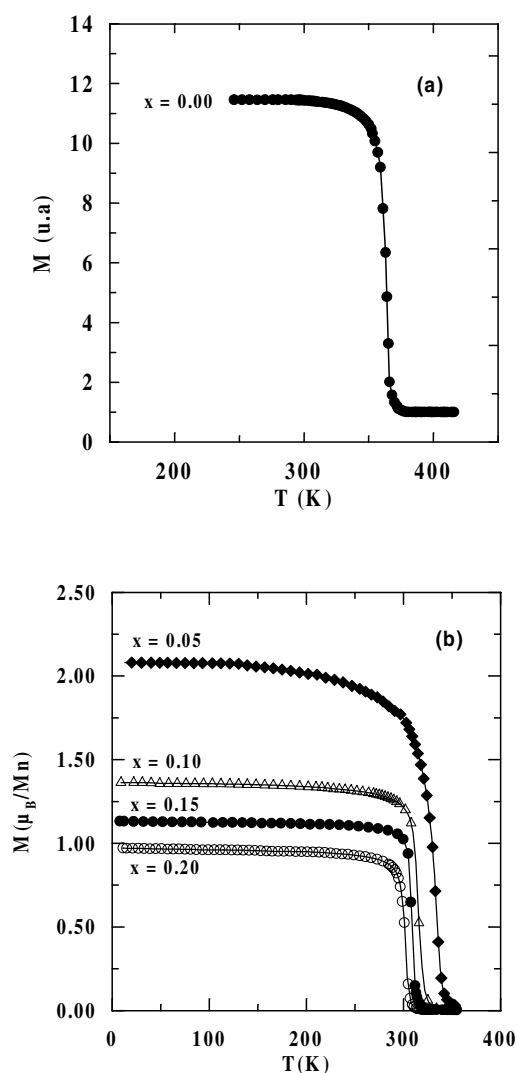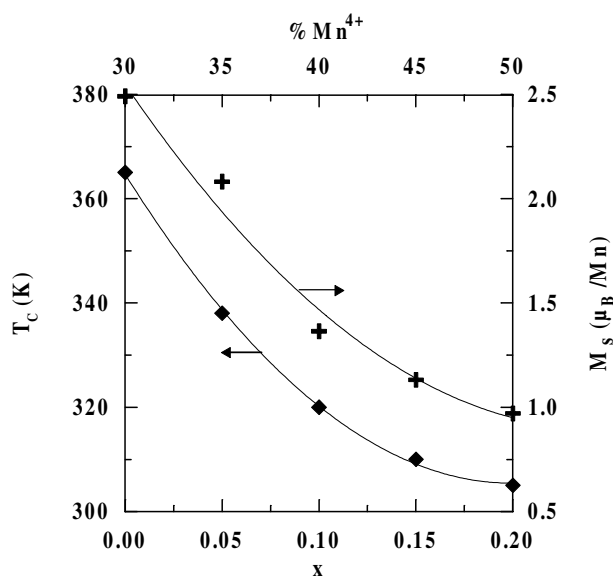
Figure 3. Magnetization versus temperature in an applied field of 0.05 T for $La_{0.7}Sr_{0.3-x}Na_xMnO_3$. (a) $x = 0$; (b) $x = 0.05$–0.2.

Derived lattice parameters are listed in table 1 from which it can be seen that, the lattice parameter a decreases with increasing x while, the angle α increases monotonically. The unit cell volume evolution with x is shown in figure 2. The volume decrease with increasing x is in concordance with the strontium substitution by sodium. In fact, the Na^+ (1.24 Å) and Mn^{4+} (0.52 Å) ionic radii are respectively smaller than Sr^{2+} (1.31 Å) and Mn^{3+} (0.70 Å) [23].

The relationship between the lattice parameters and the size of cations A and B has been confirmed by extensive structural analysis [21, 24, 25].

