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Stability of $Sr_3Ti_2O_7$ structure in $La_{1.2}(Sr_{1-x}Ca_x)_{1.8}Mn_2O_7$ and $Ca_{3-y}La_yMn_2O_7$

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Structural studies on the samples of nominal compositions of the series, $La_{1.2}(Sr_{1-x}Ca_x)_{1.8}Mn_2O_7$ and $Ca_{3-y}La_yMn_2O_7$, have been carried out using neutron and X-ray diffraction techniques. These studies show that, unlike the case of the $(La,Sr)_3Mn_2O_7$ system, the samples belonging to the $(La,Ca)_3Mn_2O_7$ system form layered $Sr_3Ti_2O_7$-type structures in a very restricted composition range. Through a systematic study on the effect of substitution of La for Ca in the layered compound $Ca_3Mn_2O_7$, the solubility of La in $Ca_3Mn_2O_7$ has been determined. The results go against the literature reports, which claim that the samples of nominal compositions $Ca_{3-y}La_yMn_2O_7$ ($1.0 \leqslant y \leqslant 2.3$) form with layered $Sr_3Ti_2O_7$ structures. The usefulness of the neutron diffraction technique in unambiguous structural characterization of the layered compounds has also been discussed.

1 Introduction

Since the discovery of colossal magneto-resistance (CMR) in the hole-doped perovskite and layered manganates[1–3] with general compositions $(R,A)MnO_3$ and $(R,A)_3Mn_2O_7$ (R = rare earth, A = divalent ion), respectively, these compounds have been subjected to extensive site selective substitutional studies.[4–17] Such studies, which have been of great help in understanding the mechanism behind the CMR, also brought to light the presence of a fine interplay between spin, charge and lattice interactions in these compounds.[4–10]

The close relation between the magnetic and electrical properties in the manganates is manifested in the observation of simultaneous onset of ferromagnetic and metallic characters as a function of temperature. This behavior, which is typical of manganates, can be explained on the basis of double exchange (DE) interaction.[18] The e_g electrons of the Mn^{3+} ions, which are coupled strongly to the core spin (d^3) by Hund's coupling, mediate ferromagnetic and metallic characters as they undergo hopping between the Mn^{3+} ($t_{2g}{}^3e_g{}^1$) and the Mn^{4+} ($t_{2g}{}^3e_g{}^0$), with their spin remaining parallel to the core spin. For these manganates, the Mn–O–Mn bond angle and the dimensionality of the DE interaction can effectively control the one electron bandwidth of the e_g electrons and thus have significant influence on their magnetic and the transport properties. A decrease in the one electron bandwidth, resulting from a decrease in the Mn–O–Mn bond angle and a reduced dimensionality of the DE interaction, leads to the suppression of ferromagnetic and metallic characters. Thus, the layered manganates, $(La,Sr)_3Mn_2O_7$, with reduced dimensionality of the DE interaction in the layered structure, show lower values of ferromagnetic transition temperature (T_C) than the corresponding perovskite manganates, $(La,Sr)MnO_3$. Among the layered manganates, the maximum value of T_C is exhibited by the compound $La_{1.2}Sr_{1.8}Mn_2O_7$, which is 124 K,[3] whereas in the case of $(La,Sr)MnO_3$ compounds, the maximum value of T_C is as high as 380 K.[15]

