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LETTER TO THE EDITOR

The limiting value of x in the ferromagnetic compositions $La_{1-x}MnO_3$

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Abstract

Studies on a large number of compositions among the ferromagnetic self-doped manganites, $La_{1-x}MnO_3$, show that the ferromagnetic Curie temperature increases with x and reaches a maximum value for $x = 1/7$. T_c remains independent of x for $x \geqslant 1/7$ and the maximum value of the magnetization is obtained for $x = 1/8$. The presence of a second phase, due to Mn_3O_4, whose contribution increases with x, is observed in the powder x-ray diffraction patterns for $x > 1/8$ and the lattice parameters remain independent of x for $x > 1/8$. The results indicate that the limiting value of x or the extent of self-doping possible in $La_{1-x}MnO_3$ is $x = 1/8$.

One of the important aspects of the La–Mn–O perovskite system is the wide range of non-stoichiometry possible and the related intriguing properties. The magnetic and transport properties of the self-doped manganites $La_{1-x}MnO_3$ resemble those of the divalent-element-doped CMR manganites $La_{1-x}D_xMnO_3$ [1]. This is because self-doping or vacancy doping in the La site of the perovskite $LaMnO_3$ also produces Mn^{4+} in the lattice, as in the case of $La_{1-x}D_xMnO_3$, which can explain the evolution of the interesting magnetic and electrical properties, including the CMR of $La_{1-x}MnO_3$, in terms of the double-exchange interactions. Compared to the large number of studies on $La_{1-x}D_xMnO_3$, there are not many reports in the literature on the self-doped compositions. In particular, the phase diagram of $La_{1-x}MnO_3$ is not yet established. Some researchers, after studying a few compositions, have fixed the limiting value of x in $La_{1-x}MnO_3$ as 0.1, based on the observation of Mn_3O_4 as an impurity phase for $x > 0.1$ [2–4]. However, there are still many reports in the literature on studies of the self-doped compositions in the doping range $0 \leqslant x \leqslant 0.33$ [5–10]. In most of these studies, minor amounts of a second phase due to Mn_3O_4 are usually observed and this is ignored while discussing the properties of the highly doped compositions. Similarly, in most cases, the ferromagnetic Curie temperature remains constant for higher values of x and this is also

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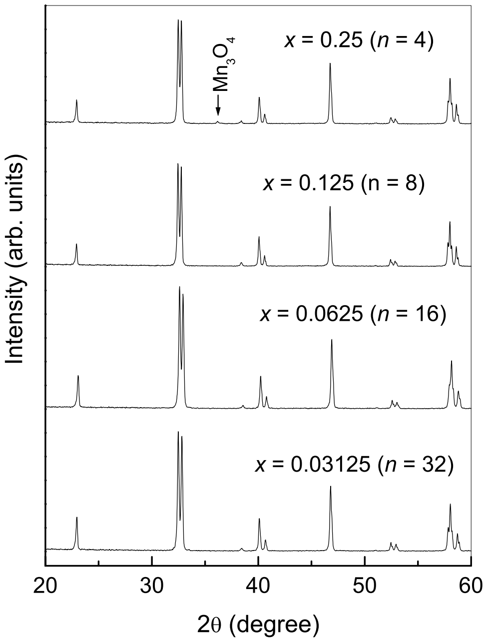

Figure 1. Powder XRD patterns of a few compositions in the $La_{1-x}MnO_3$ series ($n = 1/x$). The reflection marked by an arrow is due to Mn_3O_4.

ignored while discussing the properties of the compositions studied. To investigate whether the observation of a second phase due to Mn_3O_4 has any role in determining the limiting value of x (a fraction y of Mn_3O_4 means the absence of three times as much Mn or a larger La/Mn ratio in the perovskite than expected), we have studied the magnetic and structural characteristics of a number of compositions in the series $La_{1-x}MnO_3$.

