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LETTER TO THE EDITOR

Magnetic properties of Co-rich compositions ($x > 0.5$) in the $LaMn_{1-x}Co_xO_3$ series

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Abstract

The magnetic properties of Mn-rich and Co-rich compositions in the $LaMn_{1-x}Co_xO_3$ series, processed at different temperatures, have been compared. The ferromagnetic Curie temperature increases with x up to $x = 0.5$. For compositions with $x > 0.5$, weak magnetic transitions at the Curie temperature of one of the two ferromagnetic phases with $x = 0.5$ is observed, depending on the processing temperature, indicating mixed-phase behaviour for $x > 0.5$. The results can explain the anomalies reported in the magnetic properties of $LaMn_{1-x}Co_xO_3$.

The substituted perovskite-type manganites $LaMn_{1-x}M_xO_3$, where M is a transition metal ion, show interesting magnetic properties similar to those of the well known colossal-magnetoresistive manganites $La_{1-x}A_xMnO_3$, where A is a divalent ion. The La-site- and Mn-site-substituted compounds show ferromagnetic properties when compared to the anti-ferromagnetic behaviour of $LaMnO_3$. Extensive studies have been made of the magnetic properties of $La_{1-x}A_xMnO_3$ since the discovery of colossal magnetoresistance in this class of compounds and the results are well documented in the literature (Coey *et al* 1999). On the other hand, there are relatively few studies on the Mn-site-substituted compounds and their magnetic properties are not yet understood properly. For example, Goodenough *et al* (1961) found a two-phase region for $0.4 \leqslant x \leqslant 0.6$ and Jonker (1966) observed the presence of two phases from x-ray diffraction measurements for $x > 0.5$ in $LaMn_{1-x}Co_xO_3$. However, Troyanchuk *et al* (2000) recently reported the coexistence of ferromagnetic domains with ordered Mn and Co ions and ionically disordered spin-glass domains for $0.2 \leqslant x \leqslant 0.8$ in $LaMn_{1-x}Co_xO_3$, with an unusually low value of the Curie temperature for $x = 0.35$ and identical Curie temperatures for $0.4 \leqslant x \leqslant 0.6$. Similar characteristics are also observed for the $LaMn_{1-x}Ni_xO_3$ system. In a recent report, Blasco *et al* (2001) have shown that the composition $LaMn_{0.25}Ni_{0.75}O_3$ ($x = 0.75$) forms a single-phase structure with weak ferromagnetic and spin-glass characteristics, contrary to the previous report (Asai *et al* 1979)

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that compositions with $x > 0.5$ in the $LaMn_{1-x}Ni_xO_3$ series are biphasic with contributions from $LaMn_{0.5}Ni_{0.5}O_3$ and $LaNiO_3$. Blasco *et al* (2001) have observed multiple magnetic transitions in $LaMn_{0.25}Ni_{0.75}O_3$, with a weak ferromagnetic transition close to the magnetic transition temperature of $LaMn_{0.5}Ni_{0.5}O_3$.

Recent studies (Joy *et al* 2000b) showed that two ferromagnetic phases of $LaMn_{0.5}Co_{0.5}O_3$, in single-phase forms, can be stabilized at low and high processing temperatures (700 and 1300 °C). The compound had to be synthesized by a low-temperature method to obtain one of the phases, having a higher Curie temperature, in single-phase form. Mixed-phase behaviour was observed for samples prepared by the conventional solid-state method of synthesis as well as for the low-temperature-synthesized sample processed at intermediate temperatures. The two phases of the compound show different ferromagnetic transition temperatures, due to the difference in spin state of Mn and Co (Joy *et al* 2000a, Joly *et al* 2001). To investigate whether compositions with $x > 0.5$ in the $LaMn_{1-x}Co_xO_3$ series are really ferromagnetic with unexpectedly larger transition temperatures as reported or a mixture of different phases due to insufficient processing, and to study the effects of processing temperature on their magnetic properties, we have prepared different compositions ($0.1 \leqslant x \leqslant 0.8$) by two different methods. In this letter, we show that for $x > 0.5$, samples processed at different temperatures always contain either of the two phases of $LaMn_{0.5}Co_{0.5}O_3$ in small amounts whose contribution decreases with increasing x and the reported magnetic behaviours of these compositions are those of mixed phases.

