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The origin of ferromagnetism in $\text{LaMnO}_{3+\delta}$

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Abstract

Studies on different $\text{LaMnO}_{3+\delta}$ samples have revealed that there is no correlation between the magnetic properties and large values of δ (Mn^{4+} content) or the rhombohedral structure of the material. From powder x-ray diffraction studies, it was found that those $\text{LaMnO}_{3+\delta}$ samples showing well defined ferromagnetic transitions are of mixed-phase character: an $\text{La}_{1-x}\text{MnO}_{3+\delta}$ phase and minor amounts of an La-rich phase. The results give sufficient evidence to conclude that the self-doped, La-deficient, phases formed are responsible for ferromagnetism in $\text{LaMnO}_{3+\delta}$.

1. Introduction

Magnetic and electrical properties of the non-stoichiometric compound $\text{LaMnO}_{3+\delta}$ have been studied extensively for the past five decades [1], after Jonker and Van Santen [2], in 1950, first observed the effect of Mn^{4+} in determining the magnetic properties of LaMnO_3 . In the La–Mn–O perovskite system, the stoichiometric compound LaMnO_3 , in which Mn is present in its trivalent form, Mn^{3+} , is an antiferromagnetic material. The antiferromagnetic transition at $T_N \approx 100\text{--}140$ K is reported in the literature [3–7], with some of the samples containing small amounts of Mn^{4+} (0–10%). Generally, it is not possible to obtain the compound in stoichiometric form under the general preparation conditions (heating oxides of La and Mn in air), due to the tendency of Mn to form tetravalent ions, so the formula is generally written as $\text{LaMnO}_{3+\delta}$, which takes care of the presence of Mn^{4+} ions. Jonker and Van Santen [2] had commented that the tendency to take up excess oxygen might be an indication of a region of mixed crystals extending from LaMnO_3 to $\text{La}_{2/3}\text{MnO}_3$. As the perovskite structure cannot accommodate excess oxygen, there have been attempts to elucidate the structure and composition of the non-stoichiometric compound. Tofield and Scott [8], in 1974, from neutron diffraction studies, found that the actual composition of $\text{LaMnO}_{3.12}$ is $\text{La}_{0.94}\text{Mn}_{0.98}\text{O}_3$ ($\approx \text{La}_{0.96}\text{MnO}_3$), which is an La-deficient compound. Later on, Van Roosmalen *et al* [9], in 1994, from refinement of their neutron diffraction data on $\text{LaMnO}_{3+\delta}$, argued that

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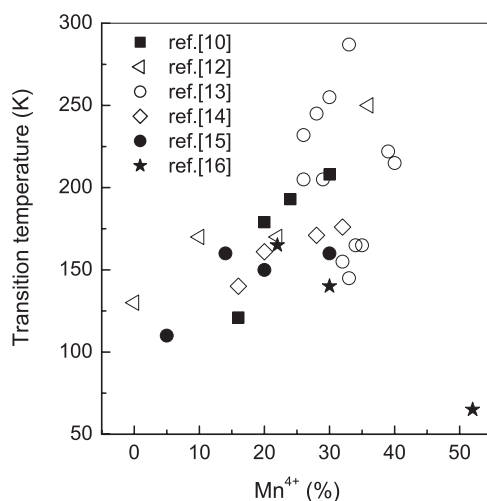


Figure 1. Comparison of the transition temperature of $\text{LaMnO}_{3+\delta}$ as a function of Mn^{4+} content, from different reports in the literature.

the studied composition contains equal amounts of La and Mn deficiency (La and Mn in 1:1 ratio), $\text{La}_{1-y}\text{Mn}_{1-y}\text{O}_3$, though they obtained a lower residual factor for unequal La and Mn deficiency as found by Tofield and Scott.