Different compositions of $La_{1-x}MnO_3$ (the values of x were taken as fractions in the range $1/32 < x < 1/3$ and the number $n = 1/x$ is used when discussing the results) were synthesized by the ceramic method from the corresponding oxides La_2O_3 and MnO_2. The mixture of oxides, taken in the appropriate stoichiometric ratio, were initially heated at 1000 °C for 48 h with an intermediate grinding. The polycrystalline materials obtained were then heated at 1200 °C for 48 h with an intermediate grinding and then pressed into the form of a pellet, and finally heated at 1200 °C for 24 h. All compositions were prepared under identical conditions, as the properties and Mn^{4+} content are known to be sensitive to the preparation conditions. The final compounds were characterized by magnetic and powder x-ray diffraction (XRD) studies. The temperature variation of the magnetization was measured, using a vibrating sample magnetometer, after cooling the samples in zero magnetic field from room temperature to 80 K and then recording the magnetization at $H = 50$ Oe, while warming at a constant rate to 300 K (zero-field-cooled, ZFC, magnetization). The field dependence of the magnetization was measured, at 82 K, with a maximum applied field of 15 kOe. For all samples, magnetic saturation at this temperature was observed for $H > 5$ kOe. Powder XRD measurements were performed on a Philips 1830 powder x-ray diffractometer using Cu Kα radiation. The Mn^{4+} concentrations in the samples were estimated by the standard iodometric titration technique [11].

The powder XRD patterns of some compositions $La_{1-x}MnO_3$ are shown in figure 1. The diffraction patterns correspond to a rhombohedral perovskite structure, and all compositions

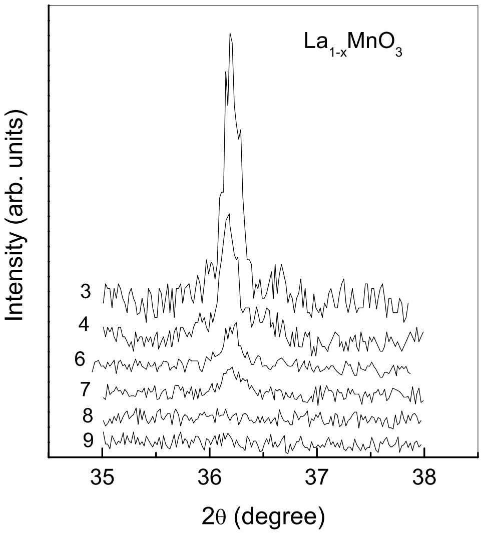

Figure 2. Powder XRD patterns of some compositions La$_{1-x}$MnO$_3$, recorded at a very slow scan rate, in the 2θ region where the most intense peak of Mn$_3$O$_4$ is observed. The numbers on the curves indicate the values of $n = 1/x$.

in the range $1/32 \leqslant x \leqslant 1/3$ showed reflections due to a rhombohedral perovskite lattice. Maignan *et al* [12] found that though the powder XRD patterns of their La$_{0.9}$MnO$_3$ samples could be indexed on the classical rhombohedral cell $R\bar{3}c$, the actual symmetry of the composition was found to be monoclinic with space group $I2/a$ and additional weak reflections due to this symmetry change were observed only in the electron diffraction patterns. No additional reflections due to monoclinic symmetry are observed in the present XRD patterns. The presence of an additional weak reflection at $2\theta = 36.2°$, due to Mn$_3$O$_4$, is indicated in the XRD pattern of the $x = 1/4$ sample. This weak reflection due to Mn$_3$O$_4$ is observed for all compositions for $x > 1/8$, and the intensity of this reflection is found to increase with increasing x above $x > 1/7$. The XRD patterns of some compositions, in the 2θ region where the most intense peak of Mn$_3$O$_4$ is observed, are compared in figure 2. The patterns shown in figure 2 were recorded at a very slow scan rate, as this procedure [13] is known to be highly efficient in detecting very small quantities of impurity phases. It may be seen that the peak due to Mn$_3$O$_4$ impurity suddenly appeared when $x > 1/8$. The rhombohedral angle, α, decreases initially with increasing x and then becomes almost constant for $x > 1/8$, as shown in figure 3. These results point to $x = 1/8$ possibly being the limiting value for vacancy doping in La$_{1-x}$MnO$_3$ and suggest that at larger values of x, the composition of the self-doped manganite is adjusted to this value of $x = 1/8$ and the excess Mn used is converted to Mn$_3$O$_4$. The increasing intensity of the reflection from Mn$_3$O$_4$ and the constancy of the lattice parameter with increasing x above 1/8 is in agreement with this conclusion.

