Magnetic Behaviour in the System $La_{1.33}Na_xMn_xTi_{2-x}O_6$

Ana Isabel Ruiz,*[a] Javier Campo,[b] María Luisa López,[a] José Luis Martínez Peña,[c] Carlos Pico,[a] and María Luisa Veiga[a]

Keywords: Perovskite phases / Neutron diffraction / Magnetic properties

A series of perovskite-type complex oxides of general formula $La_{1.33}Na_xMn_xTi_{2-x}O_6$ (x = 0.66, 0.55 and 0.44) have been obtained and characterised. Magnetic susceptibility measurements on these phases follow a Curie–Weiss-like dependence at high temperatures, although a more complex variation is observed at lower temperatures. The thermal variation of M/H from zero-field-cooled and field-cooled susceptibility measurements shows irreversible processes and magnetisation isotherms that differ from typical ferromagnetic behaviour. Neutron diffraction data collected at low temperature show no extra magnetic contribution in the nuclear peaks nor extra reflections. All the measurements carried out on this series, such as magnetic susceptibility (dc and ac), magnetisation and neutron diffraction can be interpreted as being due to a spin-glass behaviour.

Introduction

Perovskite-type oxides have the general formula ABO_3 and it is well-known that this structure allows a great number of cation substitutions at the A and/or B sites. In this way, both A and B sites can accommodate two different metal ions, with different oxidation states, that are expressed by the nominal compositions $AA'B_2O_6$,[1,2] $A_2BB'O_6$ [3,5] and $AA'BB'O_6$.[6–8] These systems have been the subject of intense research efforts due to the fact that they exhibit a wide variety of electrical and magnetic properties (high temperature superconductors, ferromagnetic and piezoelectric materials, magnetoresistors, etc.) that depend on variations in the chemical composition, stoichiometry and structure of the material.

In particular, hole-doped perovskite-type manganese oxides have attracted considerable interest in recent years motivated by the apparition of colossal magnetoresistance and the great variety of magnetic and transport properties in this class of materials.[9] Among the La-based systems, the ground state of the stoichiometric parent compound $LaMnO_3$ shows remarkable insulating A-type antiferromagnetic properties, which are attributed to a cooperative effect of orbital ordering and superexchange interactions.[10]

For these reasons, we have carried out previous research on the system $La_{1.33}Na_xMn_xTi_{2-x}O_6$ ($x = 0.66$, 0.55 and 0.44) oriented towards structural characterization by neutron diffraction[6] and electrical properties.[11] The aim of the present work was to analyse additional physical properties of these compounds by studying their magnetic behaviour.

Results and Discussion

Chemical Composition and Structural Results

Samples of the series $La_{1.33}Na_xMn_xTi_{2-x}O_6$ ($x = 0.66$, 0.55 and 0.44) were synthesised as polycrystalline powders. Table 1 gathers the Mn^{III} and Mn^{IV} concentrations present for the different compositions, which agree well with the respective nominal manganese content. From these results it is deduced that the amounts of Mn^{IV} are practically negligible in the $x = 0.55$ and 0.44 samples.

Table 1. Composition of manganese in the series $La_{1.33}Na_xMn_xTi_{2-x}O_6$

x	Mn^{III}	Mn^{IV}
0.66	0.55	0.11
0.55	0.50	0.05
0.44	0.39	0.05

All these compounds have characteristic diffraction patterns of the perovskite structure, in which some reflections are split indicating a noticeable distortion from the ideal cubic symmetry. It can be seen from neutron powder diffraction data[6] that an interesting structural transition be-

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[a] Departamento de Química Inorgánica I, Facultad de Ciencias Químicas, Universidad Complutense,
28040 Madrid, Spain
E-mail: anairuiz@quim.ucm.es
[b] Institut Max Von Laue – Paul Langevin (ILL),
38042 Grenoble Cedex 9, France
[c] Departamento de Propiedades Ópticas, Magnéticas y de Transporte, Instituto Ciencia de Materiales, Consejo Superior de Investigaciones Científicas,
Cantoblanco 28049 Madrid, Spain

tween the orthorhombic (space group *Ibmm*) and rhombohedral (space group $R\bar{3}c$) symmetries takes place between 400 and 600 K in the $x = 0.66$ sample. In contrast, the phases $x = 0.55$ and 0.44 adopt a rhombohedral symmetry (space group $R\bar{3}c$) as is deduced from the X-ray diffraction results.[6]

These materials do not show any superlattice lines corresponding to an ordered distribution of the cations at the A and B sites. Taking into account the structural results, both lanthanum and sodium cations and vacancies are located at the A-sites, and manganese and titanium cations occupy, at random, the B-sites of the perovskite structure.

