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LETTER TO THE EDITOR

Does the LaMnO$_3$ phase accept Ce-doping?

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Abstract. Recent reports, that the samples of nominal compositions, La$_{1-x}$Ce$_x$MnO$_3$, form single-phase compounds with orthorhombically distorted perovskite structure, are questionable. Our studies on the sample of nominal composition, La$_{0.7}$Ce$_{0.3}$MnO$_3$, and careful analysis of the structural data available in the literature, suggest that the above mentioned samples actually form multi-phase mixtures comprising hole doped lanthanum deficient lanthanum manganate phases and cerium oxide (CeO$_2$).

Recently a number of reports [1–6] on the studies of the magnetic, electrical and structural behaviours of the samples of nominal compositions, La$_{1-x}$Ce$_x$MnO$_3$, have been published. Das and Mandal [1–2] and Mandal and Das [3], reported for the first time that the sample, La$_{0.7}$Ce$_{0.3}$MnO$_3$, formed a single-phase compound with GdFeO$_3$-type structure and showed ferromagnetic and insulator-to-metal (I–M) transitions. Philip and Kutty [6] reported a detailed study on the structural, magnetic and electrical properties of the samples of nominal compositions, La$_{1-x}$Ce$_x$MnO$_3$, with a wide range of compositions ($0.05 \leqslant x \leqslant 0.8$). The observations of ferromagnetic and I–M transitions in the La$_{0.7}$Ce$_{0.3}$MnO$_3$ sample have been explained by Das and Mandal [1–2] on the basis of double exchange (DE) type interaction between Mn$^{3+}(t_{2g}^3 e_g^1)$ and Mn$^{2+}(t_{2g}^3 e_g^2)$. According to them, the Mn^{2+} ions are generated in this compound as a result of the substitution of tetravalent Ce ions for the trivalent La ions, which at a constant oxygen content level leads to doping of electrons. Thermo-power studies on this compound by the same authors, however, showed that it is not in an electron doped state but in a hole doped state. The hole-like nature of the carriers in the La$_{1-x}$Ce$_x$MnO$_3$ ($0.05 \leqslant x \leqslant 0.8$) samples, was also concluded by Philip and Kutty [6] from thermo-power studies and, according to them, the observed ferromagnetic and metallic properties of these compounds are determined by the DE interaction between the Mn^{3+} and Mn^{4+} ions. They have explained the presence of Mn^{4+} ions in the Ce-substituted samples prepared by them on the basis of increased oxygen content in the presence the Ce^{4+} ions at the La sites [6].

In this letter, we show that the above mentioned reports [1–6] are questionable. Our study on the sample of nominal composition, La$_{0.7}$Ce$_{0.3}$MnO$_3$, suggests that the La$_{1-x}$Ce$_x$MnO$_3$ samples do not form single-phase compounds with perovskite structure, as reported in [1–6]. Instead, they form multi-phase mixtures comprising La-deficient lanthanum manganates (La$_{1-x}$MnO$_3$) with perovskite structures and CeO$_2$. The ferromagnetic and I–M transitions exhibited by these samples are a result of the presence of the hole doped La$_{1-x}$MnO$_3$-phases [7].

We have attempted to synthesize the samples of nominal compositions, La$_{0.7}$Ce$_{0.3}$MnO$_3$ and La$_{0.7}$MnO$_3$, following the solid state reaction route. The powder x-ray diffraction (XRD) patterns of the samples were recorded on a Philips diffractometer (Model PW 1820) using CuK$_\alpha$

