Comment on `The metal-insulator transition and ferromagnetism in the electron-doped layered manganates $La_{2.3-x}Y_xCa_{0.7}Mn_2O_7$ (x = 0.0,0.3,0.5)'

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COMMENT

Comment on 'The metal–insulator transition and ferromagnetism in the electron-doped layered manganates $La_{2.3-x}Y_xCa_{0.7}Mn_2O_7$ ($x = 0.0, 0.3, 0.5$)'

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Abstract

We show that the report of Raychaudhuri *et al* (1998 *J. Phys.: Condens. Matter* **10** L191), that the samples of nominal compositions $La_{2.3-x}Y_xCa_{0.7}Mn_2O_7$ ($x = 0.0, 0.3, 0.5$) are electron doped layered manganates, is incorrect. Rietveld profile refinement of the x-ray diffraction data of the sample $La_{2.3}Ca_{0.7}Mn_2O_7$ ($x = 0.0$) synthesized by us following the same synthesis process as reported by Raychaudhuri *et al* clearly shows that it forms a multiphase mixture comprising hole doped perovskite manganates and lanthanum oxide.

Recently Raychaudhuri *et al* [1] reported that the samples of nominal compositions $La_{2.3-x}Y_xCa_{0.7}Mn_2O_7$ ($x = 0.0, 0.3, 0.5$), form as electron doped layered compounds with ferromagnetic transitions in the temperature range 160–170 K. Ferromagnetic ordering and colossal magneto-resistance in the layered manganates was discovered by Morimoto *et al* [2] in the tetragonal $La_{2-x}Sr_{1+x}Mn_2O_7$ compounds with $I4/mmm$ symmetry. The $x = 0.40$ compound of the series exhibits a maximum ferromagnetic ordering temperature (T_C) of about 125 K. Substitution of smaller ions at the (La, Sr) site in these compounds lead to a decrease in the ferromagnetic transition temperature, T_C [3–5]. In contradiction with this trend, the reports in the literature, that the $La_{2-2x}Ca_{1+2x}Mn_2O_7$ compounds with similar layered structure show ferromagnetic transitions in the temperature range 150–260 K [1, 6, 7], are quite intriguing. Recently it has been shown by us [8, 9] that $x = 0.25$ and 0.40 members of this series, i.e. the samples of nominal compositions $La_{1.5}Ca_{1.5}Mn_2O_7$ and $La_{1.2}Ca_{1.8}Mn_2O_7$, respectively, do not form with layered tetragonal structure with $I4/mmm$ symmetry as reported in the literature [6, 7]. Instead, they remain as multiphase mixtures comprising ferromagnetic hole doped perovskite manganates as the majority phases and CaO as the minority phase [8, 9]. In this comment, we prove that the compounds $La_{2.3-x}Y_xCa_{0.7}Mn_2O_7$ ($x = 0.0, 0.3, 0.5$), reported by Raychaudhuri *et al* [1] as electron doped ferromagnets with layered structure, are also multiphase mixtures comprising hole doped perovskite manganates as the majority phases.

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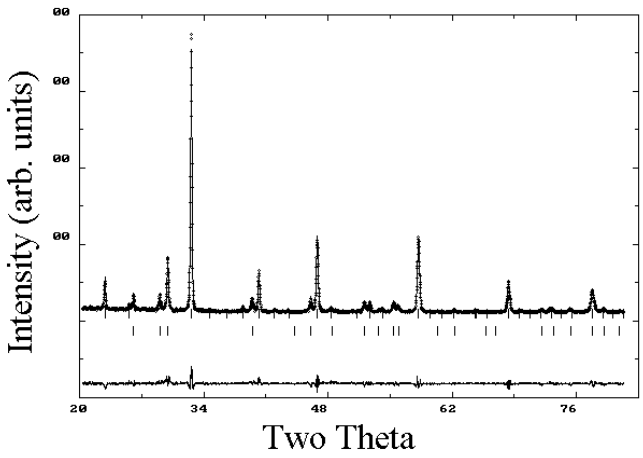

Figure 1. The Rietveld refinement of the XRD data of the sample with nominal composition $La_{2.3}Ca_{0.7}Mn_2O_7$. The lower bars indicate the peak positions for the phase La_2O_3.