3.2. Magnetic characterization

Magnetization curves versus temperature registered in a low magnetic field (0.05 T) reveal that all the samples exhibit a single magnetic transition from a paramagnetic to ferromagnetic

Figure 4. Maximum of magnetization, M_S, at 10 K, in a field of 0.05 T, and Curie temperature, T_C, versus x for La$_{0.7}$Sr$_{0.3-x}$Na$_x$MnO$_3$ solution.

phase as T decreases (figure 3). We used the maximum slope of the curve $M(T)$ as a criterion to determine the Curie temperature T_C. T_C shifts from 365 to 305 K when x increases from 0 to 0.2 (figure 4). The maximum magnetization, M_S, at 10 K decreases from 2.49 to 0.97 μB/Mn with increasing Na$^+$ content (figure 4). The variations of T_C and M_S can be interpreted in terms of the increase in Mn^{4+} content above 30%, which produces a decrease in the double exchange interaction and favours the super-exchange interaction (Mn^{4+}–O– Mn^{4+}). On the other hand, Sr^{2+} substitution by Na$^+$, of smaller radius, induces also a decrease in the average size $\langle r_A \rangle$, causing a lowering of the Curie temperature.

3.3. Electrical characterization

The variation in resistivity with temperature for La$_{0.7}$Sr$_{0.3-x}$Na$_x$MnO$_3$ samples is shown in figure 5 for a zero applied magnetic field. All the samples exhibit metallic behaviour ($\mathrm{d}\rho/\mathrm{d}T > 0$) at low temperatures ($T < T_\rho$) and semiconductor-like characteristics above T_ρ. The conduction in the ferromagnetic phase ($T < T_\rho$) is generally understood according to the double exchange theory. The Mn^{3+}–O–Mn^{4+} coupling produces conduction through charge transfer from the half-filled to empty e_g orbital. The resistivity transition temperature T_ρ decreases from 340 to 270 K and the maximum of the resistivity, ρ_{max}, increases with increasing x. The reduction in the M_s and T_C values, and the increases of ρ_{max} in the La$_{0.7}$Sr$_{0.3-x}$Na$_x$MnO$_3$ compounds are further evidence of a weak double exchange interaction due to the increase of Mn^{4+} content above 30% and the decrease of $\langle r_A \rangle$. Moreover, and according to La$_{1-x}$Na$_x$MnO$_3$ [19] and La$_{1-x}$Sr$_x$MnO$_3$ [26] studies, the rhombohedral La$_{0.7}$Sr$_{0.3-x}$Na$_x$MnO$_3$ compounds would be characterized by both a weak Hund coupling and a weak electron–phonon interaction. So, the T_ρ decrease and the ρ_{max} increase may indicate a slight increase of electron–phonon coupling as the Na$^+$ content is increased.

Figure 6, shows the evolution of T_C and T_ρ as a function of x, where it can be seen that there is no coincidence between the two critical temperatures. T_C is found to be higher
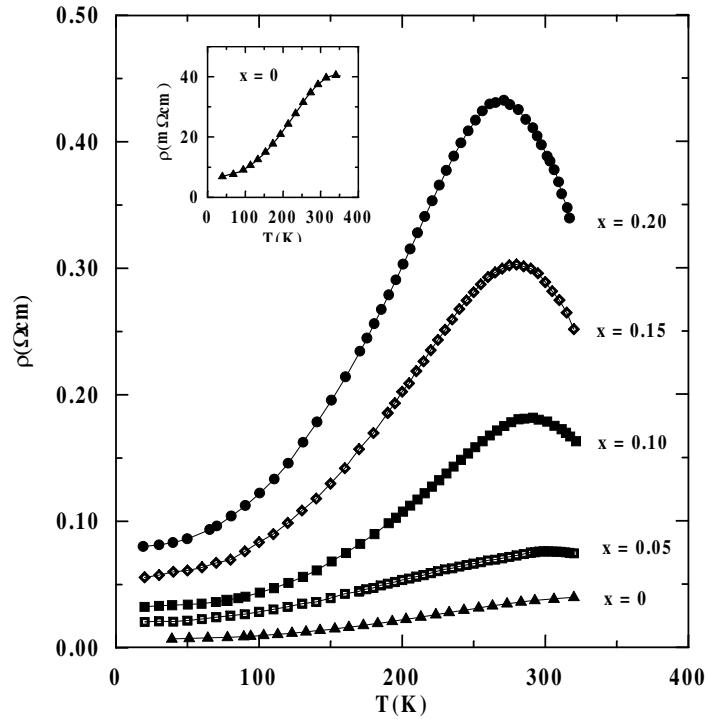
Figure 5. Resistivity versus temperature for $La_{0.7}Sr_{0.3-x}Na_xMnO_3$ compounds in zero magnetic fields. Inset: resistivity versus temperature for $La_{0.7}Sr_{0.3}MnO_3$.