Magnetic Properties

Magnetic measurements were carried out on all the above compounds. Figure 1 shows the temperature dependence of magnetic susceptibility (a) and its reciprocal (b). Reciprocal susceptibility data can be fitted to a Curie−Weiss law [M/H = C/(T − θ)] over a relatively narrow temperature range that decreases as the x value increases, from which the experimental and theoretical magnetic moments and parameters C and θ were obtained (Table 2). The experimental magnetic moment should diminish in the same way as the Mn^{3+} concentration in the sample. However, a noticeable difference between the calculated (3.85 μ_B) and observed (3.43 μ_B) values is encountered for the $x = 0.66$ phase, whereas both values are practically the same for the $x = 0.44$ composition. Thus, some magnetic interactions between the paramagnetic Mn^{3+} ions are to be expected in the first case and, possibly, in the intermediate composition $x = 0.55$. These assumptions seem to be supported by the fact that the respective Weiss constants are positive and decrease in good agreement with the Mn content in the sample. Figure 1b shows the increase in the value of the critical temperature, T_c, at which a magnetic phase-transition takes place; these increase as the manganese content increases (i.e., from 260 K for $x = 0.44$ to 310 K for $x = 0.66$). It is likely that this variation in T_c is due to magnetic dilution within the B sublattice.

Table 2. Magnetic data for $La_{1.33}Na_xMn_xTi_{2-x}O_6$

x	T range (K)	μ_{calc} (μ_B)	μ_{exp} (μ_B)	θ (K)
0.66	340−390	3.85	3.43	228
0.55	315−390	3.63	3.55	128
0.44	300−390	3.25	3.24	107

In order to analyse the nature of the proposed cooperative interactions, field-cooled (FC) and zero-field-cooled (ZFC) susceptibility measurements are compared in Figure 2 for the $x = 0.66$ sample; they were obtained at an applied field (H_e) of 500 Oe. As the temperature is lowered from around 300 K, both FC and ZFC magnetisation curves increase and are basically identical in a wide region, $T_r \leq T \leq T_c$, implying a reversibility of the magnetisation. Below the temperature, T_r, at which the FC and ZFC graphs diverge, the ZFC magnetisation shows a broad maximum at 12.4 K that is taken as the spin freezing temperature, namely as T_{sg}, while the FC variation shows a bend and increases slightly. Thus the irreversibility appears far below T_c, a behaviour that is typical of reentrant spin-glass systems,[12] as in cluster-glass systems the irreversibility starts just below T_c and the difference between FC and ZFC magnetisation is usually much higher, reflecting the presence of ferromagnetic order within the clusters.[13]

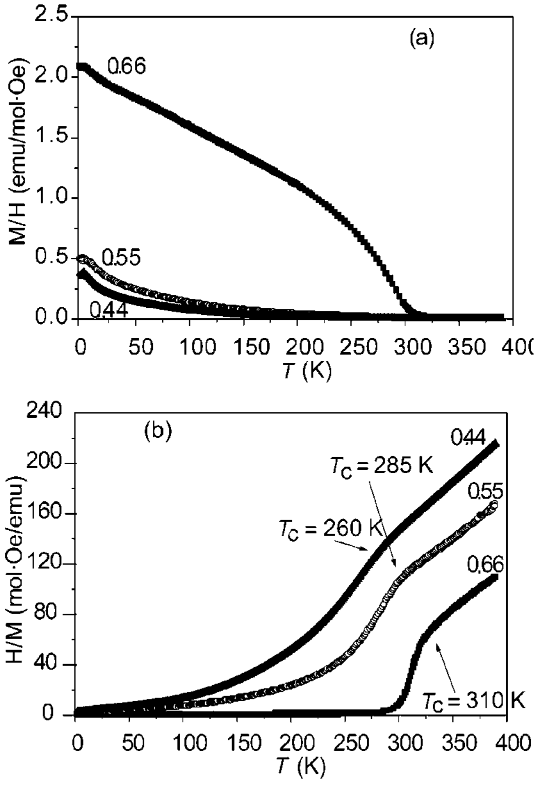

Figure 1. Susceptibility (a) and reciprocal susceptibility variations (b) for the system $La_{1.33}Na_xMn_xTi_{2-x}O_6$ ($x = 0.66$, 0.55 and 0.44)