Among the layered manganates, the compound $La_{1.2}Sr_{1.8}Mn_2O_7$ (with the maximum value of $T_C = 124$ K) has been studied most extensively.[3,19–22] Studies on the series $La_{1.2}Sr_{1.8-x}Ca_xMn_2O_7$ show that in the single-phase region, *i.e.* in the composition range $0.0 \leqslant x \leqslant 0.8$, the values of T_C and the insulator to metal transition temperature (T_P) decrease monotonically with an increase in the concentration of Ca.[16] Similar is the case for the $La_{1.4}(Sr_{1-x}Ca_x)_{1.6}Mn_2O_7$[17] system, for which the ferromagnetic transition of the parent compound occurs at 100 K. In contravention of this trend, reports in the literature claiming that the samples of nominal compositions $Ca_{3-y}La_yMn_2O_7$ ($1.0 \leqslant y \leqslant 2.3$) form with layered structures and show ferromagnetic transitions in the temperature range 160–240 K,[23–27] are of an intriguing nature. Recently, our systematic XRD study on samples of $La_{1.2}(Sr_{1-x}Ca_x)_{1.8}Mn_2O_7$ ($0.00 \leqslant x \leqslant 1.00$) showed that a drastic change in the XRD pattern and the magnetic properties occurred at $x = 0.65$, the composition where the layered structure breaks down, resulting in a multiphase mixture comprising hole-doped perovskite manganates as the majority phases and CaO as the minority phase.[28] The magnetic and the transport properties of the resultant multiphase mixtures in the composition range $0.65 \leqslant x \leqslant 1.00$ are thus determined not by the layered phase but by the presence of the hole-doped perovskite manganates as the majority phases. Rietveld refinement of the XRD data of the $x = 1.0$ sample, *i.e.*, $La_{1.2}Ca_{1.8}Mn_2O_7$, and also of the samples $La_{1.5}Ca_{1.5}Mn_2O_7$ and $La_{2.3}Ca_{0.7}Mn_2O_7$ shows that, contrary to the literature reports, they form multiphase mixtures comprising hole-doped perovskite manganates as the majority phases.[28–31] The compound $Ca_3Mn_2O_7$ has been well characterized and is known to form with the layered structure.[32,33] In the light of our earlier observation that compounds $La_{3-y}Ca_yMn_2O_7$ with $y = 0.7$, 1.5 and 1.8 do not form single-phase compounds with a layered structure, it would be most interesting to study the solubility of lanthanum in the parent compound $Ca_3Mn_2O_7$ and the stability of the

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layered structure in the samples of nominal compositions $Ca_{3-y}La_yMn_2O_7$.

In this paper, we confirm our earlier results on $La_{3-y}Ca_yMn_2O_7$ (y=0.7, 1.2, 1.5) and $La_{1.2}(Sr_{1-x}Ca_x)_{1.8}Mn_2O_7$ ($0 \leqslant x \leqslant 1$) (based on the X-ray diffraction technique) by performing neutron diffraction measurements on the same samples. Further, a systematic study of the structural properties of the samples of nominal compositions $Ca_{3-y}La_yMn_2O_7$ with ($0 \leqslant y \leqslant 2.3$) has been carried out using X-ray and neutron diffraction techniques. These studies show that the samples $Ca_{3-y}La_yMn_2O_7$ form single-phase layered compounds with the $Sr_3Ti_2O_7$ structure only in the composition range of ($0 \leqslant y \leqslant 0.2$).

2 Experimental

The samples with nominal compositions $La_{1.2}(Sr_{1-x}Ca_x)_{1.8}Mn_2O_7$ (x=0.00, 0.60, 1.00) and $Ca_{3-y}La_yMn_2O_7$ (y=0.0, 0.2, 0.4, 0.8, 1.5, 2.3) were prepared by the solid state reaction. Stoichiometric amounts of MnO_2 (Aldrich, 99.9%), $CaCO_3$ (Aldrich 99%), $Sr(NO_3)_2$ (Aldrich 99%) and La_2O_3 (Aldrich 99.99%) were mixed together thoroughly using a mortar and pestle and were then calcined at 1300 °C for 12 h. The calcined products were then made into pellets and sintered at 1300 °C for one week with several intermittent grindings. La_2O_3 was dried at 1000 °C prior to the reaction. Room temperature powder X-ray diffraction (XRD) patterns of the samples were recorded using a 12 kW rotating anode-based Rigaku powder diffractometer using Cu-Kα radiation. Room temperature powder neutron diffraction (ND) patterns were collected at a neutron wavelength of 1.278 Å using the position sensitive detector-based Hi-Q diffractometer at Dhruva reactor, Trombay.[34] A Cu(111) monochromator was used which gave a second order contribution with an intensity ratio of 0.004. Rietveld refinement was carried out using the program FULLPROF.[35] The parameters to be refined were first varied individually and then in groups; care was taken to avoid refinement of highly correlated parameters at the same time.

