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Structure, magnetic and transport properties in La$_{0.7-x}$Bi$_x$Ca$_{0.3}$MnO$_3$ (0.05 $\leqslant$ x $\leqslant$ 0.7) perovskites

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Abstract. Structure, magnetic and transport properties of La$_{0.7-x}$Bi$_x$Ca$_{0.3}$MnO$_3$ (0.05 $\leqslant$ x $\leqslant$ 0.7) manganites have been studied. Samples with $x \leqslant 0.15$ show ferromagnetic behaviour. For higher concentrations an important influence of antiferromagnetic interactions has been observed. The La$_{0.5}$Bi$_{0.2}$Ca$_{0.3}$MnO$_3$ sample shows an antiferro–ferromagnetic transition induced by the applied field and the Bi$_{0.7}$Ca$_{0.3}$MnO$_3$ composition is an antiferromagnet, but ferromagnetic interactions are still present. The resistivity of the samples shows a semiconductor–metallic transition for $x \leqslant 0.15$. For $x = 0.2$ and 0.7 the compounds exhibit insulating behaviour down to 10 K, but a field induced transition to a metallic state is found in La$_{0.5}$Bi$_{0.2}$Ca$_{0.3}$MnO$_3$. The results are discussed in terms of the charge localization probably due to the covalent character of the Bi.

1. Introduction

The observation of giant magnetoresistance (GMR) in hole doped perovskites with formula A$_{1-x}^{3+}$A$_x'^{2+}$MnO$_3$ (A = La, Sm, Nd, . . . , A$'$ = Ca, Pb, Sr, . . .) gave rise to a new investigation subject of great interest, due to the fundamental aspects of transport phenomena in ordered materials and also to their possible technological applications [1]. The ferromagnetic properties measured in this type of compound, for several specific compositions, were observed already in the 1950s years and explained by means of the double exchange mechanism (DE) that involves Mn^{3+}–O–Mn^{4+} bonds [2]. The appearance of magnetoresistance [3] is related to the simultaneous presence of ferromagnetism and metallic state.

An essential factor in order to understand the behaviour of these compounds is that the actual crystallographic structure presents an orthorhombic distortion of the classic cubic symmetry of the perovskite-like compounds [4], as recent neutron diffraction studies have elucidated for the classical composition La$_{0.7}$Ca$_{0.3}$MnO$_3$ as well as for many others compositions. As a consequence, the octahedral coordination of oxygens around Mn is distorted and therefore the Mn–O bond length turns out to be different in the three spatial directions, leading to a clear example of Jahn–Teller-type distortion. It has been also found that many compounds with different metals in the A$'$ site show magnetoresistance behaviour with changes in the magnetic and transport properties that the DE theory is not able to explain. The average size of metal A$'$, keeping constant the ratio A^{3+}/A$'^{2+}$, plays a fundamental role in the T_C (Curie temperature) and T_{SC-M} (semiconductor–metal transition temperature) values and MR (magnetoresistance) ratio. In some cases a drastic change of the magnetic behaviour and the appearance of metamagnetic state as in the (PrCaSr)MnO$_3$ system was observed [5].

Thus, a direct relation between the average ionic radii of metal A$'$ with the Mn–O bond length was established. However, when doping these compounds with different ions still the correlation between structure and magnetic and transport properties is not completely well understood, and so we have focused our effort on this important issue.

Bi^{3+} is expected to substitute La^{3+} in the ordinary composition $LaMnO_3$ perovskite because of its valence and ionic radius. However, the magnetic properties of the $BiMnO_3$ perovskite are rather different from the La manganite ones. The $BiMnO_3$ perovskite is ferromagnetic below 103 K with spontaneous magnetic moment close to the theoretical value corresponding to the Mn^{3+} ion [6]. In this work we study the substitution of La^{3+} atoms by Bi^{3+} ones in the classical composition $La_{0.7}Ca_{0.3}MnO_3$. Structure variations and magnetic behaviour for the composition range $(La_{1-x}Bi_x)_{0.5}Ca_{0.5}MnO_3$ [7] and also for $Bi_{1-x}Ca_xMnO_3$ [8] were examined in the late 1960s. In those studies the authors reported strong anomalies in the magnetic behaviour. Bismuth does not belong to the lanthanides which are commonly used for substitutions of the trivalent metal. On the other hand bismuth is stable with an oxidation state 3+ and has an average ionic radius consistent with the geometrical rule of the tolerance factor [9]. This similarity has been exploited by other authors which have produced $Bi_{1-x}Ca_xMnO_3$ single crystals almost isostructural with the corresponding composition with La [10]. Taking into account all these factors, we have chosen Bi^{3+} for substituting La in the production of samples and we have studied the modifications produced in the magnetic and structural properties.