Figure 4 shows the ZFC magnetization curves of the different La$_{1-x}$MnO$_3$ compositions. Some of the important features are: (a) a monotonic increase in the ferromagnetic transition temperature with increasing x up to $x = 1/7$ ($n = 7$ in the figure) and (b) increasing sharpness of the magnetic transition as x is increased. The trend in the variation of T_c as a function of x is shown in figure 5. T_c is defined as the temperature at which $\mathrm{d}M/\mathrm{d}T$ is maximum. T_c increases almost linearly with increasing value of x and a maximum $T_c = 251$ K is observed for $x = 1/7$, after which T_c remains almost constant. Similarly, the saturation magnetization,

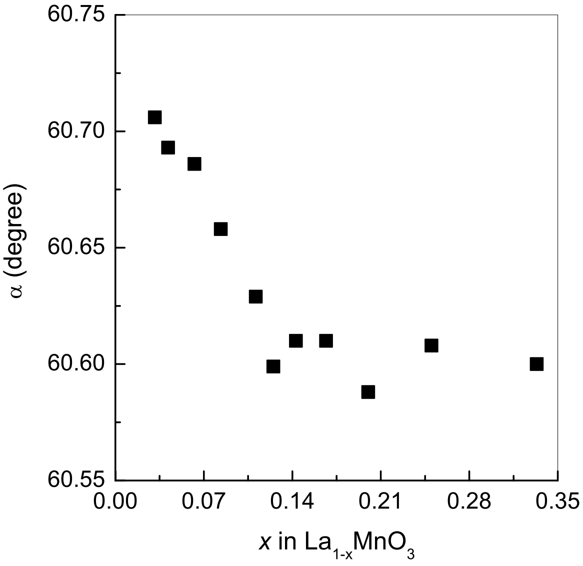

Figure 3. Variation of the rhombohedral angle, α, as a function of x in $La_{1-x}MnO_3$.

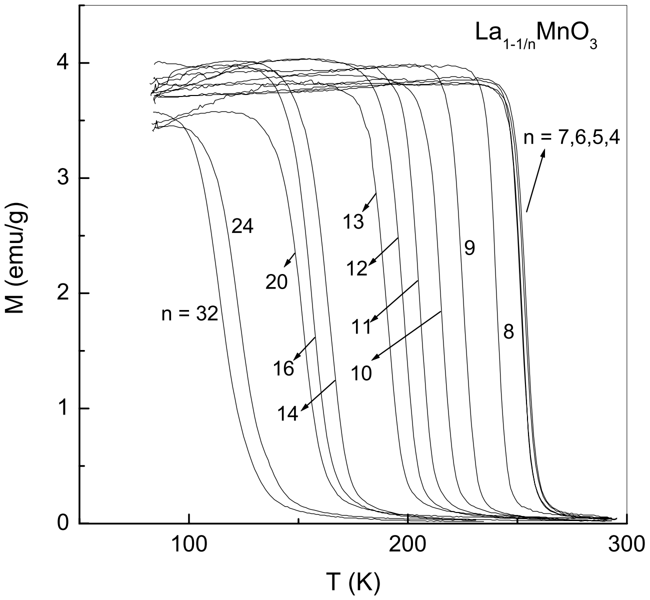

Figure 4. Temperature dependences of the ZFC magnetization of $La_{1-x}MnO_3$ ($H = 50$ Oe) for various values of x. The numbers on the curves indicate the values of $n = 1/x$.

measured at 82 K and a maximum applied field of 15 kOe, as a function of x, shows the same trend as in the case of T_c, as shown in the figure. The magnetization increases with increasing x until $x = 1/8$ and then decreases and becomes constant. The lower values of M for $x > 1/8$ may be due to the presence of the impurity phase Mn_3O_4 which is not ferromagnetic at 82 K.

The Mn^{4+} concentrations in the different compositions, as a function of x, are compared in figure 5 with the expected Mn^{4+} concentration assuming the formula $La_{1-x}MnO_3$.