Two sets of $LaMn_{1-x}Co_xO_3$ samples ($0.1 \leqslant x \leqslant 0.8$) were prepared by different methods. One set of samples were prepared by the conventional ceramic (solid-state) method by heating stoichiometric mixtures of La_2O_3, MnO_2 and CoC_2O_4 at 1000 °C for four days with five intermediate grindings. The powders obtained were then heated at 1100 and 1200 °C for one day each and then at 1300 °C for five days with intermediate grindings. The second set of samples were prepared by a low-temperature method, as discussed previously (Joy *et al* 2000b). In short, the powder samples obtained after initial decomposition of a mixture of the solutions of the corresponding metal nitrates and glycine, at ∼200 °C, were further heated at 700, 800, 1000 and 1300 °C for 24 hours each. The samples were characterized by powder x-ray diffraction (XRD), oxygen analysis and magnetic measurements. The temperature variation of the magnetization was measured in the temperature range 80–300 K, at $H = 50$ Oe, after cooling the samples from room temperature in zero applied field. M versus H measurements were performed at 82 K up to a maximum field of 15 kOe.

The zero-field-cooled (ZFC) magnetization curves of the two sets of $LaMn_{0.4}Co_{0.6}O_3$ ($x = 0.6$) and $LaMn_{0.2}Co_{0.8}O_3$ ($x = 0.8$) samples, heated at different temperatures, are compared in figure 1 and figure 2, respectively. The magnetization curves of the two phases of $LaMn_{0.5}Co_{0.5}O_3$ are also shown in figure 1 for comparison. For both the ceramic and the low-temperature-synthesized samples with $x = 0.6$ and 0.8, a magnetic transition is observed at the T_c (∼230 K) of the high-T_c phase of $LaMn_{0.5}Co_{0.5}O_3$, for samples processed below 1100 °C. Similarly, the samples processed at higher temperatures show a magnetic transition at the T_c (∼150 K) of the low-T_c phase of $LaMn_{0.5}Co_{0.5}O_3$. For $x = 0.8$, no magnetic transition is observed for the low-temperature-synthesized sample processed at higher temperatures, though the corresponding ceramic sample shows a weak magnetic transition at ∼150 K. For $x = 0.8$, $T_c \approx 140$ K is reported by Troyanchuk *et al* (2000). The value of the magnetization is lower for $x = 0.8$ when compared to that for $x = 0.6$ and the magnetization is lower for the low-temperature-synthesized samples.

To show the effect of preparation conditions on the magnetic properties of Mn-rich compositions, the magnetization curves of $LaMn_{0.7}Co_{0.3}O_3$, prepared by the two different methods and processed at low and high temperatures, are shown in figure 3. The ceramic

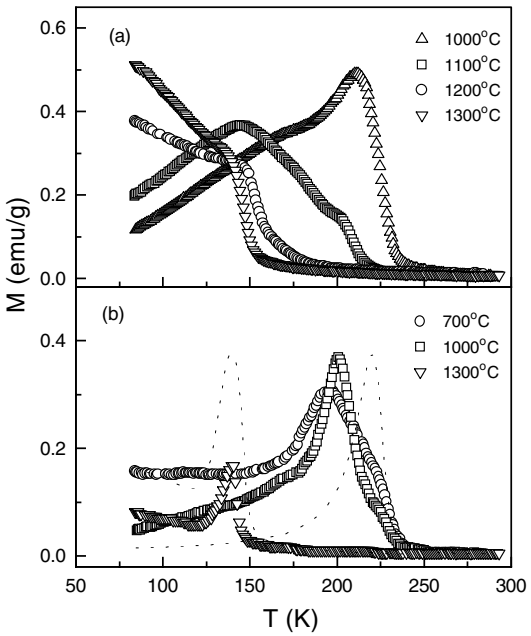

Figure 1. Comparison of the ZFC magnetization curves of $LaMn_{0.4}Co_{0.6}O_3$ samples prepared by ceramic (a) and low-temperature (b) methods and annealed at different temperatures. The magnetization curves of the two phases of $LaMn_{0.5}Co_{0.5}O_3$ are shown as dotted lines.

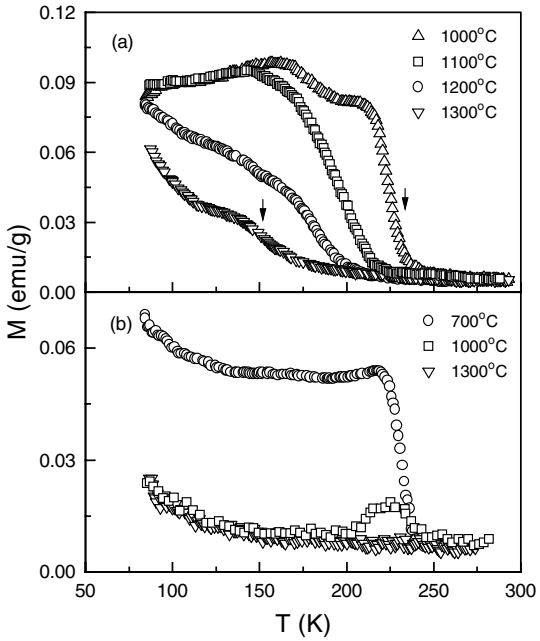

Figure 2. Comparison of the ZFC magnetization curves of $LaMn_{0.2}Co_{0.8}O_3$ samples prepared by ceramic (a) and low-temperature (b) methods and annealed at different temperatures. The arrows indicate the Curie temperatures of the two phases of $LaMn_{0.5}Co_{0.5}O_3$.