Table 1. Structural parameters obtained from Rietveld refinement of the room temperature x-ray diffraction data for $La_{2.3}Ca_{0.7}Mn_2O_7$.

Parameter	$La_{0.65}Ca_{0.35}MnO_3$	La_2O_3
a (Å)	5.482(2)	3.9334(3)
b (Å)	5.481(3)	3.9334(2)
c (Å)	7.752(5)	6.1285(5)
V (Å^3)	233.2(3)	95.0(2)
Space group	$Pbnm$	$P-\bar{3}m1$
(La, Ca) (1) $\{x, y, z\}$	{0.995(3), 0.021(3), 0.25}	
Mn $\{x, y, z\}$	{0.5, 0, 0}	
O1 $\{x, y, z\}$	{0.037(6), 0.499(7), 0.25}	
O2 $\{x, y, z\}$	{0.658(5), 0.278(7), 0.016(4)}	
La $\{x, y, z\}$		{0.333, 0.667, 0.250}
O1 $\{x, y, z\}$		{0, 0, 0}
O2 $\{x, y, z\}$		{0.333, 0.667, 0.650(6)}
B (Å^2)	1.57	1.87
R-factors (%)		
R_p	20.9	
R_{wp}	22.8	
R_{exp}	16.2	
R_B	6.35	14.9
Goodness of fit	1.98	
DW statistics	$d = 1.0285$, $Q = 1.8884$	

The $x = 0.0$ member of the series $La_{2.3-x}Y_xCa_{0.7}Mn_2O_7$, i.e. the sample $La_{2.3}Ca_{0.7}Mn_2O_7$, was synthesized by following the synthesis procedure reported in [1]. The room temperature x-ray diffraction (XRD) pattern of the sample, taken on a Philips diffractometer (PW 1820) with Ni filtered Cu Kα radiation, looks similar to the pattern reported in [1] for the same sample. Analysis of the XRD pattern shows that this sample does not form as layered manganates but remains as a multiphase mixture comprising perovskite manganates and lanthanum oxide. Rietveld refinement of the XRD pattern assuming the sample as a mixture of $La_{0.65}Ca_{0.35}MnO_3$ and La_2O_3 results in a fairly good fit as shown in figure 1. This

assumption was made to satisfy the stoichiometry of the starting composition of the sample.

$$La_{2.3}Ca_{0.7}Mn_2O_7 = 2La_{0.65}Ca_{0.35}MnO_x + 1/2La_2O_3.$$

The refined parameters are given in table 1.

In [1], the XRD pattern for the sample with $x = 0.3$ is not given but it has been claimed that it forms with layered monoclinic structure. The XRD pattern of the sample with $x = 0.5$ is shown in [1] and its structure has been reported to be the same as that of $La_{1.5}Ca_{1.5}Mn_2O_7$ [6], i.e. the layered tetragonal structure with $I4/mmm$ symmetry. However, since it has already been shown by us that the sample of nominal composition $La_{1.5}Ca_{1.5}Mn_2O_7$ does not form with layered tetragonal structure [9], the reported structure of the sample with $x = 0.5$ appears questionable. A large change in XRD pattern from $x = 0.00$ to $x = 0.50$ actually results from a decrease in the La_2O_3 content as a result of the substitution of Y for La and not due to a structural change from monoclinic to tetragonal symmetry as reported in [1].

The magnetic, electrical and electronic properties of these samples reported in [1] are determined by the presence of hole doped perovskite manganate phases. The insulator to metal (I–M) transition, which is not shown by the Y-free sample, is exhibited by the Y-doped samples, as they contain a lesser amount of lanthanum oxide than the Y-free sample.

In conclusion, we have shown that the claim of Raychaudhuri *et al* that the samples $La_{2.3-x}Y_xCa_{0.7}Mn_2O_7$ ($x = 0.0$, 0.3 and 0.5) form as electron doped layered manganites is questionable. These samples actually are multiphase mixtures comprising hole doped perovskite manganates as the majority phases, which in fact determine their magnetic, electronic and electrical properties.

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