Studies on $\text{LaMnO}_{3+\delta}$ gained momentum after the discovery of CMR in $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ [1] and there are many reports, in the recent literature, on the studies of the electronic and magnetic properties of the non-stoichiometric compound. Ferromagnetism and metal-insulator transition are observed in $\text{LaMnO}_{3+\delta}$ with high Mn^{4+} content and this has been explained in terms of the double exchange interactions between Mn^{3+} and Mn^{4+} ions, as in the case of the divalent-ion-substituted CMR manganites. It is generally considered that the ferromagnetic Curie temperature increases with increasing Mn^{4+} content in $\text{LaMnO}_{3+\delta}$, due to the increasing strength of the double exchange interactions [10].

One of the important aspects of the La–Mn–O perovskite system is the wide range of non-stoichiometry and the related interesting properties. The self-doped, La-deficient, compositions $\text{La}_{1-x}\text{MnO}_{3+\delta}$ are ferromagnetic because of the presence of Mn^{4+} ions. The ferromagnetic transition temperature increases with increasing x or with increasing Mn^{4+} content for a particular value of x [11, 12]. The latter observation (increasing T_c with Mn^{4+} content) is similar to that also observed for $\text{LaMnO}_{3+\delta}$. Both $\text{LaMnO}_{3+\delta}$ and $\text{La}_{1-x}\text{MnO}_{3+\delta}$ are reported to be orthorhombic for lower Mn^{4+} concentrations (<20%) and rhombohedral for higher Mn^{4+} content [12].

A comparison of the data reported on $\text{LaMnO}_{3+\delta}$, in the literature, suggests that the general assumption of the Curie temperature increasing with Mn^{4+} concentration is not true. The transition temperature as a function of Mn^{4+} content, observed by different researchers [10, 12–16], is compared in figure 1. Verelst *et al* [13] found varying transition temperatures (the metal-insulator transition temperatures are reported; the ferromagnetic T_c s are noted to be 10–15 K higher) for $\text{LaMnO}_{3+\delta}$ samples synthesized by different methods and having identical Mn^{4+} concentrations. For example, for compositions containing 33% Mn^{4+} , transition temperatures of 145, 167 and 287 K are reported for samples synthesized by three different low-temperature methods and higher transition temperatures are found for low- Mn^{4+} -containing compositions. Similarly, Ritter *et al* [15] have found a non-monotonic change in the Curie temperature of $\text{LaMnO}_{3+\delta}$ with increasing Mn^{4+} content. $T_c = 125$ K

is reported by Ranno *et al* [6] for a composition containing 31% of Mn^{4+} . Contrary to the general observations, there are also reports of continuously decreasing Curie temperature with increasing Mn^{4+} content [16]. Karavay [17] found that, with the decrease in the degree of crystal lattice distortions, the ferromagnetic phase content increases at the expense of the antiferromagnetic phase; Hauback *et al* [18] found that for $\delta = 0.08$ (16% Mn^{4+}) the structure of the compound is orthorhombic with a ferromagnetic transition at 125 K, whereas when the structure is rhombohedral with 30% Mn^{4+} ions the compound is not ferromagnetic. These and many other results suggest that no two reports agree on the Curie temperatures of $\text{LaMnO}_{3+\delta}$ containing identical Mn^{4+} contents and the Curie temperature depends on processing conditions. Higher transition temperatures are generally reported for samples synthesized at lower temperatures. This implies that reasons other than the Mn^{4+} concentration or crystal structure may be responsible for ferromagnetism in $\text{LaMnO}_{3+\delta}$.

To understand the origin of ferromagnetism and to investigate the absence of ferromagnetic ordering in certain compositions despite the right structure and Mn^{4+} concentrations, we have studied the magnetic properties of $\text{LaMnO}_{3+\delta}$ in detail. Studies on the magnetic properties and x-ray diffraction data of the compounds gave convincing evidence for the fact that $\text{LaMnO}_{3+\delta}$ is in fact La-deficient compositions and the observed properties are those of $\text{La}_{1-x}\text{MnO}_{3+\delta}$.

