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Stability of the layered $\text{Sr}_3\text{Ti}_2\text{O}_7$ structure in $\text{La}_{1.2}(\text{Sr}_{1-x}\text{Ca}_x)_{1.8}\text{Mn}_2\text{O}_7$

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Abstract. Samples with nominal compositions $\text{La}_{1.2}(\text{Sr}_{1-x}\text{Ca}_x)_{1.8}\text{Mn}_2\text{O}_7$ ($x = 0.00, 0.25, 0.50, 0.65, 0.80$ and 1.00) have been prepared and characterized by x-ray diffraction (XRD) and ac susceptibility techniques. Drastic changes in the XRD pattern and in the ac susceptibility versus temperature behaviour at $x = 0.65$ indicate that single phase compounds with layered $\text{Sr}_3\text{Ti}_2\text{O}_7$ structure are formed only up to $x = 0.50$. Rietveld refinement of the XRD patterns of $x = 1.00$ composition suggests that the compositions with $x \geq 0.65$ form multiphase mixtures comprising hole doped perovskite manganates as majority phases and CaO as the minority phase. These results are at variance with the literature reports that the compound $\text{La}_{1.2}\text{Ca}_{1.8}\text{Mn}_2\text{O}_7$ forms with layered $\text{Sr}_3\text{Ti}_2\text{O}_7$ structure.

1. Introduction

The hole doped perovskite and layered manganates are now being subjected to extensive study because they exhibit colossal magneto-resistance (CMR) and a rich variety of magnetic and electrical properties [1–3]. The origin of these properties lies in the presence of a fine interplay between spin, lattice and Coulomb interactions in them. Substitutional studies which can influence those interactions and thus, can give a better insight into the mechanisms responsible for different physical properties, have been carried out in detail for perovskite manganates with general formula $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{R} = \text{rare earth}$, $\text{A} = \text{divalent ion}$) [4–8]. These compounds can have varying amount of lattice distortions determined by the value of the tolerance factor, t , which is defined as $R_{(R-O)}/1.414R_{(Mn-O)}$, where $R_{(R-O)}$ and $R_{(Mn-O)}$ are rare earth–oxygen and manganese–oxygen bond distances, respectively. A decrease in value of t from its ideal value of $t = 1$ leads to a decrease in the Mn–O–Mn bond angle from 180° . As the magnetic and electrical properties of these compounds depend critically on the Mn–O–Mn bond angle, substitution of ions at the rare earth site, which can modify the value of the tolerance factor, has significant influence on those physical properties [4–8]. The compounds with $t \approx 1$ exhibit simultaneous onset of ferromagnetism and metallic character mediated by a double exchange (DE) process [9]. The e_g electrons of the Mn^{3+} ions which are coupled strongly to the core spin (d^3) by Hund's coupling, mediate ferromagnetism as they undergo hopping between Mn^{3+} ($t_{2g}^3 e_g^1$) and Mn^{4+} ($t_{2g}^3 e_g^0$) ions with their spin remaining parallel to the core spin. A decrease in the Mn–O–Mn bond angle due to a decrease in tolerance factor results in a decrease in one-electron bandwidth and electron transfer probability of the e_g electrons, and this results in suppression of the DE interaction. This, in turn, leads

to suppression of ferromagnetism and the insulator-to-metal (I–M) transition temperature, and stabilization of other competing interactions like charge ordering and antiferromagnetism [4, 5].