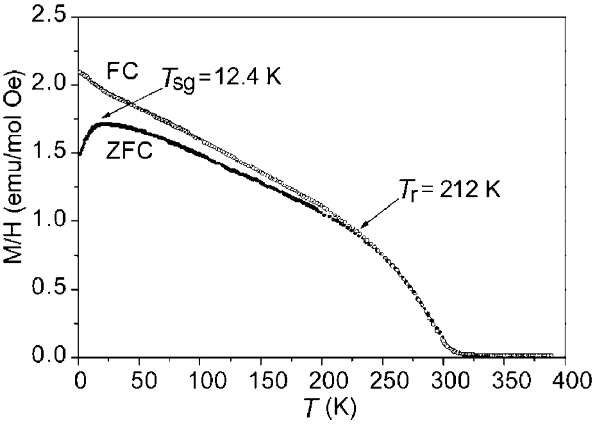

Figure 2. Temperature dependence of the magnetic susceptibility for $La_{1.33}Na_{0.66}Mn_{0.66}Ti_{1.34}O_6$ measured after zero-field cooling (ZFC) and field cooling (FC)

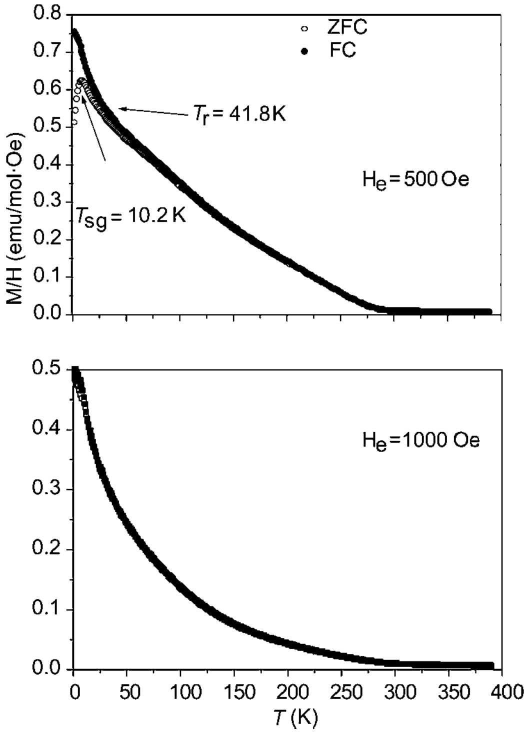

Figure 3. FC and ZFC M/H for $La_{1.33}Na_{0.55}Mn_{0.55}Ti_{1.45}O_6$ measured with an applied field (H_e) of 500 and 1000 Oe