2. Experiment

Polycrystalline samples of composition $La_{0.7-x}Bi_xCa_{0.3}MnO_3$ with $x = 0.05, 0.10, 0.15, 0.20$ have been prepared using the standard experimental procedure for solid state reaction. La_2O_3, Bi_2O_3, $CaCO_3$ and MnO_2 in stoichiometric proportions were mixed and calcinated at 900 °C for 8 h. After grinding, the powders were pressed into pellets with a pression of 2 tonnes cm^{-2} and subsequently annealed at 1200 °C for 6 h. All final products were checked by x-ray powder diffraction analysis indicating the presence of an unique phase with perovskite-type structure. This structural characterization was carried out using Cu Kα radiation ($\lambda = 1.5418$ Å), with 0.05° step and 4 s counting time. The indexing of the x-ray powder patterns was performed using the TREOR software [11].

A sample of composition $Bi_{0.7}Ca_{0.3}MnO_3$ has been also prepared in the same way but in this case the reaction time was 10 h. On the other hand, the sample with classical composition $La_{0.7}Ca_{0.3}MnO_3$ was studied by the authors in a previous work [12].

Magnetic and resistance measurements were performed on an MPMS-7 (Quantum Design) magnetometer in a temperature range from 10 to 400 K and a maximum applied field of 7 T. The zero field cooling (ZFC) and field cooling (FC) curves were performed under a field of 8 kA m^{-1}. $M(T)$ curves at 1 T applied field and hysteresis loops at 10 K and up to 7 T were also obtained. The resistance versus temperature measurements were carried out using a conventional four-wire automatic measurement system, with the current flowing parallel to the applied field. The pellets obtained from the synthesis procedure were cut in square shape ($\approx 4.5 \times 4.5$ mm^2) and silver dag contacts at the corners were used.

3. Results

3.1. Structural study

In figure 1 the x-ray diffraction patterns for the series of compounds as well as for $Bi_{0.7}Ca_{0.3}MnO_3$ composition are shown. A remarkable fact from the comparison of these
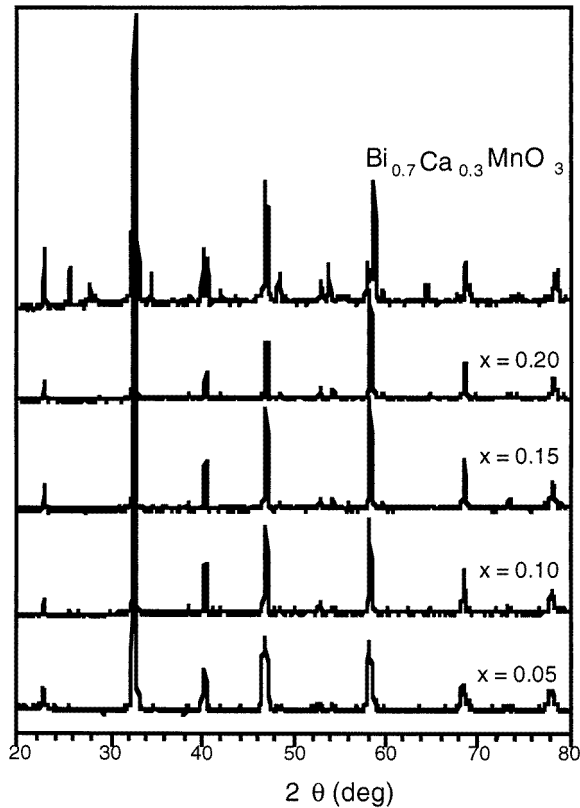
Figure 1. X-ray diffraction patterns for the La$_{0.7-x}$Bi$_x$Ca$_{0.3}$MnO$_3$ series composition.