Studies on the series of the layered manganates with formula $(\text{La, Sr})_{n+1}\text{Mn}_n\text{O}_{3n+1}$ ($n = 1$ and 2) reveal that a reduced dimensionality of the Mn–Mn interaction in these compounds, as compared to that of the perovskite manganates, results in a reduced itinerancy of the e_g electrons and consequently a weakened DE interaction [10]. Ferromagnetic and metallic characters are not observed in $\text{La}_{2-x}\text{Sr}_x\text{MnO}_4$ compounds with K_2NiF_4 structure, which belong to the $n = 1$ member of the series [11]. The $\text{La}_{2-x}\text{Sr}_{1+x}\text{Mn}_2\text{O}_7$ compounds belonging to the $n = 2$ member of the series and with $\text{Sr}_3\text{Ti}_2\text{O}_7$ type tetragonal structure, on the other hand, show simultaneous occurrence of ferromagnetism and metallic conductivity [10]. A maximum value of the ferromagnetic transition temperature, T_C , and the I–M transition temperature, T_P , of about 125 K is observed for the compound with $x = 0.40$ [10]. As in the case of perovskite manganates, ferromagnetic and metallic properties of these compounds are also suppressed as a result of a decrease in the average size of the ions at the La(Sr) sites [12–14]. This behaviour can be attributed to a decrease in the one-electron bandwidth of the e_g electrons resulting from an increased distortion in the layered structure. Thus, for the compounds $\text{La}_{1.4}(\text{Sr}_{1+x}\text{Ca}_x)_{1.6}\text{Mn}_2\text{O}_7$, a decrease in the values of T_C and T_P is observed as the concentration of Ca increases from $x = 0.00$ to 0.30 [13]. In contravention of this trend, according to various literature reports, ferromagnetic transitions for the layered $\text{La}_{2-x}\text{Ca}_{1+x}\text{Mn}_2\text{O}_7$ compounds with the compositions $x = 0.5$ and $x = 0.8$ occur at 215 K and 242 K, respectively [15–19]. This anomalous behaviour of these layered compounds, i.e., observation of higher values of T_C in the compounds with lower value of the average size of the ions at the La(Sr) sites, is quite intriguing, and motivated us to perform a systematic study on the structural and magnetic properties of the compounds $\text{La}_{1.2}(\text{Sr}_{1-x}\text{Ca}_x)_{1.8}\text{Mn}_2\text{O}_7$ in the composition range ($0.00 \leq x \leq 1.00$). Unlike the earlier study on $\text{La}_{1.4}(\text{Sr}_{1+x}\text{Ca}_x)_{1.6}\text{Mn}_2\text{O}_7$ compounds [13], we have substituted Ca for Sr in the entire concentration range. We have observed that the layered $\text{Sr}_3\text{Ti}_2\text{O}_7$ -type structure of the parent compound is observed only up to $x = 0.5$. The samples with $x \geq 0.65$ form multiphase mixtures comprising hole doped perovskite manganates as the majority phases and CaO as the minority phase. The magnetic properties of the samples in this composition range are thus determined not by the layered phase but by the presence of the hole doped perovskite manganates as the majority phases. These results are at variance with the literature reports that the sample $x = 1.00$ forms with layered $\text{Sr}_3\text{Ti}_2\text{O}_7$ -type structure.

2. Experiment

The samples with nominal compositions $\text{La}_{1.2}(\text{Sr}_{1-x}\text{Ca}_x)_{1.8}\text{Mn}_2\text{O}_7$ ($x = 0.00, 0.25, 0.50, 0.65, 0.80$ and 1.00) were prepared by solid state reaction. Stoichiometric amounts of MnO_2 (Aldrich, 99.9%), CaCO_3 (Aldrich 99%), $\text{Sr}(\text{NO}_3)_2$ (Aldrich 99%) and La_2O_3 (Aldrich 99.99%) were mixed together thoroughly with the help of mortar and pestle and were calcined at 1350°C for 12 hours. The calcined products were then made into pellets and sintered at 1370°C for one week with several intermittent grindings and pelletizations. La_2O_3 was dried at 1000°C prior to the reaction. The x-ray powder diffraction (XRD) patterns of the compounds were recorded on a Phillips (model PW 1820) diffractometer using $\text{Cu K}\alpha$ radiation and a graphite monochromator. The lattice parameters of the compounds were calculated by indexing and refining the XRD patterns using the program PowdMult [20]. The structural parameters of the $x = 1.00$ sample were refined from the XRD data by the Rietveld method, using the program FULLPROF [21]. The parameters varied were scale factor, zero point and