than T_ρ a difference possibly due to the grain size effect. In fact, the grain sizes determined by scanning electron micrographs for both $La_{0.7}Sr_{0.3}MnO_3$ and $La_{0.7}Sr_{0.1}Na_{0.2}MnO_3$ samples are 3.59 and 2.97 μm respectively. Mahendiran *et al* [27] have discussed the role of the grain sizes in $La_{0.7}Sr_{0.3}MnO_3$. They obtained three $La_{0.7}Sr_{0.3}MnO_3$ samples possessing different particle sizes by applying different heat treatments. The particle sizes of the three samples were 0.25, 0.40 and 3.5 μm, respectively. Interestingly, these samples showed similar ferromagnetic transition temperatures of 360, 370 and 390 K, but differing T_ρ values of 190, 200 and 370 K respectively. According to this report, there are ferromagnetic clusters (consisting mostly of Mn^{4+} and Mn^{3+}) within grains for $T < T_\rho$ and Mn^{3+} regions between the grains, the latter having a predominantly antiferromagnetic super-exchange interaction. The observed metal–insulator transition would depend on the relative contributions from the insulating regions and the metallic ferromagnetic clusters. As the grain size of our samples decreases, the relative contribution of the insulating regions increases, leading to a decrease of T_ρ.

In the low temperature ferromagnetic regime, the temperature dependence of the resistivity for all of the samples can be well fitted by the equation $\rho(T) = \rho(0) + AT^2$ ($T \leqslant 230$ K) (figure 7). The resistivity seems to be governed by the electron–electron scattering process associated with spin fluctuations. A similar result has been reported by Urushibara *et al* on $La_{1-x}Sr_xMnO_3$ single crystals, as reported in [28]. The variation in the coefficient A, and the maximum resistivity, ρ_{max}, is shown as a function of x in figure 8. The remarkable phenomenon is the observation of a correlation between A and ρ_{max}, implying that the electron correlation would be inherent in our manganite oxides up to T_ρ [29].
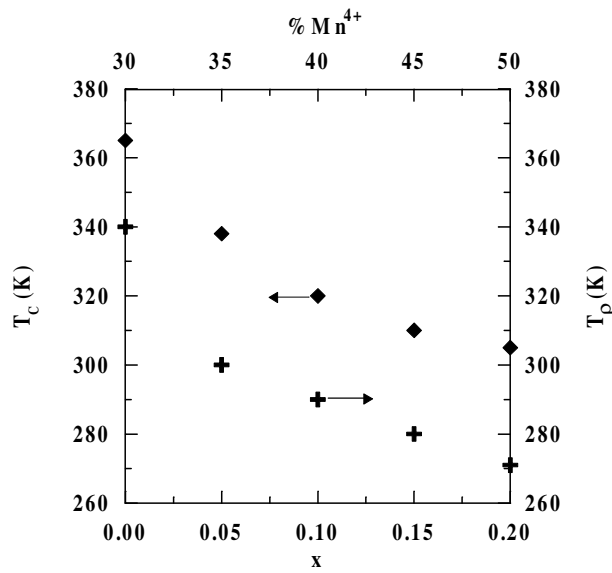
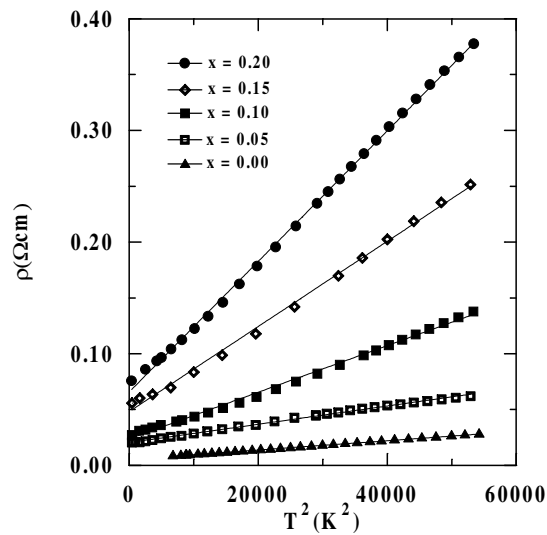**Figure 6.** Transition temperatures T_C and T_ρ versus x for La$_{0.7}$Sr$_{0.3-x}$Na$_x$MnO$_3$.

