Colossal magnetoresistance of Nd-doped LaCaMnO$_3$ polycrystalline ceramics

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Abstract

The cation doped polycrystalline compound La$_{0.5}$Nd$_{0.15}$Ca$_{0.35}$MnO$_3$ has been synthesized by a conventional solid state reaction method. The Rietveld analysis of the powder XRD of the composites reveals an orthorhombic structure with Pbnm space group symmetry. The cell parameters are a = 5.4505 Å, b = 5.4457 Å and c = 7.6876 Å. The AC magnetization studies show a semiconducting paramagnetic to metallic ferromagnetic transition at a temperature below the Curie temperature T$_C$ which is found to be 206.3 K. It is also observed that metal to semiconductor transition temperature T$_{MS}$ is very close to T$_C$. The sample also possesses high magnetoresistance, which is revealed in MR studies.

Keywords: La$_{0.5}$Nd$_{0.15}$Ca$_{0.35}$MnO$_3$, magnetization, ferromagnetic, magnetoresistance

I. Introduction

The polycrystalline compounds of positive and negative magnetoresistance have been actively investigated for long period of time because of its potential applications [1–6]. Many of these compounds have perovskite ABX$_3$ structure. In the case of aristotype perovskite structures, B cations form the octahedral framework, and these octahedral combines to the 3D network with A cations by arranging them in 12 coordinates of octahedral cavities maintaining this framework of the 3D network [7–9]. Distortions from these aristotopic structures have significant impact on physical, magnetic, electrical and optical properties. Octahedral tilting distortion is present in 80–90% of these perovskites and it occurs if A cation is too small in octahedral cavities [10–14]. These distortions change the conduction bandwidth and strength of magnetic superexchange interactions, which intern helps to fine-tune the magnetic, electrical and optical properties [15–17].

In addition to the structural diversities, these composites possess compositional flexibility [9]. Chemical substitutions are possible in all three sites of these perovskite structures. The present study is interested in cationic substitutions, which can cause ordered or random arrangements in the structural framework to engineer new materials [17,18]. Cation ordering is realized with either A or B site cations and there exists a clear difference in each of these attempts [9–17]. In comparison with B cation ordering, A cation ordering is less investigated [9–19] and this study is focused to explore the possible potential of A cation ordering.

LaCaMnO$_3$ is a well-studied ceramics because of the appearance of colossal magnetoresistance (CMR) [20,21]. The most interesting topics in this perovskite system are different interrelated phenomena such as insulator-metal transition, orbital ordering, charge ordering, double exchange, lattice, and magnetic polaron and so on [22]. The problem of the interplay of magnetic, structural and transport properties is old one [23,24], but the invention in high-temperature superconductivity brought it once again at the forefront. In high T$_C$ compounds magnetic ordering is mainly antiferromagnetic, but in CMR it is ferromagnetic [22–24]. There are many reports on the doping of metal ions in manganites which may lead to potential fluctuations of electrons in σ^* bond, due to the larger difference in valance between La^{3+} and doped metal ions [25,26]. Therefore the study of doped perovskite manganites may lead to the invention of new compounds that exhibits fairly good CMR effects. In this paper, we report the colossal magnetic behaviour of cation doped LaCaMnO$_3$.

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II. Experimental

Solid state reaction technique was used in the preparation of the powder samples $La_{0.5}Ca_{0.5}MnO_3$ and $La_{0.5}Nd_{0.15}Ca_{0.35}MnO_3$. The raw materials of high reagent graded (99.9%) purity chemicals used for the sample preparation were lanthanum oxide (La_2O_3), neodymium oxide (Nd_2O_3), calcium carbonate (Ca_2CO_3) and manganese oxide (Mn_2O_3). These chemicals were weighed in stoichiometric amounts and ball milled for 48 h. The obtained mixtures were physically mixed further in a medium of cyclohexane repeatedly in an agate mortar for one week to obtain the required homogeneity. The powders were then calcined at 1250 K repeatedly with intermittent grindings. Finally, these powders were uniaxially pressed into pellet under pressure of 10 MPa and sintered at 1375 K. The copper contacts are made on the sintered pellets for resistivity measurements.

Room temperature X-ray diffraction pattern of the $La_{0.5}Ca_{0.5}MnO_3$ and $La_{0.5}Nd_{0.15}Ca_{0.35}MnO_3$ powders were collected on Bruker diffractometer (D8 Advance) using Cu Kα radiation. The measurements were done in 2θ range from $10°$ to $100°$ with a step size of $0.02°$. Morphology of the $La_{0.5}Nd_{0.15}Ca_{0.35}MnO_3$ sample was observed by scanning electron microscopy (SEM, JEOL-JSM 6390). The AC magnetic susceptibility of the sintered $La_{0.5}Nd_{0.15}Ca_{0.35}MnO_3$ sample was measured against temperature for a range of 10–300 K using the Evercool SQUID Magnetometer. The magnetoresistance studies of the sintered $La_{0.5}Nd_{0.15}Ca_{0.35}MnO_3$ sample were taken by means with the help of superconducting magnets and four-probe arrangements having Advantest current source and Kiethely Nano-Voltmeter.