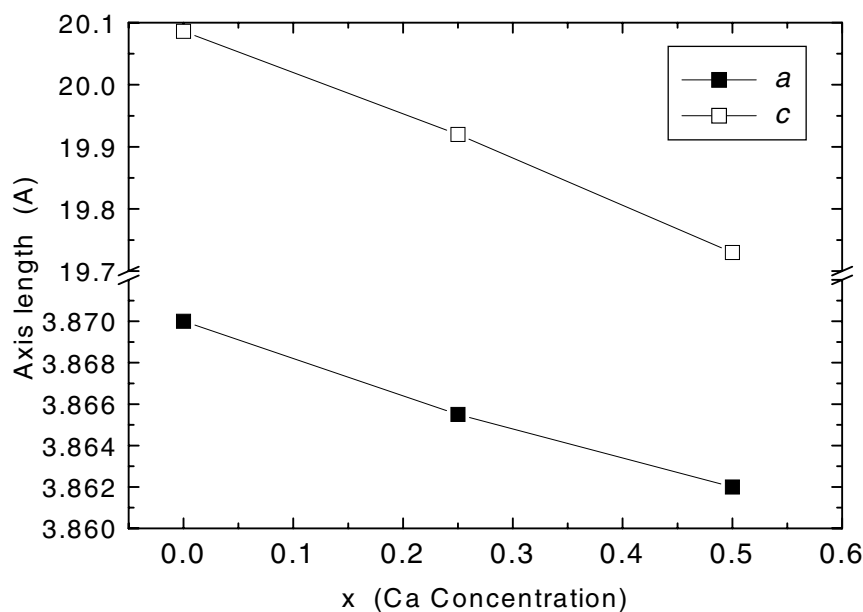


Figure 2. Variation of lattice parameters a and c with the concentration of Ca for the compounds in the composition range $0.00 \leq x \leq 0.50$.

Significant changes in the XRD pattern occur at $x = 0.65$, which are indicated by dotted lines in figure 1. For example, the position of the peak indexed as (101) shifts to a lower 2θ value by about 0.5° , which cannot be accounted for by the contraction of the lattice resulting from the substitution of Ca for Sr. The (116) reflection vanishes and new peaks appear at ≈ 37.3 and 40.6 degrees. Our attempts to index the patterns for $x \geq 0.65$ on the basis of the $\text{Sr}_3\text{Ti}_2\text{O}_7$ structure resulted in a poor agreement between calculated and experimental values of the peak positions. These observations indicate that a drastic change in the structure occurs at $x = 0.65$. It was also observed that the patterns of the samples with $x = 0.65, 0.80$ and 1.00 are similar to those obtained by Kamenev *et al* [17] for the compound $\text{La}_{1.2}\text{Ca}_{1.8}\text{Mn}_2\text{O}_7$, where it has been claimed that this compound could be indexed on the basis of $\text{Sr}_3\text{Ti}_2\text{O}_7$ structure. In order to obtain more definite information on the relative intensities, we attempted Rietveld refinement of the XRD data for the $x = 1.0$ sample based on $\text{Sr}_3\text{Ti}_2\text{O}_7$ structure. Expectedly, we obtained a poor fit with respect to the peak positions as well as peak intensity values. In particular, the peak indexed as (101) does not fit even after repeated refinement of cell parameters. This is an important observation since (101) is a key reflection in the $I4/mmm$ space group. Also, there are certain peaks (32.2, 38.8 and 53.9 degrees) in the observed pattern that are not present in the $\text{Sr}_3\text{Ti}_2\text{O}_7$ structure. This shows that the indexing of the XRD pattern by Kamenev *et al* [17] is incorrect. On closer observation, it is seen that except for certain low intensity peaks, which could be identified to arise from the presence of CaO, the XRD pattern of the $x = 1.0$ sample has a close resemblance to that of perovskite manganates (figure 1) with orthorhombic structure [24]. Also, the ferromagnetic ordering temperature of the $x = 1.0$ sample falls in the range of ferromagnetic ordering temperature of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ compounds [25]. Hence, there is a strong reason to believe that instead of forming with $\text{Sr}_3\text{Ti}_2\text{O}_7$ structure, this sample forms a multiphase mixture comprising hole doped perovskite manganates and CaO. Rietveld profile refinement of the XRD pattern of $x = 1.00$ sample presuming it as a mixture of