patterns is that the systematic substitution of La by Bi does not produce relevant effect on them. The reflections in these powder diffraction patterns are consistent with a pseudocubic perovskite-type structure and they can be indexed using a cubic cell with double dimensions respect to the perovskite cell ($a = 2a_p$). By increasing the amount of Bi a slight contraction of the cell parameter is observed: from $a = 7.730$ for the $x = 0.05$ composition to $a = 7.719$ for the $x = 0.20$ one. However, if the cell volume between these two compositions is compared, we find a reduction of only 0.45%. This can be explained considering the similar dimension of the two cations La^{3+} (ionic radius = 1.302 Å) and Bi^{3+} (ionic radius = 1.30 Å) [13].

In the x-ray pattern of Bi$_{0.7}$Ca$_{0.3}$MnO$_3$ some reflections are split owing to the monoclinic distortion. The cell parameters obtained by indexing calculation are $a = 7.730(1)$, $b = 7.698(2)$, $c = 7.729(5)$ and $\beta = 91.01(7)$. This monoclinic distortion leads to a drastic change of the transport properties (regarding to the corresponding composition La$_{0.7}$Ca$_{0.3}$MnO$_3$) as will be discussed in the following.

However, x-ray diffraction experiments carried out by conventional diffractometers detect only the contribution of the heavy atoms giving rise to the doubling of the perovskite cell. On the other hand, the information concerning distortion of the octahedra is not observable owing to the small contribution of the oxygen atoms to the intensity of the reflections. For this reason, the reflections which indicate that orthorhombic distortion are either extremely weak or slightly splitted. So, the diffraction pattern gives only partial information about the structural
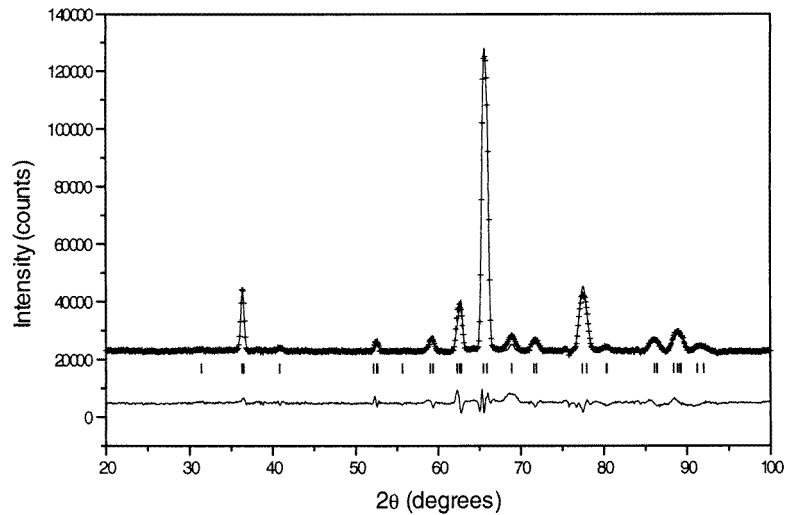
Figure 2. Rietveld refinement of the $La_{0.5}Bi_{0.2}Ca_{0.3}MnO_3$ neutron diffraction spectrum obtained at 170 K (the intensity is in arbitrary units). No magnetic contribution has been taken into account. Difference between adjustment and experiment is around 1.83%.

Table 1. Rietveld refinement results for neutron diffraction pattern of the $La_{0.5}Bi_{0.2}Ca_{0.3}MnO_3$ composition.