3 Results and discussion

ND patterns of the $La_{1.2}(Sr_{1-x}Ca_x)_{1.8}Mn_2O_7$ (x=0.00, 0.60, 1.00) samples are shown in Fig. 1. A number of earlier neutron diffraction studies[19–22] have reported that the x=0.00 composition forms a single-phase compound with a layered $Sr_3Ti_2O_7$-type structure (space group *I*4/*mmm*). Our repeated attempts to synthesize a single-phase compound were not successful and the presence of impurity phases was always observed. The impurity phases could be identified as the perovskite $(La,Sr)MnO_3$ phases (space group *Pbnm*), and Rietveld refinement of the neutron diffraction pattern of this sample based on the presence of the perovskite phases as impurities resulted in a reasonably good fit (Fig. 2). The pattern is similar to ND patterns reported by Moritomo *et al.*[14] and Chi *et al.*[36] on the compounds $(La_{0.9}Nd_{0.1})_{1.4}Sr_{1.6}Mn_2O_7$ and $La_{1.4}Sr_{1.6}Mn_2O_7$, respectively. While Moritomo *et al.*[14] showed the refinement of the neutron diffraction data by excluding the regions where the peaks due to the perovskite phase appeared, Chi *et al.*[36] fit the ND data on the basis of both the layered and perovskite phases. Since none of the above-mentioned reports on $La_{1.2}Sr_{1.8}Mn_2O_7$[19–22] shows the observed ND patterns, we are unable to compare our pattern with those obtained by them. The difference in the phase-purity obtained by us to that reported in refs. 19–22 could arise from the difference in the synthesis conditions followed, since it is known that the phase-purity of the layered compounds is extremely sensitive to the synthesis conditions. The existence of the perovskite phases in $La_{1.2}Sr_{1.8}Mn_2O_7$ is not noticeable in its XRD pattern[28] for two reasons. Firstly, these phases are present with low volume fraction, and secondly, their most intense peaks, *i.e.* (020, 200), overlap very closely with those of the layered compounds, *i.e.* (105, 110). This is not the case for the ND patterns in Fig. 1, where a wide separation (*ca.* 2.0 degrees) of the positions of the most intense peaks of the perovskite phase (020, 220) and the layered phase (116) is observed.

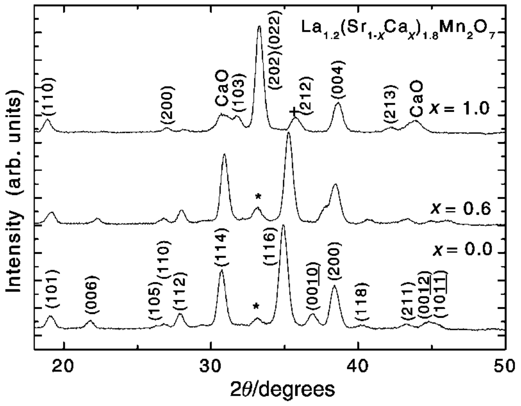

Fig. 1 Neutron diffraction patterns for the compounds $La_{1.2}(Sr_{1-x}Ca_x)_{1.8}Mn_2O_7$ (x=0.0, 0.6, 1.0). Indexing for x=0.0 is based on a tetragonal structure and for x=1.0, the indices represent an orthorhombic structure. The asterisks indicate peaks due to the perovskite phase; '+' indicates the position of the most intense peak of the layered phase.

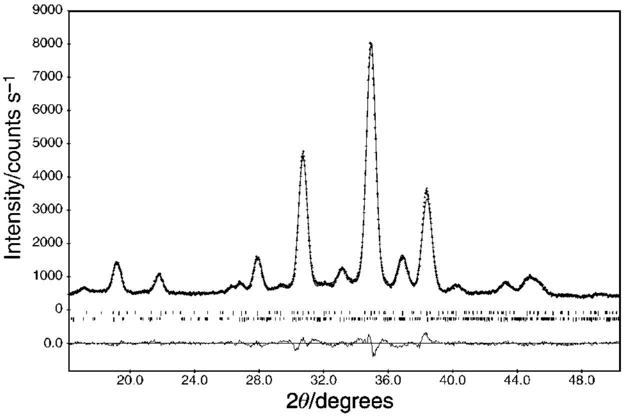

Fig. 2 Rietveld refinement of the neutron diffraction pattern for x=0.0 using two phases. R_p=4.22%, R_{wp}=5.35%, R_{exp}=3.2%, and χ^2=2.8.

