

Study of structural and electronic transport properties of Ce-doped LaMnO₃

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Abstract. The structural and electronic transport properties of La_{1-x}Ce_xMnO₃ ($x = 0.0-1.0$) have been studied. All the samples exhibit orthorhombic crystal symmetry and the unit cell volume decreases with Ce doping. They also make a metal–insulator transition (MIT) and transition temperature increases with increase in Ce concentration up to 50% doping. The system La_{0.5}Ce_{0.5}MnO₃ also exhibits MIT instead of charge-ordered state as observed in the hole doped systems of the same composition.

Keywords. Colossal magnetoresistance; La_{1-x}Ce_xMnO₃; metal–insulator transition.

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1. Introduction

Rare earth doped manganites of the general formula R_{1-x}A_xMnO₃ (R = rare earth and A = divalent cation) have been widely investigated due to their remarkable magnetic and transport properties like metal–insulator transition (MIT), colossal magnetoresistance (CMR), charge ordering etc. The parent compound RMnO₃ is a charge transfer insulator. When this system is doped with a divalent element such as Sr, Ca, Ba and Pb, a proportionate number of Mn³⁺ ions with electronic configuration $t_{2g}^3 e_g^1$ are replaced with Mn⁴⁺ having electronic configuration t_{2g}^3 . This creates holes in the e_g band. The magnetic and electrical properties have been traditionally examined on the basis of double exchange model. Therefore, by analogy with the hole-doped systems one could also have double exchange between Mn²⁺ and Mn³⁺, which results in a MI transition. Such systems are termed as electron doped systems. Almost all the earlier reports on La_{1-x}Ce_xMnO₃ [1–5] show a double peak feature in the resistivity vs. temperature plot. While in some of them no reason has been assigned for the same, it has been attributed to the double phase nature of the samples in others. In the light of all these reports we undertook the detailed study of the Ce-doped LaMnO₃ and synthesized the whole series of La_{1-x}Ce_xMnO₃ ($x = 0.0-1.0$) to analyze the structural and transport properties.

2. Experimental

Bulk polycrystalline samples of $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ ($x=0.0-1.0$) were synthesized using solid state reaction route. All the samples were characterized by X-ray diffraction (XRD) using $\text{Cu-K}\alpha$ radiation and found to be single phase. The resistivity of samples was measured using standard four-probe technique in the temperature range 77–300 K in a home-built cryostat.

3. Results and discussion

3.1 Structural analysis

The room temperature powder X-ray diffraction patterns for $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ samples for $x = 0.0-1.0$ have been recorded to analyze the structure of these samples. All the compositions exhibit the single phase nature with orthorhombic crystal symmetry. Figure 1 shows the XRD patterns for $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ ($x = 0.0-1.0$). The lattice parameters of LaMnO_3 change considerably with Ce doping. The value of a decreases with increasing Ce concentration and reaches a value of 4.701 Å for CeMnO_3 while for LaMnO_3 its value was 5.582 Å. There is a slight increase in b parameter on 10% Ce doping but further doping results in decrease, which continues up to the end member of the series CeMnO_3 . It is to be noted that the values of b remain higher than that of the undoped sample up to 60% Ce doping. The c parameter decreases on doping from $x = 0.0-0.8$. This decrease is gradual relative to that for a and b .

The c parameter shows an increased value for $\text{La}_{0.1}\text{Ce}_{0.9}\text{MnO}_3$, but it decreases again for CeMnO_3 . We observed no peak for CeMnO_3 before 49.8° . The unit cell volume decreases with increase in the Ce concentration, obviously due to the size mismatch of La and Ce ions. We have summarized all these observations in table 1. The earlier reports regarding the XRD patterns of $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ are contradictory. Mandal and Das [1], and Philip and Kutty [3] claimed this system as orthorhombic. Ganguly *et al* [4] and Zhao *et al* [5] emphasized the presence of an impurity phase of CeO_2 to which they attributed the three peaks observed by them at 28.47 , 47.47 and 56.33° . We observed no such peaks for the whole series of samples. In our case the three peaks, which lie close to these values are at 29.8 , 48.0 and 57.6° . But, we are able to index them on the basis of orthorhombic symmetry.

3.2 Transport analysis

The resistivity vs. temperature plots of $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ ($x = 0.0, 0.2, 0.3, 0.5$) are shown in figure 2. We observed no metal–insulator transition for LaMnO_3 . The plot, however, flattens at lower temperatures, which may be due to the ferromagnetic ordering of spins. The doping with Ce induces a metal–insulator transition and as such $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$ exhibits a MIT at $T_p = 240$ K. The value of T_p goes on increasing with increasing concentration of Ce and for 30% of Ce doping T_p becomes 274 K. $\text{La}_{0.5}\text{Ce}_{0.5}\text{MnO}_3$ does not show any