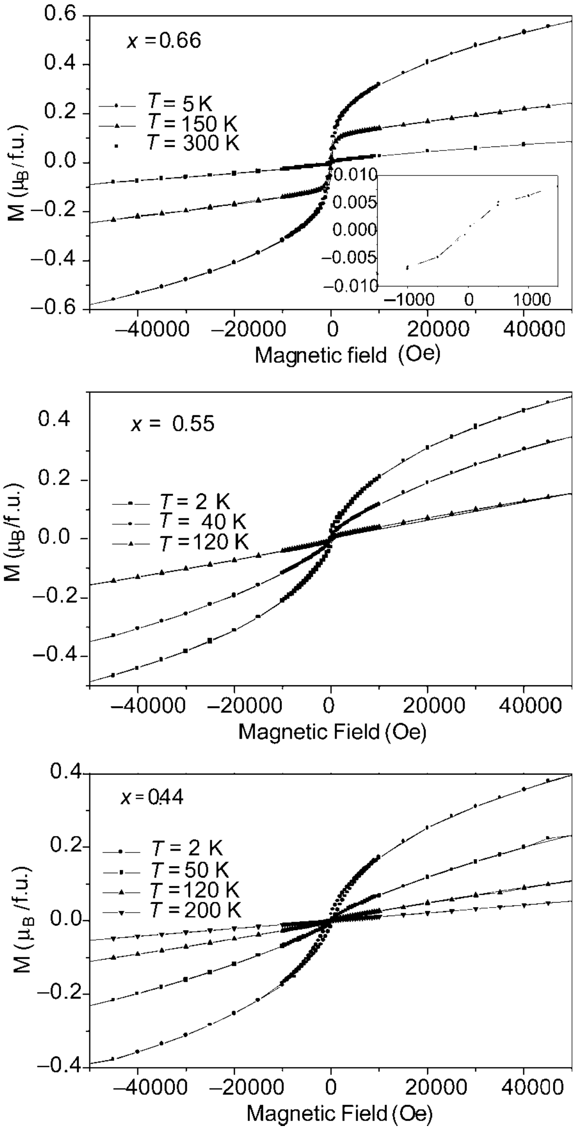

Figure 4. Magnetisation isotherms obtained at different temperatures for the system $La_{1.33}Na_xMn_xTi_{2-x}O_6$ (x = 0.66, 0.55 and 0.44)

With respect to the remaining compositions, Figure 3 shows the shape of the M_{FC} and M_{ZFC} curves for $x = 0.55$ at two different fields of 500 and 1000 Oe. Only a clear T_{sg} is detected for the lower field measurements; a similar behaviour was obtained for the sample $x = 0.44$ (not shown). However, when the manganese doping decreases in the sample, T_{sg} drops slightly and the respective cusp is less pronounced, suggesting that the magnetic interaction diminishes (12.4 K for $x = 0.66$ and 10.2 K for $x = 0.55$); the maximum is not observed for $x = 0.44$ at the same external field of 500 Oe. These changes suggest that the magnetic transitions below T_c in this system are very sensitive to the applied field and that they are completely suppressed by increasing H_e. Such a behaviour has also been reported for some other perovskite-type oxides[4,13,14] and was assumed to originate from the formation of a spin-glass.

Magnetisation measurements provide useful information about the magnetic behaviour of these systems and the isotherms obtained at different temperatures are depicted in Figure 4. Characteristic S-shaped curves were obtained in all cases and they do not saturate even in fields as high as 50 kOe. Curves below T_c show a clear ferromagnetic component with increasing importance when the temperature is lowered. Such a behaviour is evidence for a disordered spin-state (spin-glass-like state) induced by disorder and frustration due to competing ferro- and antiferromagnetic exchange interactions. The very narrow hysteresis loops indicate that these materials behave as weakly ferromagnetic. Finally, the low values of magnetisation could be explained by recalling that both paramagnetic Mn^{3+} and diamagnetic Ti^{4+} ions are randomly distributed over the B sites, thus preventing the establishment of a long-range ordering in these materials.[9]

In order to evaluate the importance of the above cooperative interactions, neutron diffraction experiments were carried out on these systems and Figure 5 shows thermal patterns for the sample $x = 0.66$ in the temperature range 1.6−262 K. Only a very weak ferromagnetic contribution could be observed near 2θ = 70°, whose intensity is practically negligible (see inset in Figure 5), so it was not possible to obtain a ferromagnetic component. Therefore it is more realistic to assume that no extra magnetic contributions (in the intensity of nuclear peaks nor extra peaks) are observed at low temperatures and, consequently, that there is no long range magnetic ordering in these materials.

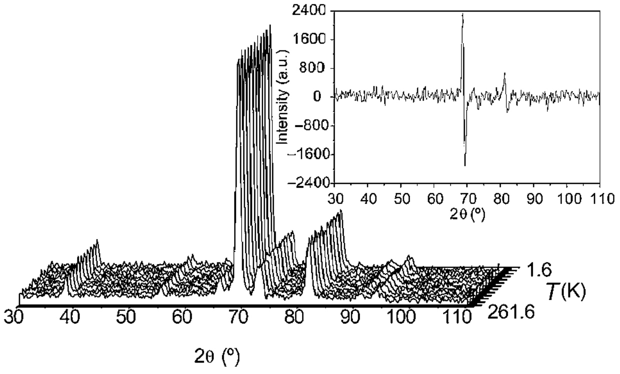

Figure 5. Neutron thermodiffractograms of $La_{1.33}Na_{0.66}$-$Mn_{0.66}Ti_{1.34}O_6$ between 1.6 and 262 K and angular range 30−110°; the inset shows the difference diagram between 1.6 and 261.6 K (inset)

Finally, to gain a deeper insight into the spin-glass behaviour of this series, thermal variations of the ac susceptibility, χ_{ac}, at different frequencies were performed and they are depicted in Figure 6 for the sample $x = 0.66$. This demonstrates that the real part of χ_{ac} exhibits a broad maximum at about 67 K which decreases in intensity as the frequency increases (from 1 to 1000 Hz), as is expected for spin-glass systems,[15] thus confirming the above assumptions.