2. Experiment

$\text{LaMnO}_{3+\delta}$ was prepared by the ceramic method from La_2O_3 (preheated at 1000 °C for 12 h) and MnO_2 or Mn_2O_3 , taking La and Mn in a 1:1 stoichiometric ratio. Some compositions of $\text{La}_{1-x}\text{MnO}_{3+\delta}$ were also prepared from MnO_2 . The compounds were characterized by powder x-ray diffraction (XRD), oxygen (Mn^{4+} content) analysis and magnetic measurements. Temperature variation of 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. Mn^{4+} concentration was determined by the standard iodometric titration procedure [2, 8].

3. Results and discussion

The temperature dependence of the magnetization of LaMnO_3 , synthesized from MnO_2 (LMO1) and Mn_2O_3 (LMO2) and heated at 1000 °C (sample A) and 1200 °C (sample B) for 48 h each, is shown in figure 2. The Mn^{4+} concentrations in the two samples A and B of LMO1 were found to be 33 and 26%, respectively. However, there are no well defined magnetic transitions for these two samples, as expected from the high Mn^{4+} concentrations, as shown in figure 1. The magnetization at low temperatures is larger for sample A compared with that of sample B. On the other hand, well defined magnetic transitions are observed for the two samples of LMO2 heated at 1000 (A) and 1200 °C (B), below 200 and 150 K, respectively. Both these samples showed an Mn^{4+} concentration of 26%. The magnitude of magnetization is almost five times larger for LMO2 when compared with that of LMO1. From the results on LMO1 and LMO2, it is obvious that the amount of Mn^{4+} is not the controlling factor in determining the ferromagnetic properties of $\text{LaMnO}_{3+\delta}$.

The powder XRD patterns of the two samples (A and B) of LMO1 and LMO2 are shown in figures 3 and 4, respectively. All patterns are due to a rhombohedral perovskite structure. This is expected because of the high Mn^{4+} content in the samples, though there are no ferromagnetic transitions in LMO1. Previous studies have shown that $\text{LaMnO}_{3+\delta}$ adopts a rhombohedral structure for $\delta > 0.1$ (>20% Mn^{4+}). Two very weak reflections close to $2\theta = 28^\circ$ are observed for LMO1A (indicated by arrows in figure 3) on close examination of the powder

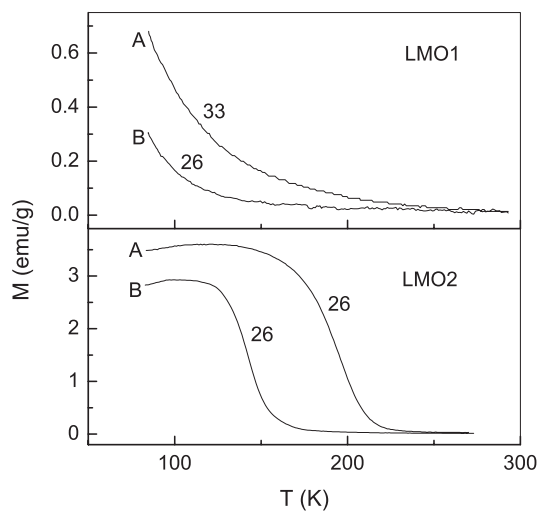


Figure 2. Temperature variation of the magnetization ($H = 50$ Oe) of LMO1 and LMO2, heated at 1000°C (A) and 1200°C (B). The numbers on the curves are the Mn^{4+} concentrations of the particular sample.

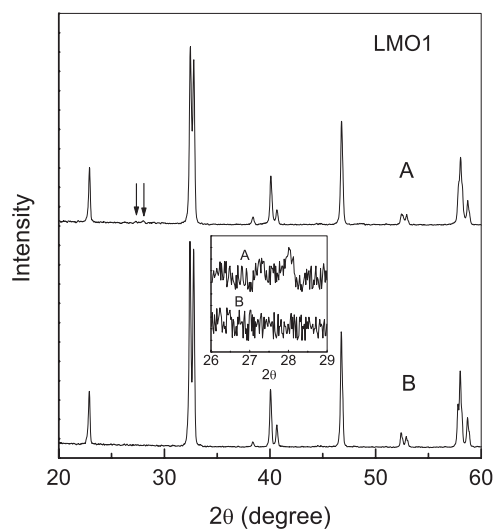


Figure 3. Powder XRD patterns of LMO1, heated at 1000°C (A) and 1200°C (B). The arrows indicate weak reflections due to $\text{La}(\text{OH})_3$. Inset: expanded patterns clearly showing reflections due to $\text{La}(\text{OH})_3$ in LMO1A.