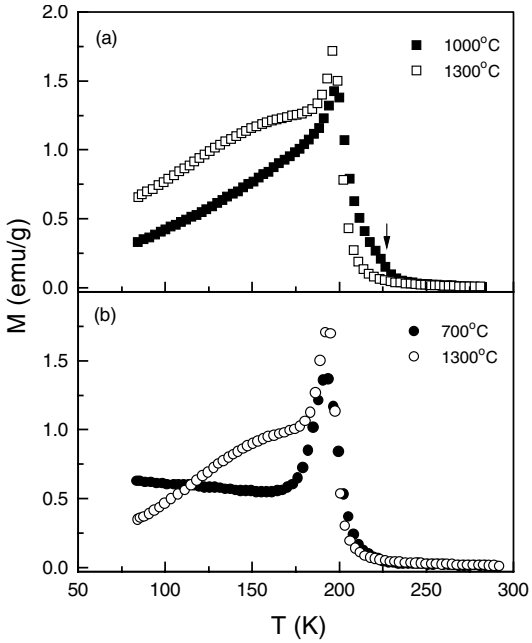

Figure 3. Comparison of the ZFC magnetization curves of $LaMn_{0.7}Co_{0.3}O_3$ samples prepared by ceramic (a) and low-temperature (b) methods and annealed at two different temperatures. The arrow indicates T_c for the high-T_c phase of $LaMn_{0.5}Co_{0.5}O_3$.

samples processed at lower temperatures show a small increase in magnetization at the T_c of the high-T_c phase of $LaMn_{0.5}Co_{0.5}O_3$, whereas no such mixed-phase behaviour is observed for the sample prepared by the low-temperature method. The two sets of samples show magnetic transitions at almost identical temperatures, at a temperature different to the T_cs of the two phases of $LaMn_{0.5}Co_{0.5}O_3$. Similar results were obtained for other compositions also for $x < 0.5$.

For compositions with $x < 0.5$, the transition temperatures are found to be independent of the processing temperature for low-temperature-synthesized samples and for the ceramic samples heated above 1100 °C. On the other hand, for $x > 0.5$, samples processed at different temperatures show weak and broad magnetic transitions. The magnetic transitions of these compositions processed at low temperatures are at the T_c (230 K) of the high-T_c phase for $x = 0.5$ and at the T_c (150 K) of the low-T_c phase for $x = 0.5$ when processed at high temperatures. Magnetic transitions are observed at intermediate temperatures (between 150 and 230 K) for the samples heated in the temperature range 700–1300 °C. When such a difference in the transition temperatures is observed for $x > 0.5$, for samples processed at different temperatures, the observed magnetic transition temperature for a particular composition processed at a given temperature cannot be considered as the true magnetic transition temperature of that composition.

The magnetization curves of some compositions, with $x < 0.5$ and $x > 0.5$, synthesized by the low-temperature method and heated at 1000 °C are compared in figure 4. For $x < 0.5$, single sharp magnetic transitions are observed at different temperatures and the Curie temperature varies with x. On the other hand, for $x > 0.5$, a weak magnetic transition with decreasing magnitude of magnetization with increasing x is observed at the T_c of the high-T_c phase for $x = 0.5$. This suggests that the $x > 0.5$ samples are not truly homogeneous

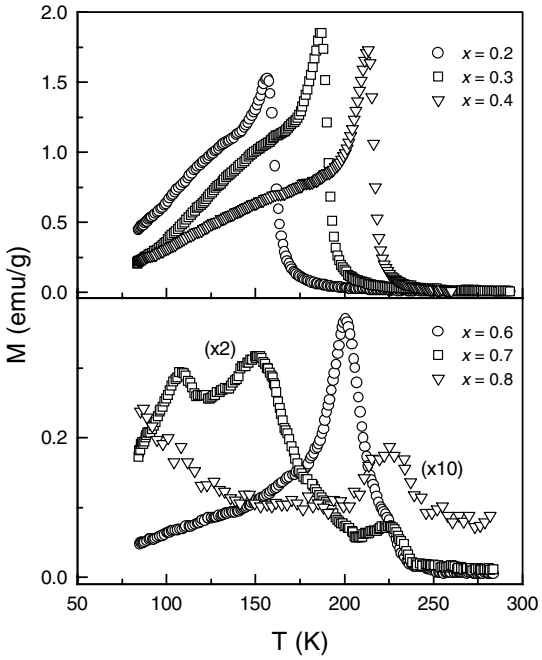

Figure 4. Magnetization curves for $x < 0.5$ and $x > 0.5$, synthesized by the low-temperature method and heated at 1000 °C. The curves for $x = 0.7$ and 0.8 are multiplied by 2 and 10, respectively, to show the weak magnetic transition at ∼230 K.