Space group			*Pbmn*
a			5.413(1)
b			5.460(1)
c			7.645(1)
R_p			1.83
R_{wp}			2.74
S			4.35
Atom	x	y	z
La/Ca/Bi	0.5021(3)	0.5339(4)	0.25
Mn	0.5	0	0
O1	0.0645(7)	0.4905(6)	0.25
O2	0.7158(1)	0.2768(5)	0.0339(7)

distortion. In order to obtain more information we have performed a very preliminary neutron diffraction experiment on the D20 apparatus ($\lambda = 2.41$ Å) at the Institute ILL (Grenoble, France) on the sample with composition $La_{0.5}Bi_{0.2}Ca_{0.3}MnO_3$ at 170 K. The neutron diffraction pattern reveals that the crystal structure belongs to the orthorhombic space group *Pbnm*. The orthorhombic cell is obtained from the cubic one by tilting $45°$ around the c axis. No magnetic contribution was observed because the diffraction experiment was performed above its Curie temperature. The Rietveld refinement carried out by using DBWS-9006 software, reported in figure 2, was done using the structural model described in table 1. It is in good agreement with the experimental data ($R = 1.87\%$) except for the peak at $2\theta = 68.89°$. The high intensity of this peak could be due to a charge ordering contribution. This fact can also explain the insulator behaviour observed for $La_{0.5}Bi_{0.2}Ca_{0.3}MnO_3$ in the absence of any applied magnetic field H (see below).

3.2. Magnetic behaviour

Figures 3 and 4 show the magnetic behaviour observed from ZFC and FC measurements for all the compositions studied in this work. These ZFC curves allow us to determine the order temperature, T_C, for each sample, as the temperature where the minimum of the dM/dT derivative occurs. There is a remarkable similarity in this behaviour for all samples in the range of compositions $0.05 \leqslant x \leqslant 0.15$, hinting at the fact that the magnetization processes involved at low applied field values are very similar: the obtained curves split just below T_C and suggest the existence of non-homogeneous magnetic systems [14], and are in fact similar to the $x = 0$ composition previously studied by the authors [12].
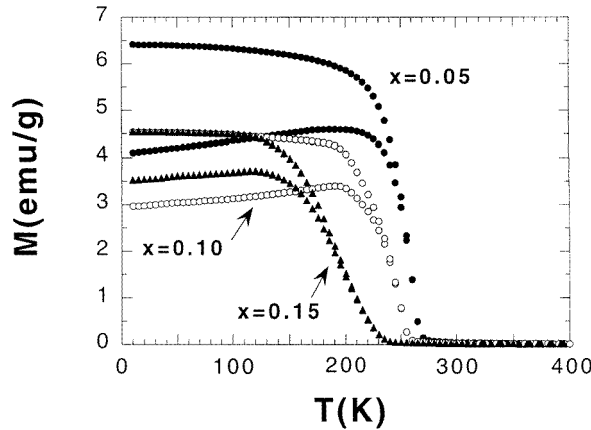

Figure 3. Zero field cooling (upper branch) and field cooling (lower branch) curves measured for the compositions $x = 0.05, 0.10$ and 0.15.

For the case $x = 0.2$, the measured behaviour is very close to the observed one for the $La_{0.5}Ca_{0.5}MnO_3$ composition [15, 16]. The ZFC curve presents three possible transitions at temperatures 200 K, 100 K (ordering temperature) and 50 K, respectively. The transition at 200 K is not well resolved but it is evident a small shoulder in the susceptibility curve. It can be attributed to an antiferromagnetic ordering temperature, but can be also interpreted as a charge ordering transition (that also appears in the $La_{0.5}Ca_{0.5}MnO_3$ composition) which sometimes looks very similar [10]. A neutron diffraction experiment performed at 170 K for this composition (as described in 3.1) also supports this idea. The ordering temperature T_C is clearly observed at 100 K in the $1/\chi$ curve. The transition at 50 K could be due to the appearance of antiferromagnetic components or any other kind of magnetic inhomogeneity. This last issue is supported by the splitting between the ZFC and FC curves. Using the inverse susceptibility curve and the corresponding Curie–Weiss fit ($\chi = C/(T - \theta_p)$) in the high temperature paramagnetic region, we found a positive paramagnetic Curie temperature $\theta_p = 200$ K. This is close to the value obtained for $La_{0.5}Ca_{0.5}MnO_3$ (see, i.e., [16]).