patterns of LMO1A and LMO1B (samples heated at 1000 and 1200°C). This region of the XRD pattern of the two samples is shown in the inset of figure 3, which clearly shows two weak reflections in sample A and no reflections in this 2θ region for sample B. These two reflections are not expected for the rhombohedral perovskites and have been identified as those of the two most intense reflections of $\text{La}(\text{OH})_3$ (see figure 5). For LMO2A, showing a clear ferromagnetic transition below 200 K, these two reflections are of larger intensity (figure 4) with some other additional reflections also, which are again due to $\text{La}(\text{OH})_3$. Though no additional reflections

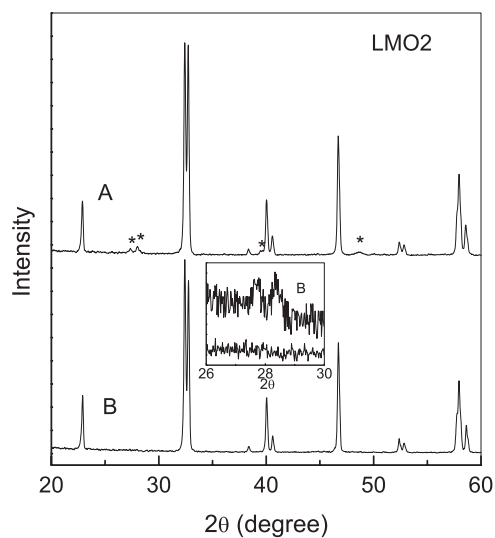


Figure 4. Powder XRD patterns of LMO2, heated at 1000 (A) and 1200 °C (B). Reflections marked by * are due to $\text{La}(\text{OH})_3$. Inset: comparison of the pattern of LMO2B recorded at the normal and a slow scan rate, showing weak reflections due to $\text{La}(\text{OH})_3$ in the slow scanned spectra of the sample.

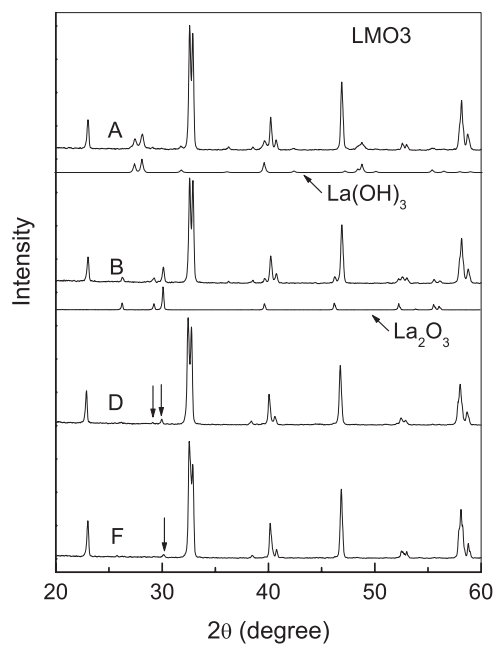


Figure 5. Powder XRD patterns of LMO3, initially heated at 1000 °C for 24 h (A) and then for different durations: at 1000 °C 2 h (B) and 24 h (D) and at 1200 °C for 48 h (F). The arrows indicate the reflections due to La_2O_3 .

are observed for LMO2B, the two weak reflections could be detected when the diffraction pattern was recorded at a very slow scan rate [19]. This is shown in the inset of figure 4 for LMO2B, which shows a ferromagnetic transition below 150 K.