Figure 7. Temperature dependence of the resistivity in the low temperature ferromagnetic regime ($T \leqslant 230$ K) for La$_{0.7}$Sr$_{0.3-x}$Na$_x$MnO$_3$.

Damay *et al* [30] have shown that La$_{0.5}$Sr$_{0.5-x}$Ca$_x$MnO$_3$ samples ($x \geqslant 0.15$ and $\langle r_A \rangle \leqslant 1.243$ Å) characterized by an Mn^{3+}/Mn^{4+} ratio equal to one, exhibit a paramagnetic–ferromagnetic transition followed by a ferromagnetic–antiferromagnetic one when T decreases. However our La$_{0.7}$Sr$_{0.1}$Na$_{0.2}$MnO$_3$ sample characterized by the same Mn^{3+}/Mn^{4+} ratio and an average size of the A site cations, $\langle r_A \rangle = 1.23$ Å, does not present the ferromagnetic–antiferromagnetic transition at low temperature. This result confirms that the magnetic behaviour at low temperature may be also governed by the mismatch effect
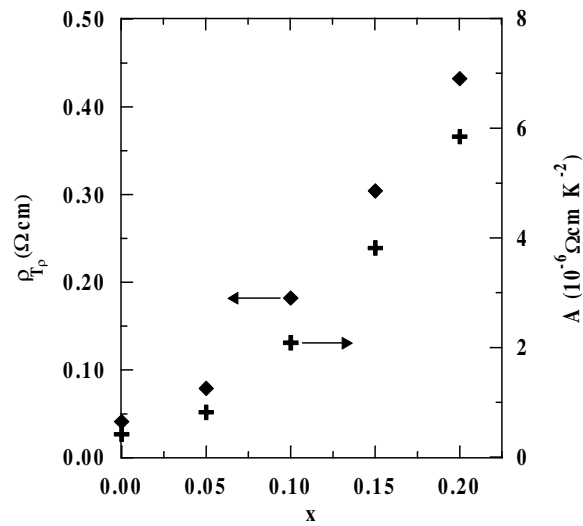
Figure 8. (◆) Resistivity at T_ρ ($\rho_{T\rho}$) versus x for $La_{0.7}Sr_{0.3-x}Na_xMnO_3$. (+) Coefficient A versus x for $La_{0.7}Sr_{0.3-x}Na_xMnO_3$.
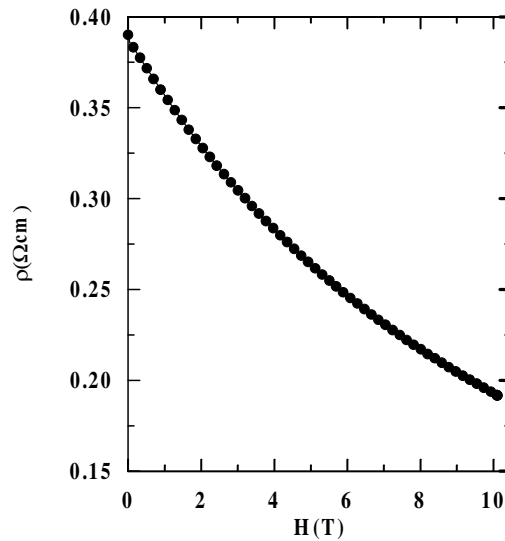
Figure 9. Resistivity versus magnetic field for $La_{0.7}Sr_{0.1}Na_{0.2}MnO_3$ at 300 K.

represented by the variance σ^2 defined by $\sigma^2 = \Sigma y_i r_i^2 - \langle r_A \rangle^2$, where r_i corresponds to the radii of the various A site cations and y_i to their fractional occupancies ($\Sigma y_{i=1}$). In fact, the variance of $La_{0.5}Sr_{0.27}Ca_{0.23}MnO_3$ ($\langle r_A \rangle = 1.23$ Å) is higher ($\sigma^2 = 10.03 \times 10^{-3}$ Å^2) than that for $La_{0.7}Sr_{0.1}Na_{0.2}MnO_3$ ($\sigma_2 = 1.29 \times 10^{-3}$ Å^2), reflecting well the differing magnetic behaviour in these compounds.