The case of the $x = 0.7$ composition turns out to be simpler: from the temperature evolution of the measured magnetization and inverse susceptibility, two transitions at 140 K (that could be also a charge ordering transition) and 45 K are clearly observed. We have also found a positive paramagnetic Curie temperature $\theta_p = 50$ K. This value indicates the existence of ferromagnetic interactions in the sample. At 45 K there is clearly an antiferromagnetic transition. The splitting between ZFC and FC curves indicates the existence of canting of antiferromagnetic moments or weak ferromagnetism.
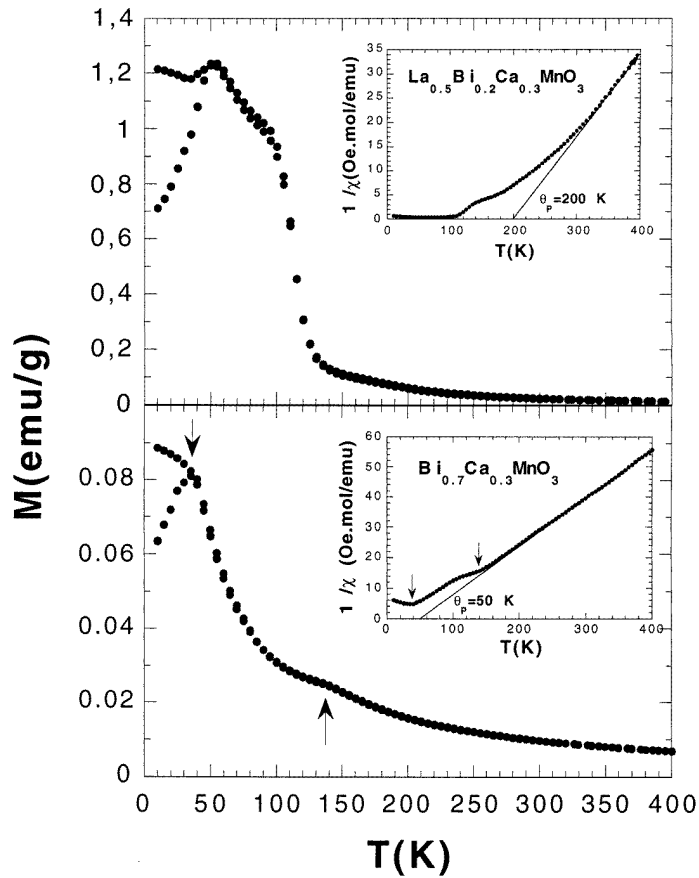
Figure 4. Zero field cooling (upper branch) and field cooling (lower branch) curves measured for the $La_{0.5}Bi_{0.2}Ca_{0.3}MnO_3$ (top) and $Bi_{0.7}Ca_{0.3}MnO_3$ (bottom) compositions. The inset shows the $1/\chi$ curve obtained from zero field cooling measurement.

Hysteresis loops have been also measured at 10 K and up to 7 T. There are several interesting features to be analysed (see figure 5): the samples corresponding to $x = 0.05, 0.10$ and 0.15 compositions behave as ordinary ferromagnetic samples. However, this is not the case for the $x = 0.20$ composition: its virgin magnetization curve reveals a canted antiferromagnet with a ferromagnetic component that increases in two steps as the applied field does. A field of 6 T is high enough to saturate the sample and subsequently to show a normal ferromagnetic behaviour. Once in the ferromagnetic state, the system remains always in this magnetic state, even when suppressing the field. This kind of magnetism is similar to a metamagnet showing an antiferro–ferromagnetic transition under field [16]. Canted antiferromagnetism is then possible as the ground state.