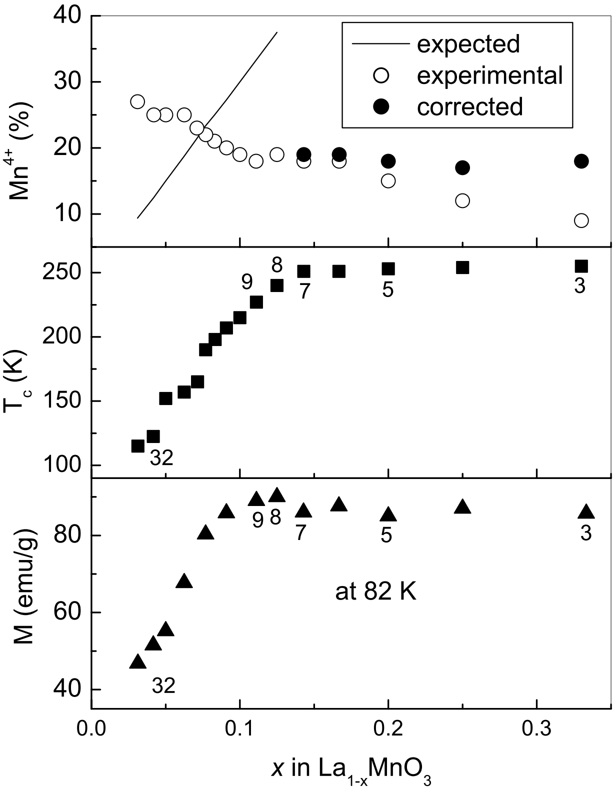

Figure 5. The variation of the Mn^{4+} concentration (upper panel), Curie temperature (middle panel), and saturation magnetization at 82 K (lower panel), as a function of x in $La_{1-x}MnO_3$. The numbers indicate the values of $n = 1/x$.

The theoretical Mn^{4+} concentration increases linearly from 0 to 100% for $x = 0$–$1/3$. On the other hand, the experimentally determined Mn^{4+} concentration, calculated neglecting the Mn_3O_4 content in the samples for $x > 1/8$, decreases continuously with increasing x, and a very low value of 9% Mn^{4+} content is obtained for $x = 1/3$. However, it is known that at lower Mn^{4+} contents, the crystal structure is orthorhombic for $La_{1-x}MnO_3$ [10]. Therefore, such a low Mn^{4+} concentration is not possible for $x = 1/3$, considering the rhombohedral structure of this compound. Assuming that $x = 1/8$ is the limiting value of x and Mn_3O_4 is formed in equivalent amounts for higher values of x, the corrected Mn^{4+} concentration in the compositions for $x \geqslant 1/7$ is found to become almost constant, approximately 18%, as shown in the figure as corrected values. This high value of the Mn^{4+} content supports the rhombohedral structure of these compositions. It may be noted that for La vacancies $x < 1/14$, the experimental Mn^{4+} concentration is much larger than the theoretical values and vice versa for $x > 1/14$.

The powder XRD studies showed the presence of unreacted Mn, in the form of Mn_3O_4, and lattice parameters independent of x for values of $x > 1/8$, and magnetic measurements show the maximum value of magnetization for $x = 1/8$ and the maximum T_c for $x = 1/7$, in $La_{1-x}MnO_3$. These results lead to the conclusion that $x = 1/8$ is the limiting value of x. The value of $x = 1/8$ corresponds to an ordered structure in which one La vacancy is present at the corner of the simple perovskite unit cell, which is shared by eight unit cells, as shown in figure 6

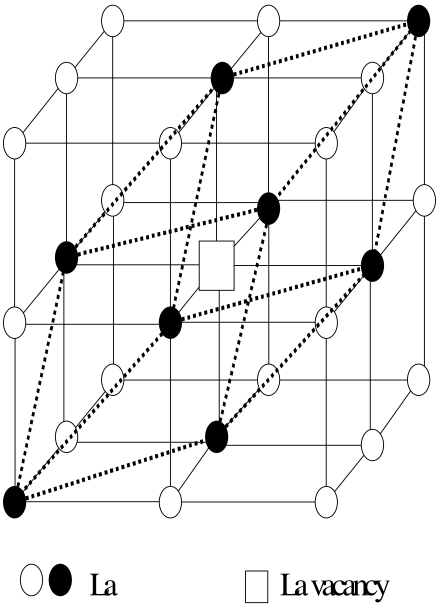

Figure 6. The structure of $La_{7/8}MnO_3$ showing one La vacancy for eight B-type basic perovskite unit cells. The actual rhombohedral unit cell is also shown for comparison.