The conductivity in the paramagnetic phase for the $La_{0.7}Sr_{0.1}Na_{0.2}MnO_3$ sample can be fitted well by a $\sigma = C \exp(-E_a/k_B T)$ law. The activation energy is found to be $E_a = 70$ meV. With applied magnetic field, the resistivity of our $La_{0.7}Sr_{0.1}Na_{0.2}MnO_3$ sample is decreased (figure 9), leading to a large magnetoresistance effect.
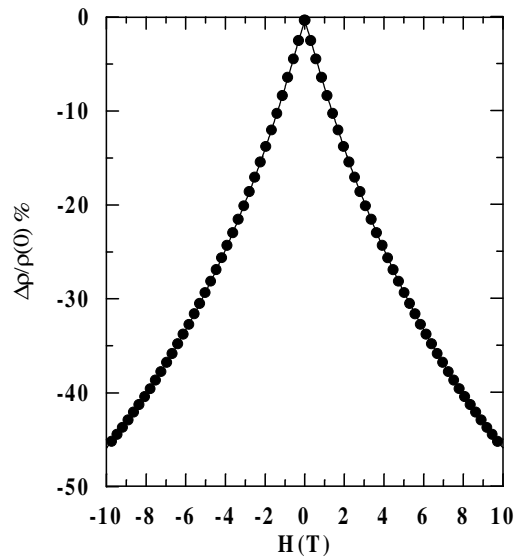
Figure 10. $\Delta\rho/\rho(H=0)\%$ ratio versus magnetic field for La$_{0.7}$Sr$_{0.1}$Na$_{0.2}$MnO$_3$ at 300 K.

In figure 10, the magnetoresistance ratio, defined as $\Delta\rho/\rho = [\rho(H) - \rho(H=0)]/\rho(H=0)$, is plotted as a function of applied field at $T = 300$ K.

Magnetoresistance ratios of approximately 46% and 33% are obtained for applied fields of 10 T and 6 T respectively at 300 K. Our results show that strontium substitution by sodium induces a decrease in T_C down to room temperature and an increase in the magnetoresistance ratio. A magnetoresistance ratio of about 20% is observed for the La$_{0.7}$Sr$_{0.3}$MnO$_3$ bulk sample in an applied field of 6 T at $T = 300$ K [31].

4. Conclusion

In this work, the structural, magnetic and transport properties of the manganite perovskite La$_{0.7}$Sr$_{0.3-x}$Na$_x$MnO$_3$ solution have been investigated. X-ray diffraction analysis shows that our samples crystallize in a rhombohedral structure with a decrease in the unit cell volume as x increases. Magnetic and electrical measurements show that La$_{0.7}$Sr$_{0.3-x}$Na$_x$MnO$_3$ materials exhibit ferromagnetic, metallic behaviour at low temperature ($T < T_\rho$) and semiconductor-like characteristics above T_ρ. The observed decrease in Curie temperature, T_C, can be explained by the Mn^{4+} content increase and the decrease in average size of the A site cations with alkali substitution. A magnetoresistance ratio of about 33% for $T = 300$ K and $H = 6$ T was observed for the La$_{0.7}$Sr$_{0.1}$Na$_{0.2}$MnO$_3$ ceramic sample. If the magnetoresistance response at room temperature can be improved further, it will be a promising candidate for application as a device in sensors and magnetic recording. To complete this work, a neutron measurement is essential for a deeper understanding of the crystallographic and magnetic structures of the La$_{0.7}$Sr$_{0.3-x}$Na$_x$MnO$_3$ perovskite manganites.

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