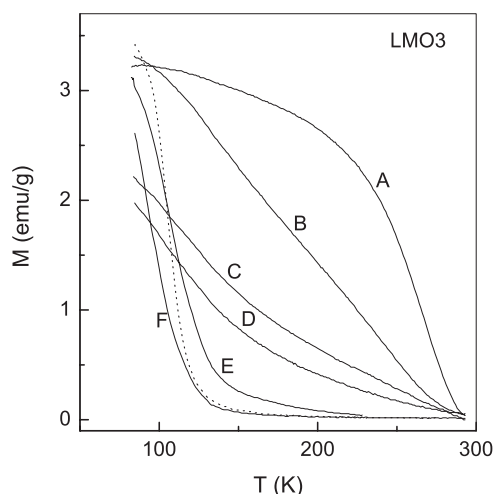
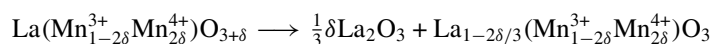


Figure 6. Temperature variation of the magnetization ($H = 50$ Oe) of LMO3, initially heated at 1000°C for 24 h (A) and then for different durations: 2 h (B), 6 h (C), 24 h (D) and at 1200°C for 24 h (E) and 48 h (F). The dotted line is the magnetization curve of $\text{La}_{0.97}\text{MnO}_{3+\delta}$.

Tofield and Scott [8] had earlier argued that perfect Mn and oxygen stoichiometry can be maintained at the expense of vacancies at the La site, i.e. the formation of $\text{LaMnO}_{3+\delta}$ can be visualized as



but the authors could not detect any second phase in the Debye–Scherrer x-ray photograph. However, from the refinement of the structure of $\text{LaMnO}_{3.12}$ from neutron diffraction data, the authors found that the true composition is $\text{La}_{0.94}\text{Mn}_{0.98}\text{O}_3$. It was reasoned that the failure to detect the presence of La_2O_3 in the sample was either due to the small amount of this phase, which is below the limit of detection of the instrument, or that during exposure of the sample to the atmosphere the moisture-sensitive La_2O_3 is converted to the poorly crystalline hydroxide $\text{La}(\text{OH})_3$, which will be difficult to detect. In the present study, we could detect the presence of small amounts of $\text{La}(\text{OH})_3$ in some of the samples.

The additional reflections due to $\text{La}(\text{OH})_3$ in the XRD patterns of $\text{LaMnO}_{3+\delta}$ (in both LMO1 and LMO2) indicate that not all La is reacted to form a 1:1 composition, even if the starting ratio of La and Mn is 1:1, and the compounds obtained are La deficient, i.e. $\text{La}_{1-x}\text{MnO}_{3+\delta}$. The samples showing higher magnetic transition temperatures have larger amounts of unreacted La and therefore the deficiency of La is larger in these samples. It is already known that the Curie temperature increases with increasing La deficiency in $\text{La}_{1-x}\text{MnO}_{3+\delta}$.

To confirm whether it is La deficiency in the samples which makes $\text{LaMnO}_{3+\delta}$ ferromagnetic and to see whether the results are reproducible, another sample of LaMnO_3 was made from MnO_2 with controlled heating. Powder XRD and magnetic measurements were made immediately after cooling the samples in the furnace to room temperature, to look for the presence of La_2O_3 in the samples.

The powder XRD patterns of some of the second set of LaMnO_3 samples prepared from MnO_2 (LMO3) and heated at different temperatures are shown in figure 5 and the magnetization curves of these samples are shown in figure 6. The La_2O_3 – MnO_2 mixture taken in the required stoichiometric ratio (La:Mn = 1:1) was initially heated at 1000°C for 24 h and stored in a

sample container for three weeks (sample A). This sample was further heated at 1000 °C for 2 h (sample B), 6 h (sample C), 24 h (sample D) and then finally at 1200 °C for 24 h (sample E) and 48 h (sample F). The powder XRD and magnetic measurements were made on sample A, and on other samples immediately after each heating schedule. For all samples, the powder patterns are found to be due to a rhombohedral perovskite structure, as in the case of LMO1. For both LMO3A and LMO3B, many weak additional reflections are observed in the XRD patterns. A comparison with the powder patterns of $\text{La}(\text{OH})_3$ and La_2O_3 indicates that all the strong reflections of $\text{La}(\text{OH})_3$ are found in the pattern of LMO3A and the reflections due to La_2O_3 are found in the pattern of LMO3B (XRD pattern recorded immediately after cooling the sample in a furnace). This indicates that a small portion of La_2O_3 is not reacted initially and this is converted to $\text{La}(\text{OH})_3$ during the course of time. The amount of unreacted La_2O_3 is decreased after each heating. After heating the sample at 1200 °C for a long time (sample F), the presence of La_2O_3 is still observed, in very small amounts, in the XRD pattern.