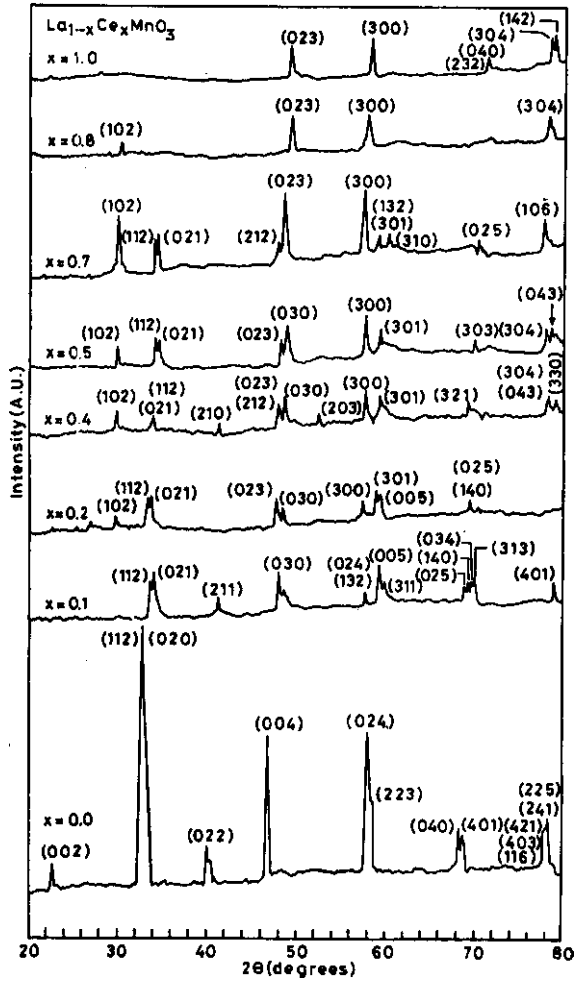


Figure 1. X-ray diffraction patterns of $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ ($x = 0.0-1.0$).

charge-ordering phenomenon as observed in the hole-doped samples of the same composition. Instead, it exhibits MIT at temperature ~ 286 K. The reason for this different behavior may be attributed to mixed valence of Ce lying between 3 and 4 as also reported for CeO_2 and $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ [6]. The earlier reports on the resistivity of $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ show a double transition. Mandal and Das have observed a shoulder-like feature at a lower temperature and a sharp peak at higher temperature [1]. They show that this shoulder-like feature grows into a peak, and its height increases with oxygen over doping. Gebhardt *et al* [2] also observed a similar double peak feature and the flattening of the sharper peak with decreasing Ce concentration. We too observed a double transition in as-prepared samples. But on reprocessing the samples we could observe only a single transition. This supports our structure analysis conforming to a single phase orthorhombic structure. Philip and Kutty

Table 1. Lattice parameters and unit cell volume for different compositions of $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$.

Composition	Crystal symmetry	a (Å)	b (Å)	c (Å)	Unit cell volume (Å ³)
LaMnO_3	Orthorhombic	5.582	5.515	7.763	238.982
$\text{La}_{0.9}\text{Ce}_{0.1}\text{MnO}_3$	Orthorhombic	4.914	5.625	7.748	214.164
$\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$	Orthorhombic	4.814	5.622	7.742	209.532
$\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$	Orthorhombic	4.801	5.582	7.701	206.381
$\text{La}_{0.6}\text{Ce}_{0.4}\text{MnO}_3$	Orthorhombic	4.768	5.572	7.685	204.170
$\text{La}_{0.5}\text{Ce}_{0.5}\text{MnO}_3$	Orthorhombic	4.756	5.553	7.656	202.196
$\text{La}_{0.4}\text{Ce}_{0.6}\text{MnO}_3$	Orthorhombic	4.782	5.516	7.641	201.551
$\text{La}_{0.3}\text{Ce}_{0.7}\text{MnO}_3$	Orthorhombic	4.774	5.509	7.637	200.853
$\text{La}_{0.2}\text{Ce}_{0.8}\text{MnO}_3$	Orthorhombic	4.739	5.412	7.624	195.536
$\text{La}_{0.1}\text{Ce}_{0.9}\text{MnO}_3$	Orthorhombic	4.735	5.364	7.672	194.858
CeMnO_3	Orthorhombic	4.701	5.298	7.657	190.705

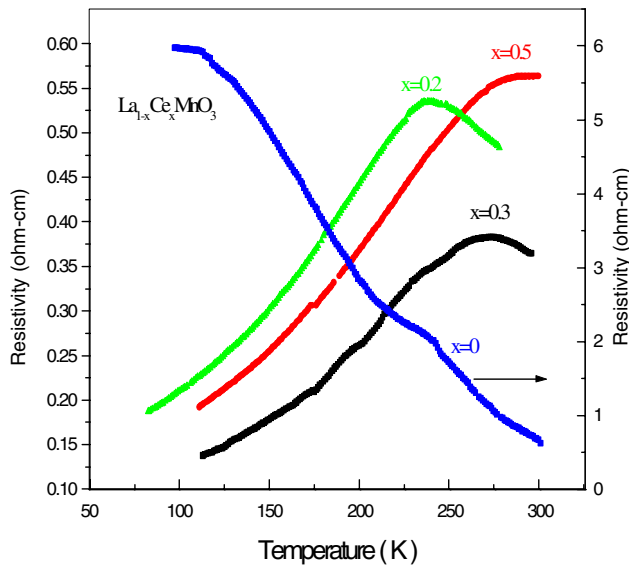


Figure 2. Temperature dependence of resistivity plots for $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ ($x = 0.0, 0.2, 0.3, 0.5$).

[3] have also reported a single transition for samples synthesized by wet chemical route involving a redox reaction.

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