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# Percolative nature of A-site disordered $La_{0.75}Ca_{0.25-x}Sr_xMnO_3$ manganites

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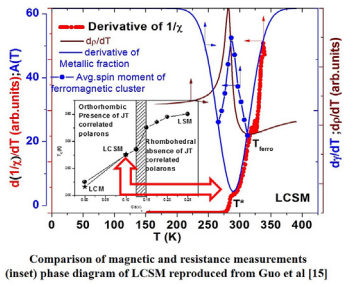
## HIGHLIGHTS

- Percolative nature of $La_{0.75}Ca_{0.25-x}Sr_xMnO_3$(x = 0, 0.10) manganites is investigated.
- $d(\chi^{-1})/dT$ is a better tool for probing the percolative nature of manganites.
- Correlation between magnetic, resistivity and magnetoresistance measurements.
- Discussed as phase separation happening in small polarons in the insulating phase.
- Attributed to the interplay of correlated polarons in orthorhombic structure.

## GRAPHICAL ABSTRACT




Comparison of magnetic and resistance measurements (inset) phase diagram of LCSM reproduced from Guo et al [15]

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## ABSTRACT

Magnetic, resistive, and magnetoresistance measurements were used to investigate the percolative nature of A-site disordered $La_{0.75}Ca_{0.25-x}Sr_xMnO_3$(x = 0, 0.10) manganites. $La_{0.75}Ca_{0.15}Sr_{0.10}MnO_3$ has an orthorhombic structure and second order magnetic phase transition indicates the presence of two prominent downturns $T^*$ and $T_{ferro}$ above the Curie temperature ($T_C$) in the derivative of the inverse susceptibility measurements. These observations are in agreement with the percolation model and the results are discussed in the light of phase separation happening in small polarons present in the insulating phase.



## 1. Introduction

The Manganese perovskites with their rich electronic and magnetic phase diagram, chemical stability, fine tunability of transition temperatures, prove to be a class of promising materials for colossal magnetoresistance applications near room temperature [1,2]. Colossal magnetoresistance (CMR) observed in manganites around $T_c$ is attributed to an interplay between spin, lattice, charge and orbital degrees of freedom [3]. CMR shows a strong dependence on the nature (order) of the magnetic phase transitions and also for external factors such as strain [4] and lattice distortion [5].

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Inadequacy of double exchange mechanism to explain the CMR in manganites has led to percolation model [6]. Metal to Insulator transition (MIT) in manganites is also reported as a percolation transition which led to the emergence of a new phase called the Griffiths phase [7]. Percolative nature is very much sensitive to variation of A site ionic radii, disorder and strain. Souza et al. have reported the fusion of small ferromagnetic polarons between the temperature T* and the Curie temperature ($T_C$). They have reported the temperature T* instead of Griffiths temperature ($T_G$) in $La_{0.7}Ca_{0.3}MnO_3$ compositions [8]. The presence of T* is identified by downturn in inverse susceptibility and the origin of this is attributed to the segregation of ferromagnetic clusters in paramagnetic matrix above the Curie temperature $T_C$ [9]. Many studies in CMR manganites support the concept of correlated polaronic nature of manganites [10] as the origin of CMR.

$La_{0.75}Ca_{0.25}MnO_3$ (LCM) is one such well-studied manganite composition showing a significant CMR around the Curie temperature [11]. Lanzara et al. have reported a cross over from intermediate Jahn–Teller (JT) polaron below Tc to coexistence of small and intermediate polarons above Tc. This cross over occurs interestingly around the MIT in LCM [12]. Synchrotron X-ray scattering measurements in manganites by Kiryukhin et al. confirms the presence of these JT correlated polarons in the orthorhombic phase but not in the rhombohedral phase [13]. It would therefore be interesting to study the electrical and magnetic properties of the composition $La_{0.75}Ca_{0.25-x}Sr_xMnO_3$ (x = 0.1) with an orthorhombic structure and with optimum change in A-site ionic radius. Magnetic measurements of $La_{0.75}Ca_{0.25-x}Sr_xMnO_3$ with compositions (x = 0, 0.1) are reported in this paper. Interestingly two downturns were observed in the derivative of the inverse susceptibility measurement above the Curie temperature in $La_{0.75}Ca_{0.15}Sr_{0.10}MnO_3$(LCSM) composition. Concomitant changes happening in resistive and magnetoresistance measurements corresponding to magnetic measurements indicate the presence of T* and temperature of formation of ferromagnetic clusters ($T_{ferro}$) which are analysed on the basis of the percolation model and discussed in the light of phase separation happening in insulating nature of small polarons.