and the broad and multiple magnetic transitions suggest mixed-phase behaviour. This may be one of the reasons for the observation of multiple magnetic transitions for $LaMn_{0.25}Ni_{0.75}O_3$ (sample processed at 900 °C) with a weak ferromagnetic transition at a temperature close to the T_c of $LaMn_{0.5}Ni_{0.5}O_3$, but with a lower value of the magnetization (Blasco *et al* 2001), similar to that observed for $x = 0.7$ in figure 4.

The magnetic transition temperature as well as the magnetization at 82 K and 15 kOe, as a function of x in $LaMn_{1-x}Co_xO_3$, are shown in figure 5, for samples synthesized by the two different methods and heated to 1300 °C. For $x = 0.5$, the phase with the higher T_c and larger magnetization is processed at 700 °C. T_c is shown only up to $x = 0.5$, because of the mixed-phase behaviour and processing temperature dependence of the transition temperature for $x > 0.5$. The Curie temperatures obtained by Troyanchuk *et al* (2000) are also shown in the figure for comparison. The lower value of the maximum T_c in the present work (for $x = 0.5$) may be due to the difference in definition of the transition temperature. In the present work, the magnetic transitions are very sharp due to phase purity and the low magnetic fields used for the measurements, and T_c is taken as the temperature at which dM/dT is maximum. The T_cs are slightly higher at lower values of x for the low-temperature-synthesized samples and this may be due to the presence of excess Mn^{4+} as generally observed in the case of $La_{1-x}A_xMnO_3$. The Curie temperature increases up to $x = 0.5$, in contrast to the very low value of T_c for $x = 0.35$ observed by Troyanchuk *et al* (2000). Moreover, the same Curie temperature is observed for $0.4 \leqslant x \leqslant 0.6$ by these authors and this may be due to the mixed-phase behaviour, with a larger amount of the high-T_c phase of $LaMn_{0.5}Co_{0.5}O_3$ present in the samples due to insufficiently careful processing. Goodenough *et al* (1961) earlier observed a two-phase region for $x = 0.4$–0.6.

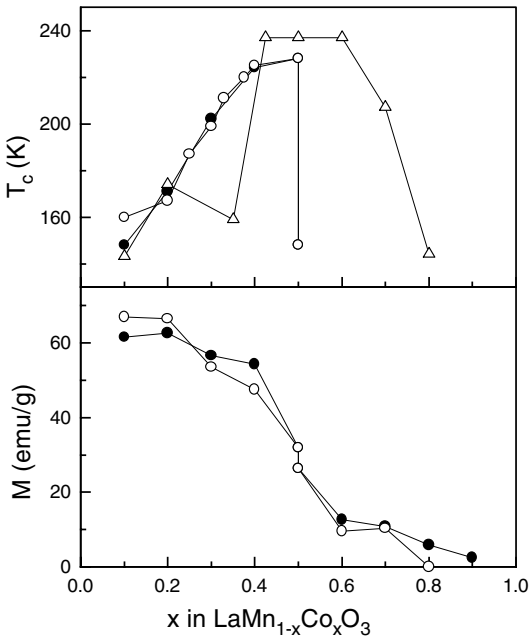

Figure 5. Variations of T_c and the magnetization (measured at 82 K and 15 kOe) as functions of x in $LaMn_{1-x}Co_xO_3$. ●: ceramic method; ○: low-temperature method; △: Troyanchuk *et al* (2000). For $x = 0.5$, T_c and M for the two phases of the compound are shown.

The present results show that in all samples for $x > 0.5$ in $LaMn_{1-x}Co_xO_3$, a fraction of one of the phases of $LaMn_{0.5}Co_{0.5}O_3$ is present depending on the processing temperature. The amount of this ferromagnetic phase decreases with increasing x and multiple magnetic transitions are observed when both of the phases for $x = 0.5$ are present together, showing an apparent value of magnetization for higher values of x due to mixed-phase behaviour. From the present results, it may be concluded that the Co-rich compositions ($x > 0.5$) in the $LaMn_{1-x}Co_xO_3$ series are not ferromagnetic, at least in the temperature range 80–300 K.

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