The magnetization curve of LMO3A shows a broad ferromagnetic transition close to 300 K (figure 6). Such a high transition temperature is expected because some of the La is not reacted and therefore the compound obtained is highly La-deficient $\text{La}_{1-x}\text{MnO}_{3+\delta}$. Samples B, C and D show a continuous increase in magnetization as the temperature is decreased, with no well defined magnetic transitions. A clear magnetic transition is observed for sample F below 120 K and the Mn^{4+} concentration in this sample was estimated as 28%. This magnetic transition temperature is less than that observed for LMO2B with 26% of Mn^{4+} (150 K) and having the same rhombohedral structure. Moreover, the low Curie temperature of this sample (LMO3F) is contrary to the various reports in the literature on the ferromagnetic properties of $\text{LaMnO}_{3+\delta}$ having a rhombohedral structure and high Mn^{4+} content.

Estimation of the true composition of sample F, from the relative intensities of the peak due to La_2O_3 and the most intense reflection of the perovskite phase, gave the value of $x \approx 0.03$ in $\text{La}_{1-x}\text{MnO}_{3+\delta}$. The magnetization curve of a sample of $\text{La}_{0.97}\text{MnO}_{3+\delta}$ processed under identical conditions and having a comparable Mn^{4+} concentration of 29% showed a magnetic transition at ~ 120 K similar to that of sample F (large values of Mn^{4+} concentrations are known for low values of x in $\text{La}_{1-x}\text{MnO}_{3+\delta}$ [12, 20]), further confirming that this $\text{LaMnO}_{3+\delta}$ sample is an La-deficient composition.

Generally, high Mn^{4+} concentration and high Curie temperatures are reported for $\text{LaMnO}_{3+\delta}$ samples synthesized by low-temperature methods [10, 13, 18]. In one such preparation (LMO4) of the 1:1 compound by the method reported by Hauback *et al* [18], the presence of small amounts of the La-rich phase, $\text{La}(\text{OH})_3$, was observed in the powder XRD pattern for a sample heated at 1000 °C and showing a ferromagnetic transition below 200 K, as shown in figure 7. When the compounds are synthesized by low-temperature methods, the particle size will be very small and it will be difficult to observe small amounts of impurity phases from the powder XRD patterns, unless due care is taken. The presence of small amounts of impurity phases may not be observed in the powder XRD pattern because of line broadening due to their smaller particle size or if the XRD patterns are recorded after the conversion of unreacted La_2O_3 to less crystalline $\text{La}(\text{OH})_3$. This is the possible reason why impurity phases are not generally detected in low-temperature-synthesized $\text{LaMnO}_{3+\delta}$ samples showing higher magnetic transition temperatures.

The temperature variation of magnetization of the four $\text{LaMnO}_{3+\delta}$ samples, heated at 1200 °C, is compared in figure 8. It is interesting to note that the final compounds obtained in the two series, synthesized from MnO_2 (LMO1B and LMO3F), have different magnetic characteristics. A clear magnetic transition for LMO3F, with a higher value of magnetization, is observed when compared with that of LMO1B. Similarly, though the Mn^{4+} content is identical for LMO1B and LMO2B, no magnetic transition is observed for the former whereas a clear