radiation and a graphite monochromator. The lattice parameters of the samples were calculated by indexing the XRD patterns and the structural parameters of the samples were refined from the XRD data by Rietveld method, using the program FULLPROF [8]. AC susceptibility against temperature behaviour in the temperature range of 15–300 K, were obtained using an APD CCR with Meissner coil assembly, in conjunction with an EG&G model 5208 Lock-in Amplifier. Measurements were taken at a frequency of 80 Hz in an ac field of 0.5 Oe.
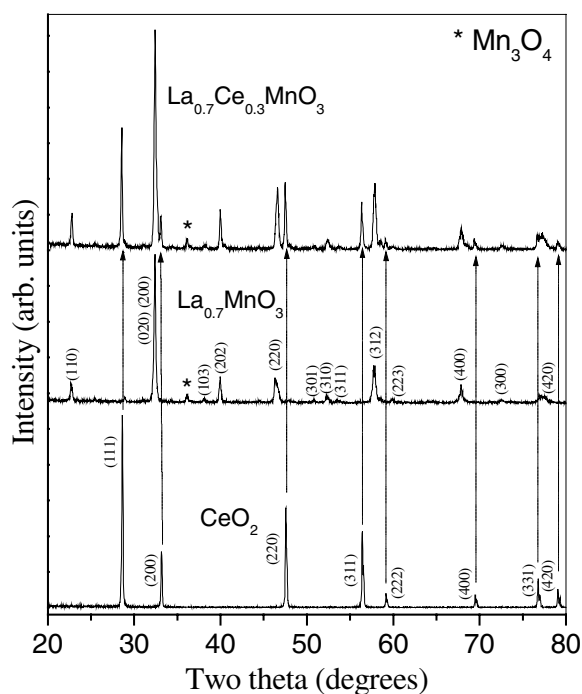
Figure 1. The x-ray diffraction (XRD) patterns for CeO_2, $La_{0.7}MnO_3$ and $La_{0.7}Ce_{0.3}MnO_3$. The dotted lines indicate the presence of the CeO_2 phase in the sample, $La_{0.7}Ce_{0.3}MnO_3$.

Figure 1 shows the XRD patterns for the samples with nominal compositions, $La_{0.7}Ce_{0.3}MnO_3$, $La_{0.7}MnO_3$ and for CeO_2. The pattern for the $La_{0.7}MnO_3$ sample shows that it is a mixture of orthorhombically distorted perovskite (GdFeO$_3$-type) lanthanum manganate and a small amount of Mn_3O_4 [7]. An inter-comparison of these three patterns clearly shows that the sample, $La_{0.7}Ce_{0.3}MnO_3$, can be considered as a mixture of orthorhombically distorted lanthanum deficient perovskite lanthanum manganates and CeO_2. For this sample, the pattern shown in figure 1 looks quite different from those reported by Das and Mandal [1, 2] and Philip and Kutty [6]. Both the reported patterns, however, not only look significantly different from each other, but also contain the three most intense peaks due to the presence of the CeO_2-phase (occurring at $28.55°$, $47.62°$ and $56.35°$). These peaks cannot be indexed on the basis of lattice parameter values reported by them considering the structure belonging to *Pbnm* space group, as it is conventionally known. To confirm the multi-phase nature of this sample, we have carried out Rietveld refinement of the XRD pattern of the sample, $La_{0.7}Ce_{0.3}MnO_3$, presuming it to be a mixture of $La_{1-x}MnO_3$ (*Pbnm* space group) and CeO_2 phases, leaving the Mn_3O_4 phase as the impurity phase. A reasonably good fit (figure 2) accounting for all the observed diffraction peaks (excluding the peak due to the Mn_3O_4 phase) could be obtained considering the sample as a mixture of CeO_2 and two perovskite manganate phases with compositions close