It is observed from Fig. 1 that the layered phase remains the majority phase only up to x=0.6. The fraction of the perovskite phase (marked by asterisks) increases from x=0.0

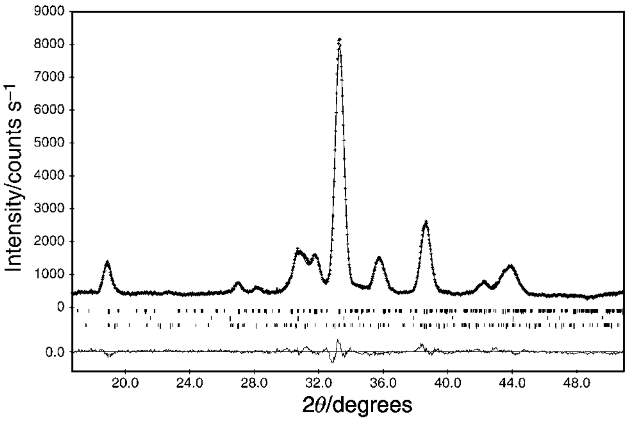

Fig. 3 Rietveld refinement of the neutron diffraction pattern for x=1.0 using three phases. R_p=5.0%, R_{wp}=6.5%, R_{exp}=3.55%, and χ^2=3.34.

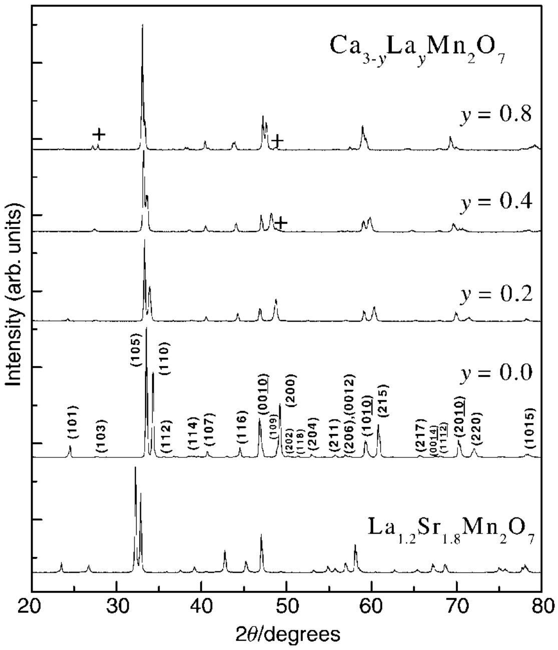

Fig. 4 X-Ray diffraction patterns for the compounds $Ca_{3-y}La_yMn_2O_7$ ($y=0.0$, 0.2, 0.4 and 0.8). '+' indicates the presence of an impurity phase. The XRD pattern of $La_{1.2}Sr_{1.8}Mn_2O_7$ is also included as a reference pattern for the layered structure.

to 0.6 and becomes the dominant one at $x=1.0$. This is clearly seen in the ND patterns where the (202, 220) reflection of the perovskite phase becomes prominent for $x=1.0$. These patterns give a clearer understanding of our earlier observation from X-ray diffraction studies that the layered structure of the parent compound ($x=0.0$) breaks down at $x=0.65$, and that a multiphase mixture with a perovskite phase as the majority phase and CaO as the minor phase is formed for the sample with $x=1.0$.[28] The Rietveld refinement of the ND pattern of the $x=1.0$ sample (Fig. 3), however, shows that in addition to the CaO and the perovskite phases, the layered manganate phase is also present as a small volume fraction. This phase was not observed in our earlier XRD patterns due to the same reasons as given above for the $x=0.00$ sample but with the roles of the layered and perovskite phases reversed. These results support our earlier reports,[28–29] which questioned the literature reports[25–26] that the sample $La_{1.2}Ca_{1.8}Mn_2O_7$ forms with a layered $Sr_3Ti_2O_7$-type structure.