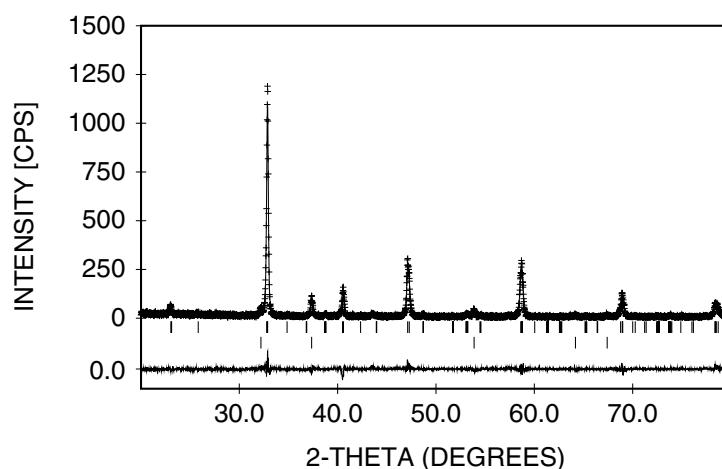
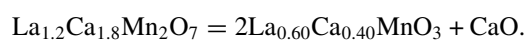


Figure 3. Rietveld profile refinement of La_{1.2}Ca_{1.8}Mn₂O₇ considering it as a mixture of La_{0.60}Ca_{0.40}MnO₃ and CaO phases. The lower bars are the peak positions for CaO.

Table 2. Structural parameters obtained from Rietveld refinement of the room temperature x-ray data for the $x = 1.00$ composition.

Parameter	La _{0.60} Ca _{0.40} MnO ₃ (major phase)	CaO (minor phase)
a (Å)	5.4420(8)	4.8071(1)
b (Å)	5.4538(7)	
c (Å)	7.6792(8)	
V (Å ³)	227.9	111.08
Space group	<i>Pbnm</i>	<i>Fm3m</i>
(La,Ca) (1) $\{x, y, z\}$	{0.994(3), 0.019(1), 0.25}	
Mn $\{x, y, z\}$	{0.5, 0, 0}	
O1 $\{x, y, z\}$	{0.056(7), 0.501(6), 0.25}	
O2 $\{x, y, z\}$	{0.746(8), 0.294(4), 0.024(4)}	
Ca $\{x, y, z\}$		{0, 0, 0}
O $\{x, y, z\}$		{0.5, 0.5, 0.5}
Overall B (Å ²)	1.33	1.33
R-factors (%):		
R_p	17.0	
R_{wp}	24.0	
R_{exp}	20.6	
R_B	7.09	9.96
Goodness of fit	1.36	
DW statistics	$d = 1.569, Q = 1.887$	

La_{0.60}Ca_{0.40}MnO₃ and CaO gave a good fit as shown in figure 3. This assumption was made to satisfy the starting compositions of the samples



The refined parameters are given in table 2. Our results, therefore, confirm that the $x = 1.0$ sample does not form with Sr₃Ti₂O₇ structure, using the synthesis protocol employed in the present study. Quantitative phase analysis for this sample shows that the weight fraction of the CaO phase is about 6.5%.