The $Bi_{0.7}Ca_{0.3}MnO_3$ sample does not reach magnetic saturation at 7 T. Magnetization curves have been performed at different temperatures (10, 20, 30 and 40 K) and Arrot plots indicate that there is no spontaneous magnetization at any temperature. This fact rules out the existence of weak ferromagnetism, but it is consistent with the existence of some ferromagnetic clusters. Quite similar behaviour has been also observed in the $Bi_{2/3}Sr_{1/3}MnO_3$ composition [17, 18] and interpreted in this way.
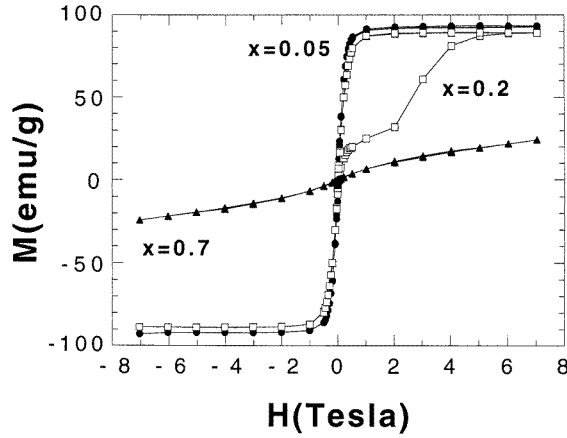
Figure 5. Hysteresis loops measured at 10 K and up to 7 T, for the $x = 0.05$, 0.2 and 0.7 compositions.

Table 2. Values of the order temperature, T_C, magnetic moment in the ordered state per transition metal atom, μ_{TM}, and transition temperature in the resistance behaviour, T_{SC-M}.

x	T_C (K)	μ_{TM} (μ_B/atom)	T_{SC-M} (K)
0.05	260	3.59	260
0.10	245	3.69	240
0.15	190	3.57	160
0.20	110	3.60	110[a]
$Bi_{0.7}Ca_{0.3}MnO_3$	$\theta_p = 50$	—	—

[a] Measured at 2 T.

The results obtained from magnetic measurements are summarized in table 2. The effect of the substitution of La atoms by Bi ones is a continuous decrease in the order temperature, but the magnetic moment measured at 10 K and 7 T applied field remains almost unchanged and quite close to the expected value of 3.7 μ_B/atom for a Mn^{4+}/Mn^{3+} ratio of 0.3/0.7.

In figure 6 the temperature dependence of the resistance measured under zero and 6 T applied fields, for the $x = 0.05$ composition, is shown. In the absence of external field a sharp resistance maximum, characteristic of a semiconductor–metal transition, has been found for all compositions at temperatures close to T_C, except for the $x = 0.20$ and $x = 0.70$ ones. In fact, other authors have already reported that the $Bi_{0.7}Ca_{0.3}MnO_3$ composition behaves as an insulator [8]. For this composition we have estimated a resistivity value $\rho \approx 0.174$ (Ω cm) at room temperature.