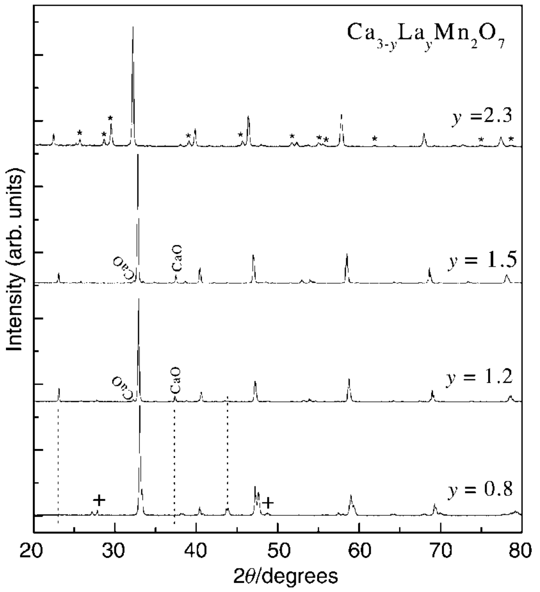

Fig. 5 X-Ray diffraction patterns for the compounds $Ca_{3-y}La_yMn_2O_7$ ($y=0.8$, 1.2, 1.5 and 2.3). Asterisks indicate the presence of La_2O_3. The pattern for $y=0.8$ is repeated for comparison.

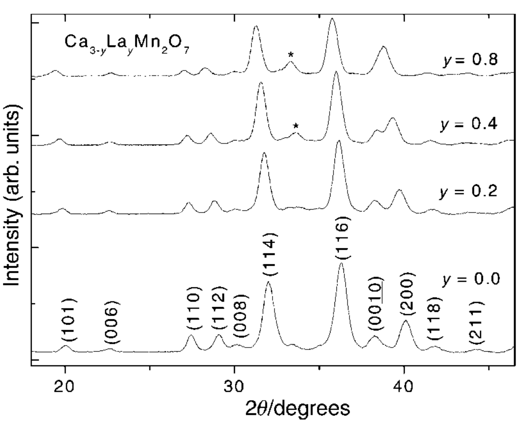

Fig. 6 Neutron diffraction pattern for the compounds $Ca_{3-y}La_yMn_2O_7$ ($y=0.0$, 0.2, 0.4 and 0.8). The peak marked by the asterisk belongs to the developing perovskite phase.

Fig. 4 and 5 show the X-ray diffraction patterns of the samples with nominal compositions $Ca_{3-y}La_yMn_2O_7$ ($y=0.0$, 0.2, 0.4, 0.8, 1.2, 1.5 and 2.3). No extra peaks, indicative of the presence of any phase other than the layered phase, are observed up to $y=0.2$ (Fig. 4). The appearance of extra peaks in the XRD pattern of the $y=0.4$ and 0.8 samples (marked as '+') indicates the presence of a second phase, the layered phase still being the majority phase (Fig. 4). A significant change in the nature of the XRD pattern (as highlighted in Fig. 5 with dotted lines) is observed at $y=1.2$, and as we have already reported[28] and discussed in the previous section, the sample with $y=1.2$ forms a multiphase mixture with perovskite as the majority phases. Therefore, the change in the XRD pattern between $y=0.8$ and 1.2 is a result of the change in the nature of the product from that of a composition with layered phases as the majority phases to that of a composition with perovskite phases as the majority phases. The sample $y=1.5$ shows similar behavior to that of the sample $y=1.2$. The minor phase in these two samples, which could be detected from their XRD patterns, is CaO, as indicated in Fig. 5 and reported by us earlier.[28–30] In the case of $y=2.3$, although the perovskite phases remain as the majority phases, the minor phase which could be detected is not CaO but La_2O_3[31] (as shown by asterisks in Fig. 5).