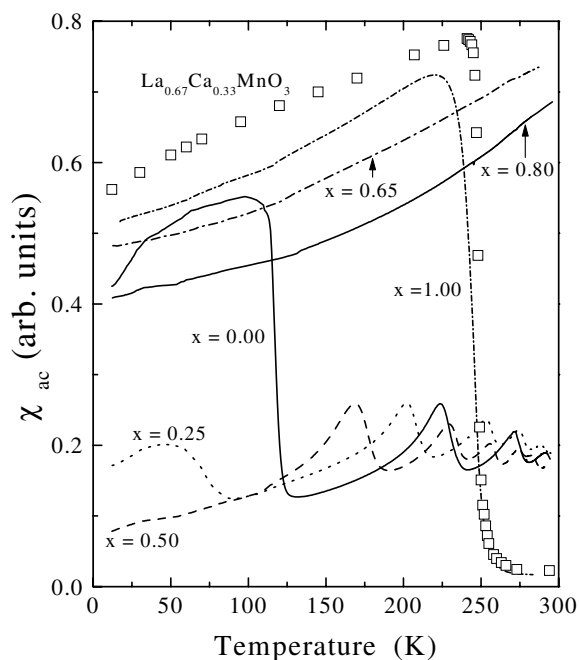


Figure 4. Ac susceptibility versus temperature plots for $\text{La}_{1.2}(\text{Sr}_{1-x}\text{Ca}_x)_{1.8}\text{Mn}_2\text{O}_7$ ($x = 0.00, 0.25, 0.50, 0.65, 0.80$ and 1.00) and for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ [24] compounds.

Ac magnetic susceptibility (χ_{ac}) versus temperature plots for all the samples are shown in figure 4. The data for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ [24] are also plotted (open squares) in the same figure for reference. All the plots were normalized with respect to the weight of the sample taken for the susceptibility measurement. The sample with $x = 0.0$, besides showing a ferromagnetic transition at 126 K, also shows a few other magnetic transitions with smaller intensities at higher temperatures, which are oscillatory in nature. The origin of these peaks is not understood yet but it was reported earlier that three dimensional long range magnetic ordering is not associated with any of these transitions [22, 23]. In the concentration region $0.0 \leq x \leq 0.5$, the ferromagnetic transition temperature decreases with increase in x , which can be explained on the basis of a decrease in one electron bandwidth of the e_g electrons due to substitution of smaller Ca ions for Sr. The compound with $x = 0.25$ shows a ferromagnetic transition at 80 K and the compound with $x = 0.50$ does not show any ferromagnetic transition down to 15 K, though broad peaks corresponding to oscillatory magnetic transitions are present at higher temperatures in both the cases.

In line with the structural changes, a drastic change in the magnetic behaviour is also observed as the concentration of Ca increases from $x = 0.50$ to 0.65 . The samples with $x = 0.65$ and $x = 0.80$ do not show any magnetic transitions, but the observation of strong magnetic signals for these samples, which increase monotonically from 15 K to 300 K, indicates that these samples are ferromagnetic with the transitions occurring at temperatures above 300 K. The $x = 1.0$ sample, on the other hand, shows a ferromagnetic transition at around 260 K. It is observed that the magnetic transition temperature of the $x = 1.0$ sample is close to that of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (figure 4), which indicates that the magnetic properties of that sample could arise from the presence of hole doped perovskite manganates with compositions close to $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$. The origin of the strong ferromagnetic signal for the samples with $x = 0.65$

and 0.80 probably lies in the presence of $La_{1-x}Sr_xMnO_3$ ($x \geq 0.20$) phases, ferromagnetic transitions of which occur at temperatures above 300 K [26]. The ac susceptibility behaviour of the compounds thus supports the results from the XRD data analysis that the samples with compositions $x \geq 0.65$ form multiphase mixtures comprising hole doped perovskite manganates as the majority phases.

4. Conclusion

In conclusion, our structural and magnetic studies on $La_{1.2}(Sr_{1-x}Ca_x)_{1.8}Mn_2O_7$ ($0.0 \leq x \leq 1.0$) demonstrate that single phase compounds with layered $Sr_3Ti_2O_7$ structure are formed only in the concentration range $0.0 \leq x \leq 0.50$. The T_C of the compounds in this range decreases with increase in Ca content. For Ca concentrations greater than 0.5, our XRD results do not provide any evidence for the formation of the compounds with layered $Sr_3Ti_2O_7$ structure in contradiction with previous reports. Instead, these samples form multiphase mixtures comprising hole doped perovskite manganates as the majority phases and CaO as the minority phase.

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