The decrease of the resistance value observed when a 6 T external field is applied allows us to use the definition of the relative negative magnetoresistance as $[R(6\text{ T}) - R(0\text{ T})]/R(0\text{ T})$ [3]. The measured magnetoresistances for all samples are shown in figure 7. In the case of the $x = 0.05$ and 0.10 samples, a quite similar behaviour has been already reported by Srinivasan *et al* [13] in a bulk polycrystalline sample of $La_{0.62}Bi_{0.05}Ca_{0.33}MnO_3$ composition. There is a continuous improvement of this MR value as Bi content increases, but the temperature at which the maximum of the MR behaviour occurs continuously decreases. In this way the 100% change in MR is reached for the $x = 0.20$ composition below $T = 130$ K. For this composition, the semiconductor–metal transition does not appear at zero applied field, but it is clearly induced by a field greater than 1 T.
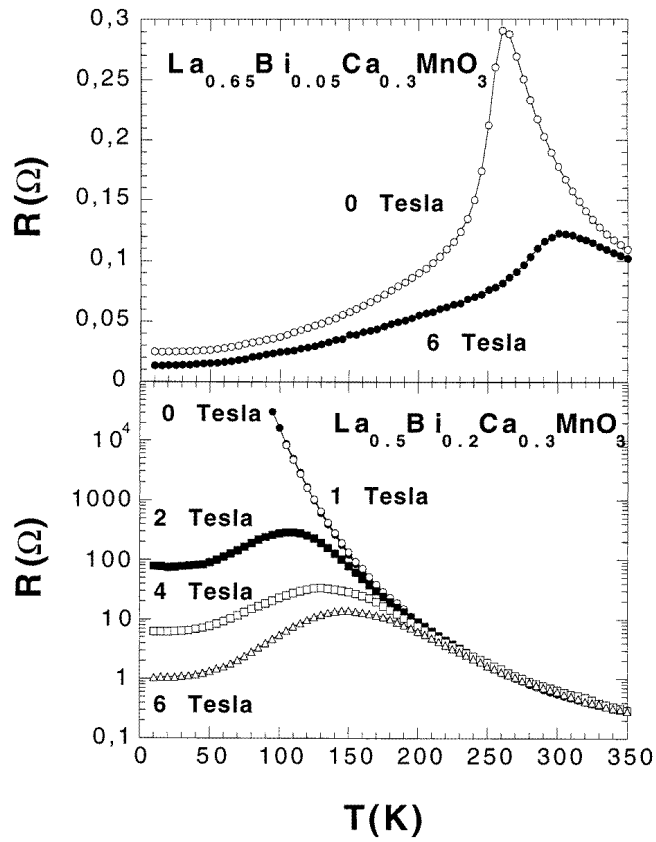
Figure 6. Resistance behaviour versus temperature for the $x = 0.05$ composition measured at 0 and 6 T applied magnetic fields (top), and for the $x = 0.2$ composition at several applied fields (bottom).
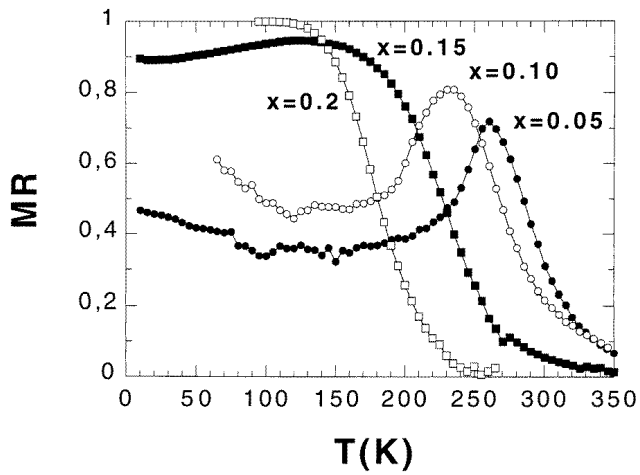

Figure 7. Magnetoresistance behaviour versus temperature for the compositions studied in this work.

4. Discussion and conclusions

In the light of our experimental work, we can affirm that doping the La$_{0.7}$Ca$_{0.3}$MnO$_3$ with low amounts of Bi atoms gives rise to quite low distortion in the structure. No static or cooperative Jahn–Teller distortion appears in the studied compositions (La$_{0.7-x}$Bi$_x$)Ca$_{0.3}$MnO$_3$, with $x = 0.05$, 0.10 and 0.15. The almost constant value of the saturation magnetic moment indicates that the number of Mn^{4+} ions and Mn^{3+}–O^2–Mn^{4+} interactions remains unchanged, following the double exchange mechanism. Within those doping levels, the Bi atom seems to be in a 3+ state and is fully equivalent to the La ions. However, the Bi weakens the ferromagnetic character of these compositions. This fact is reflected in a continuous decrease of the Curie temperature.

A drastic change in the magnetic behaviour occurs for the sample of composition La$_{0.5}$Bi$_{0.2}$Ca$_{0.3}$MnO$_3$. Antiferromagnetic interactions play an important role for this composition. The observed metamagnetic character with an antiferro–ferromagnetic transition induced by the applied field, accompanied by the insulating behaviour of this composition, indicates the existence of a charge-ordered system in spite of the high, still constant value of the saturation magnetic moment. This charge localization, that is probably responsible for the decrease of the ferromagnetic interactions and the increase of the resistivity, could be induced by the strong covalent character of the Bi.

The collapse in the ferromagnetic order as the Bi content increases is fully clear for the Bi$_{0.7}$Ca$_{0.3}$MnO$_3$ composition, which shows antiferromagnetic character in the whole range of temperature together with insulating behaviour. For this composition the distorted tetragonal cell measured for the other compositions turns out to be a monoclinic one.

The complex magnetic behaviour of these compounds, however, is far from being completely understood and merits a deeper study. In this sense, neutron diffraction experiments are now in progress in order to elucidate the magnetic structure of these compounds and the existence of charge ordering in the $x = 0.2$ sample.

Acknowledgments

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