The neutron diffraction patterns for all of these samples are shown in Fig. 6 and 7. The patterns of the samples with $y=0.0$ and 0.2 show that they are single-phase compounds with layered structure without the presence of any impurity phases

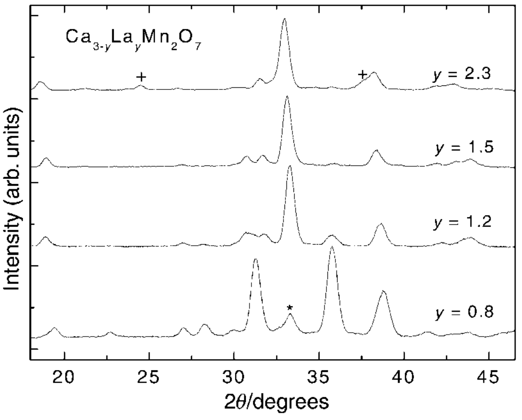

Fig. 7 Neutron diffraction pattern for the compounds $Ca_{3-y}La_yMn_2O_7$ ($y=0.8$, 1.2, 1.5 and 2.3). '+' indicates the presence of La_2O_3. The pattern for $y=0.8$ is repeated for comparison.

(Fig. 6). The perovskite phase, as the second phase, starts appearing as minority phase at $y=0.4$ and its fraction increases with increase in y up to $y=0.8$ (marked with an asterisk in Fig. 6). At $y=1.2$ it becomes the majority phase with CaO and layered phases as the minority phases (Fig. 7). These ND patterns thus give a clearer picture of what we have discussed in the light of the XRD patterns shown in Fig. 4 and 5. For example, the impurity phase observed from the XRD patterns (Fig. 4) of the samples with $y=0.4$ and 0.8 could successfully be recognized from their ND patterns as the perovskite phase. Similarly, the change in the nature of the product at $y=1.2$, from a composition with predominantly layered phase to a composition with predominantly perovskite phase, can be understood very clearly from the change in nature of the neutron diffraction pattern at that composition. As argued earlier, the reason for this is that in the case of neutron diffraction patterns, the most intense reflections of the layered phase are well separated from the most intense reflections of the perovskite phase. For both $y=1.5$ and 2.3, the layered phase is not observable within the resolution limits of our instrument, and the minor phases in these samples are CaO and La_2O_3, respectively.

The results of our neutron diffraction studies on the $Ca_{3-y}La_yMn_2O_7$ samples do not support the literature reports[25–27] that the samples of nominal compositions $La_{2-2x}Ca_{1+2x}Mn_2O_7$ ($0.0 \leqslant x \leqslant 0.5$) form with a single-phase layered structure. When considered in our representation, the above-mentioned composition range becomes $1.0 \leqslant y \leqslant 2.0$. We have shown that with the synthesis conditions followed by us, the samples $y=1.2$ and 1.5, falling in this composition range, form multiphase mixtures with perovskite manganates as the majority phases. We concur with Asano *et al.*[26] in as much as that the sample $Ca_3Mn_2O_7$ ($y=0$ in the present case) forms with a layered $Sr_3Ti_2O_7$ structure. We, therefore, believe that a detailed ND study is essential for an unambiguous understanding of the structural properties of the samples of nominal compositions $La_{2-2x}Ca_{1+2x}Mn_2O_7$ ($0.0 \leqslant x \leqslant 0.5$) as reported in the literature.[25–27]

In conclusion, our detailed room temperature X-ray and neutron diffraction studies on samples of nominal compositions $La_{1.2}(Sr_{1-x}Ca_x)_{1.8}Mn_2O_7$ ($x=0.00$, 0.60, 1.00) and $Ca_{3-y}La_yMn_2O_7$ ($0 \leqslant y \leqslant 2.3$), prepared by the solid state reaction route, indicate that the literature reports,[23–27] which suggest that that the samples of nominal compositions $Ca_{3-y}La_yMn_2O_7$ ($1.0 \leqslant y \leqslant 2.3$) form with a layered $Sr_3Ti_2O_7$ structure, may not be correct. These studies also confirm the results of our earlier XRD work on $La_{1.2}(Sr_{1-x}Ca_x)_{1.8}Mn_2O_7$.[28] Further, our studies also show that, unlike the perovskite system $La_{1-x}Ca_xMnO_3$, where solid solutions are observed over the entire concentration range, the corresponding layered phases with a $Sr_3Ti_2O_7$-type structure form solid solutions in a very restricted concentration range.

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