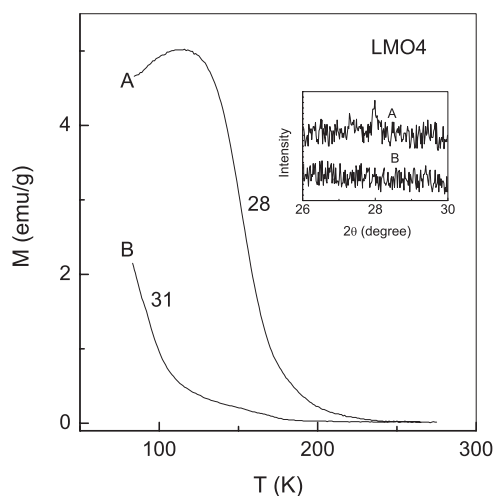


Figure 7. Temperature variation of the magnetization ($H = 50$ Oe) of LMO4, synthesized by a low-temperature method and heated at 1000 (A) and 1200 °C (B) for 24 h. Inset: the powder XRD patterns showing the impurity phase due to unreacted La in sample A. The numbers on the curves indicate the Mn^{4+} content.

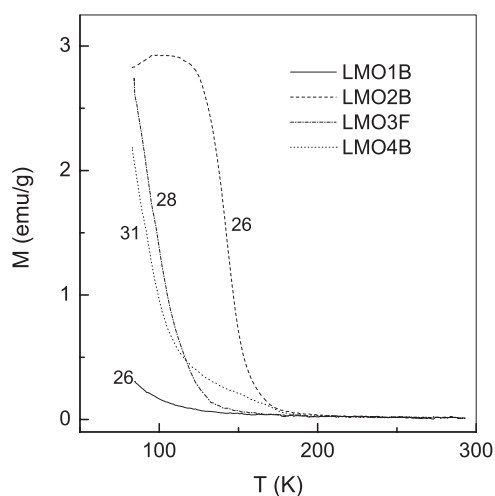


Figure 8. Comparison of the temperature variation of the magnetization ($H = 50$ Oe) of the four $\text{LaMnO}_{3+\delta}$ samples, heated at 1200 °C. The numbers indicate Mn^{4+} concentrations.

magnetic transition below 160 K is observed for the latter. These observations indicate the fact that it is not possible to reproduce the results on $\text{LaMnO}_{3+\delta}$ and this may be attributed to the formation of $\text{La}_{1-x}\text{MnO}_{3+\delta}$ with different small x values in the final products. Higher Curie temperatures are observed for $\text{La}_{1-x}\text{MnO}_{3+\delta}$, even for small values of x [20]. In the La–Mn–O perovskite system, the different compositions, $\text{LaMnO}_{3+\delta}$ and $\text{La}_{1-x}\text{MnO}_{3+\delta}$, are generally prepared by the same methods and under identical conditions, by taking the starting components in the appropriate stoichiometric ratio. This implies that La and Mn oxides can react initially to form any composition in $\text{La}_{1-x}\text{MnO}_{3+\delta}$ even if the components are taken in the 1:1 ratio, and the present results indicate that it is easier to obtain $\text{La}_{1-x}\text{MnO}_{3+\delta}$ than

$\text{LaMnO}_{3+\delta}$. This also implies that there is no control over the formation of $\text{LaMnO}_{3+\delta}$, and $\text{La}_{1-x}\text{MnO}_{3+\delta}$ with any value of x can form initially. The final small value of x is determined by this reaction and therefore cannot be reproduced. Hence the magnetic characteristics will be different for different samples.

The present results give evidence for the fact that the oxygen-excess $\text{LaMnO}_{3+\delta}$ is in fact La-deficient compositions, $\text{La}_{1-x}\text{MnO}_{3+\delta}$, as commented by Jonker and Van Santen [2] and suggested by Tofield and Scott [8], and not $\text{La}_{1-y}\text{Mn}_{1-y}\text{O}_3$ as suggested by Van Roosmalen *et al* [9]. The origin of ferromagnetism in $\text{LaMnO}_{3+\delta}$ is, therefore, due to the formation of $\text{La}_{1-x}\text{MnO}_{3+\delta}$ compositions in the samples, which are ferromagnetic due to the presence of Mn^{4+} ions.

Acknowledgments

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