to $La_{0.7}MnO_3$, and with slightly different lattice parameter values. It is clear from figure 2 that the three most intense peaks of the CeO_2-phase cannot be indexed on the basis of orthorhombic structure with *Pbnm* space group, with any lattice parameter values in the neighbourhood of those reported in the literature [1–6]. This confirms that the sample, $La_{0.7}Ce_{0.3}MnO_3$, does not form as a single-phase compound with orthorhombically distorted perovskite structure. The XRD patterns for the samples, $La_{1-x}Ce_xMnO_3$ ($0.05 \leqslant x \leqslant 0.8$), given by Philip and Kutty (figure 1 of [6]) show that the relative intensity of the peaks due to the CeO_2-phase increases monotonically with an increase in the value of x. A closer look at these patterns shows that the sample with $x = 0.05$ contains the perovskite phase as the majority phase and the CeO_2 phase as the minority phase, whereas the opposite is true for the sample with $x = 0.8$. Thus, analysis of the structural data available in the literature, along with the results obtained by us, suggest that the reports in the literature [1–6], that the samples of nominal compositions, $La_{1-x}Ce_xMnO_3$, form single phase compounds with orthorhombically distorted perovskite structures, are questionable.
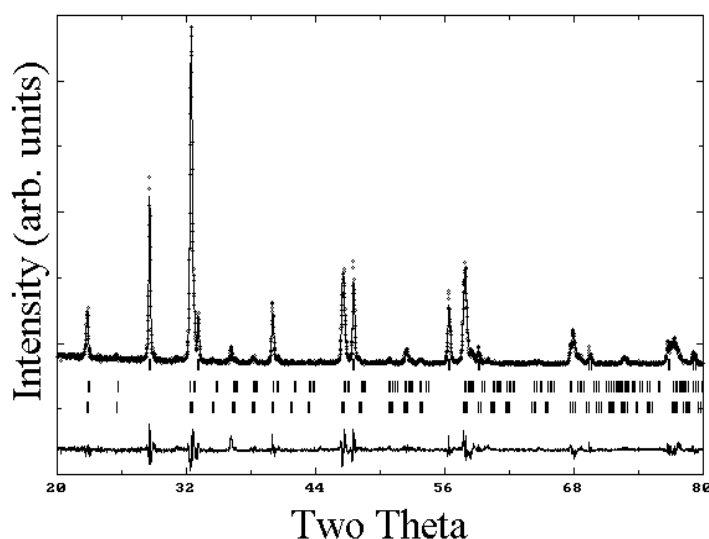
Figure 2. The Rietveld refinement of the XRD data of the sample with nominal composition, $La_{0.7}Ce_{0.3}MnO_3$. Uppermost bars indicate the peak positions for CeO_2 with *Fm3m* space group. The peak positions for the two perovskite phases with *Pbnm* space group are indicated by the two sets of lower bars. $R_p = 15.8$, $R_{wp} = 23.5$, $R_{exp} = 20.0$ and $\chi^2 = 2.49$.

Further support for these results comes from the ac-susceptibility against temperature behaviour for the samples, $La_{0.7}Ce_{0.3}MnO_3$ and $La_{0.7}MnO_3$, as shown in figure 3. The very similar signatures exhibited by these two samples suggest that the magnetic behaviour of the $La_{0.7}Ce_{0.3}MnO_3$ sample is determined by the presence of the hole doped $La_{1-x}MnO_3$-phases with compositions close to $La_{0.7}MnO_3$ [7]. The broader transition exhibited by it *vis-à-vis* the sample $La_{0.7}MnO_3$ could result from the formation of two different $La_{1-x}MnO_3$- phases (figure 2), in it in the presence of the CeO_2-phase as the impurity phase. Our results, therefore, suggest that the ferromagnetic behaviour exhibited by the samples with nominal compositions, $La_{1-x}Ce_xMnO_3$ ($0.05 \leqslant x \leqslant 0.8$) [1–6], arises from the presence of hole doped $La_{1-x}MnO_{3-\delta}$ phases in them.

In conclusion, our studies on the structural and magnetic properties of the sample of nominal composition, $La_{0.7}Ce_{0.3}MnO_3$, show that it forms a multi-phase mixture comprising
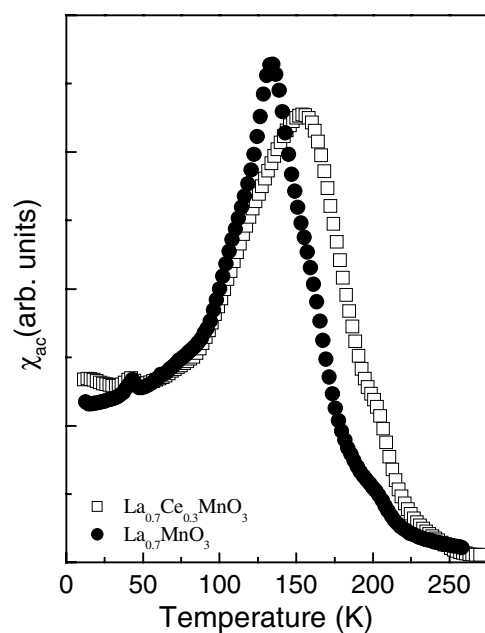
Figure 3. The ac-susceptibility (real part, χ') against temperature behaviour of the samples $La_{0.7}MnO_3$ and $La_{0.7}Ce_{0.3}MnO_3$.

hole doped lanthanum deficient lanthanum manganate phases and cerium oxide (CeO_2). This, and an analysis of the structural data available in the literature [1–6] on the samples of nominal compositions, $La_{1-x}Ce_xMnO_3$ ($0.05 \leqslant x \leqslant 0.8$), suggest that the reports [1–6] that they form single phase compounds with $GdFeO_3$-type structure, are questionable.

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