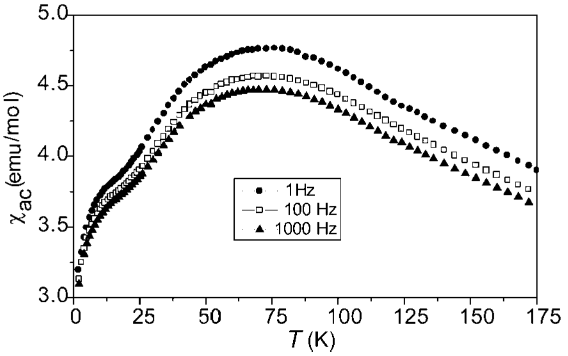

Figure 6. Thermal dependence of the ac susceptibility at different values of the excitation frequency

In summary, different magnetic and neutron diffraction measurements carried out on the series $La_{1.33}Na_xMn_xTi_{2-x}O_6$ ($x = 0.66$, 0.55, and 0.44) confirm a spin-glass behaviour that is attributed to cation disorder in the perovskite B sites. Such a disorder should contribute to the frustrated magnetic ground state and has also been found in related $AB_{1-x}B'_xO_3$ perovskite-type systems, in which the dilution of paramagnetic B cations seems to be crucial to the occurrence of spin-glass transitions at low temperatures. In the compounds under research the Ti^{4+}/Mn^{3+} ratio increases progressively from about 2 (for $x = 0.66$) to about 3.5 (for $x = 0.44$) and it becomes obvious that the effect of manganese dilution is crucial to the respective magnetic ordering. Similar features were previously observed in other related systems $LnMn_{1-x}B'_xO_3$, where lanthanum has been substituted by praseodymium or neodymium.[16,17]

Experimental Section

Polycrystalline samples of general composition $La_{1.33}$-$Na_xMn_xTi_{2-x}O_6$ ($x = 0.66$, 0.55 and 0.44) were prepared by a classical ceramic method. Stoichiometric amounts of $La(NO_3)_3{\cdot}6H_2O$, $NaNO_3$, $C_{15}H_{21}MnO_6$ [manganese(III) acetylacetonate] and $C_{10}H_{14}O_5Ti$ [titanium(IV) acetylacetonate] were used as starting materials, and heated at 973 K for several days.

The Mn^{3+}/Mn^{4+} ratio was determined by redox titration with an excess of $FeSO_4$ solution and back titration with $KMnO_4$, with the samples being dissolved in H_2SO_4/H_2O (50:50). A known amount of $FeSO_4$ was introduced into the sample solution and the excess was determined with a standard $KMnO_4$ solution to give the total manganese ; the possible Mn^{4+} content was determined by the procedure described in ref.[10]

X-ray diffraction patterns were recorded with a Philips X′Pert-MPD diffractometer and a PW 3050/00 goniometer, using Ni-filtered Cu-K_α radiation and a 2θ step size of 0.05°, with a counting time of 12.5 s for each step. The goniometer was connected to a PC controlled by the commercial program PC-APD (Analytical Powder Diffraction Software, 4.0).

The neutron powder-diffraction data were recorded on the D1A high-resolution powder diffractometer (λ = 1.9110 Å) at the Institut Laue−Langevin (Grenoble, France). The neutron and X-ray diffraction patterns were analysed by the Rietveld method and the Fullprof program.[18] The multidetector D1B powder diffractometer with a wavelength of 2.52 Å was used for thermal patterns in the 1.6−300 K temperature range.

Magnetic measurements were obtained in a SQUID (Quantum Design, MPMS-XL model) with a sensitivity of 10^{-10} emu in the temperature range 2−400 K, applying a field of 500, 1000 Oe.

Acknowledgments

One of the authors (A.I.R.) is grateful to the C.A.M. for a fellowship. We are indebted to the CICYT (MAT 2000-1585-C03-02), Spain, for financial support. We also acknowledge the I.L.L. (CRG−D1B) for collecting the neutron diffraction data.

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Received November 12, 2001
[I01448]