for a B-type perovskite-unit-cell lattice. That is, every rhombohedral perovskite unit cell in the lattice contains one La vacancy. Increasing the La vacancy content beyond this limit may collapse the perovskite structure and, therefore, $La_{1-x}MnO_3$ with a limiting value of $x = 1/8$ is formed if the initial La/Mn ratio is kept below 0.875 and excess MnO_2 remains unreacted, which is observed as Mn_3O_4 in the XRD patterns. $x = 1/8$ corresponds to a maximum possible concentration of 37.5% Mn^{4+} in $La_{1-x}MnO_3$. Interestingly, the maximum T_c in the divalent-ion-substituted manganites is observed for the composition $La_{5/8}D_{3/8}MnO_3$ [14], with a possible amount of Mn^{4+} of 37.5%.

The values of the experimental Mn^{4+} concentration for $x < 1/14$ being larger than the expected values considering the formula $La_{1-x}MnO_3$ needs further consideration. Such values of the Mn^{4+} content, larger than expected, are possible only if there are excess oxygens in the structure, as expressed by the formula $La_{1-x}MnO_{3+\delta}$. However, it is known that the perovskite structure cannot accommodate excess oxygen. Therefore, to accommodate excess Mn^{4+}, the only way is to have Mn deficiency in the compounds, as given by the formula $La_{1-x}Mn_{1-y}O_3$. The actual compositions, as calculated based on the values of x and the observed Mn^{4+} concentrations, are shown in table 1. For $x = 1/16$, the composition obtained, $La_{0.937}Mn_{0.981}O_3$, is comparable to the single-crystal composition $La_{0.936}Mn_{0.982}O_3$, reported by McCarroll *et al* [15], except that T_c for the single-crystal sample is larger than that in the present study on polycrystalline samples. The higher T_c of single crystals may be due to the ordering of La and Mn vacancies in the lattice for $x = 1/16$ $(1/8 \times 2)$. On the other hand, for values of $x > 1/14$, the Mn^{4+} concentrations are less than that expected and therefore the formula of the compound can be represented as $La_{1-x}MnO_{3-\delta}$. This indicates that Mn deficiency is most favoured to stabilize the perovskite structure of $La_{1-x}MnO_3$ at lower values of x and oxygen deficiency is favoured at higher values of x. Similar Mn deficiencies at low values of x have been observed by earlier researchers [3, 8, 9]. Ferris *et al* [16], from Rietveld refinement analysis, have shown that the Mn occupancy is less than 1 in the few $x < 0.1$ compositions studied.

Table 1. Actual compositions for different values of x in $La_{1-x}MnO_3$, based on the experimental Mn^{4+} concentrations.

x	Mn^{4+} ($\pm 1\%$)	Composition	La/Mn
0.031	27	$La_{0.969}Mn_{0.946}O_3$	1.024
0.042	25	$La_{0.958}Mn_{0.964}O_3$	0.994
0.05	25	$La_{0.950}Mn_{0.969}O_3$	0.980
0.062	25	$La_{0.937}Mn_{0.981}O_3$	0.955
0.071	23	$La_{0.929}Mn_{0.996}O_3$	0.933
0.077	22	$La_{0.923}MnO_{2.99}$	0.923
0.083	21	$La_{0.917}MnO_{2.98}$	0.917
0.091	20	$La_{0.909}MnO_{2.96}$	0.909
0.10	19	$La_{0.900}MnO_{2.94}$	0.900
0.111	18	$La_{0.889}MnO_{2.92}$	0.889
0.125	18	$La_{0.875}MnO_{2.90}$	0.875

It may be seen that the Mn deficiency is larger than the La vacancy at very low values of x. The concept of Mn deficiency, at low values of x, can explain the broadness of the ferromagnetic transitions. The deficiency of Mn will create ferromagnetic clusters. The larger the Mn deficiency, the larger the size distribution of such clusters, and the broad magnetic transition may be considered as a sum of the magnetic transitions of individual ferromagnetic clusters of varying size. This can also explain the increasing sharpness of the magnetic transition as x is increased, due to decreasing Mn deficiency.

The present studies indicate that the limiting value of x or the extent of self-doping possible in $La_{1-x}MnO_3$ is $x = 1/8$, which corresponds to an ordered structure.

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