## 2. Experimental details

Polycrystalline powder samples of $La_{0.75}Ca_{0.25-x}Sr_xMnO_3$ (x = 0, 0.10), in the following named LCM and LCSM, respectively, were prepared by the conventional solid–state reaction method [14]. Stoichiometric amount of $La_2O_3$, $CaCO_3$, $SrCO_3$ and $MnO_2$ were mixed well and calcined initially at $1200^O$ C for 24 h followed by cooling to room temperature. A second calcinations step took place at $1250^OC$ for 24 h and cooled back to room temperature. After the second calcination the samples were pelletized and sintered at $1400^OC$ for 24 h. The phase purity and crystal structure of the powder samples were checked by X-ray powder diffraction (XRD) using $CuK_\alpha$ radiation in a Bruker D8 Advance powder diffractometer, and Rietveld refinement was performed with Fullprof software. A refined pattern of LCSM is shown in Fig. 1. LCM and LCSM were both identified to crystallize in a single phase orthorhombic structure with space group *Pnma*. Chemical composition of LCSM was checked using JEOL SEM EDS analysis which indicated that the calcium composition is 2% less than the expected in LCSM composition but, the Curie temperature from magnetic measurements and structural analysis from XRD pattern of both the compositions are in accordance with the earlier reports [15]. Magnetic measurements were taken using a Lake Shore 7407 vibrating sample magnetometer in fields up to 1 T. Magnetoresistance measurements were carried out by linear four probe method using Quantum Design PPMS with a magnetic field of 12 T and temperature down to 2 K.

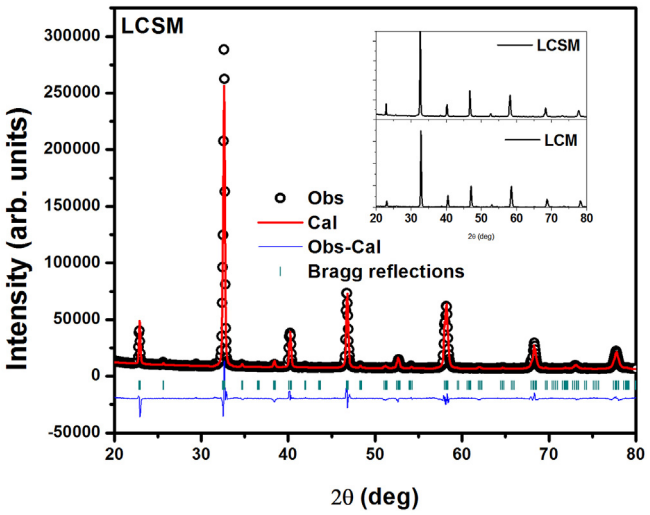


**Fig. 1.** Rietveld refinement for Powder XRD pattern of LCSM composition (Inset) XRD pattern for LCM and LCSM compositions.

## 3. Results

### 3.1. Magnetic measurements

Magnetic properties of LCM and LCSM are shown in Fig. 2. The Curie temperature of the LCM and LCSM samples were measured using maximum change in slope observed in magnetization vs temperature plot in an applied magnetic field of 0.01 T. The temperature dependence of magnetization and its differential plot for LCSM composition is as shown in top inset of Fig. 2. The observed $T_C$ for LCM and LCSM samples are 216 and 276 K respectively. Temperature dependent zero field heat capacity measurements obtained from Differential scanning calorimetry (DSC) shows a peak of the heat capacity at 277 K for the LCSM composition. The $\ln(\chi^{-1})$ vs T in Fig. 2 show no significant downturn or slope change for the LCSM while the LCM show a weak downturn around 225 K (marked by black arrow). The lower inset in Fig. 2 shows a plot of the $d(\chi^{-1})/dT$ vs. T, which indicate the presence of downturn at 225 K for LCM. In the case of LCSM two prominent downturns can be observed one at 287 K and the other at 322 K (marked with black

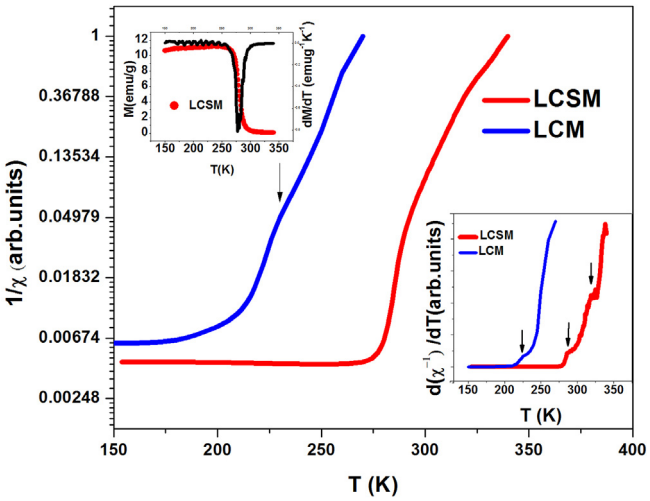


**Fig. 2.** Temperature dependence of Inverse susceptibility of LCM and LCSM compositions; (top inset) M vs. T and dM/dT of LCSM (lower Inset) Derivative of inverse susceptibility for the two samples.

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