III. Results and discussion

3.1. Structural characterization

The XRD patterns of the $La_{0.5}Ca_{0.5}MnO_3$ and $La_{0.5}Nd_{0.15}Ca_{0.35}MnO_3$ powders are shown in Fig. 1a. The sharp and intense peaks representing the perovskite structure in the pattern are indication of good crystallinity within the sensitivity limit of the diffractometer. In comparison of the observed structure with the perovskite structure of existing manganites, it can be concluded that this structure is similar to the structure with ICDD card No. 1521126 [27,28]. No secondary phase was detected in the sample which indicates the formation of a pure phase. All the observed peaks can be indexed to orthorhombic phase with space group *Pbnm*. The cell parameters of $La_{0.5}Nd_{0.15}Ca_{0.35}MnO_3$ are $a = 5.4505$ Å, $b = 5.4457$ Å and $c = 7.6876$ Å and the cell parameters of $La_{0.5}Ca_{0.5}MnO_3$ are $a = 5.4301$ Å, $b = 5.4428$ Å and $c = 7.6726$ Å. It can be seen from this observation that the unit cell volume of the $La_{0.5}Nd_{0.15}Ca_{0.35}MnO_3$ sample increases slightly from 226.76 to 228.18 Å^3 due to the replacement of Ca by Nd. This may be due to the higher value of ionic radius of Nd (0.995 Å) over Ca (0.99 Å). The cell parameters for the structural refinement were calculated by the Fullprof software package. The Rietveld refinement was performed with sixth-order Chebychev polynomial function for the background, Pseudo-Voigt profile function, lattice parameters, LP Factor, scale Factor and atomic coordinates. A good fit was obtained between the observed and calculated patterns ($R_{wp} = 0.1862$, $R_p = 0.1384$, and $\chi^2 = 1.456$) and the corresponding pattern is shown in Fig. 1b.

SEM micrograph of the $La_{0.5}Nd_{0.15}Ca_{0.35}MnO_3$ sample is presented in Fig. 2. The spherical, oval and some irregular particle shapes can be seen in the micrograph corresponding to a non-uniform morphology with a very few voids and holes scattered among particle. This image also confirms clustering and agglomeration of particles but the grain boundaries are not clearly visible.

3.2. Magnetization measurements

The AC magnetic susceptibility versus temperature of the $La_{0.5}Nd_{0.15}Ca_{0.35}MnO_3$ sample is shown in Fig. 3. Magnetic susceptibility measurement was done in ZFC and FC modes. The magnetic susceptibility increases with decreasing temperature, which is an indication of paramagnetic to ferromagnetic transition at a temperature below the Curie temperature T_C. The ferromagnetic
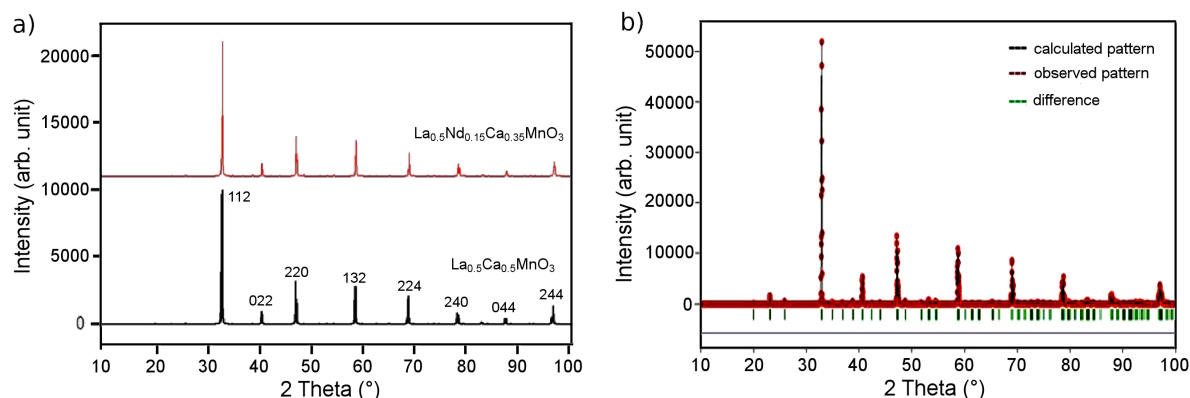

Figure 1. XRD patterns of $La_{0.5}Ca_{0.5}MnO_3$ and $La_{0.5}Nd_{0.15}Ca_{0.35}MnO_3$ powders (a) and Rietveld refined XRD pattern of $La_{0.5}Nd_{0.15}Ca_{0.35}MnO_3$ powder (b)
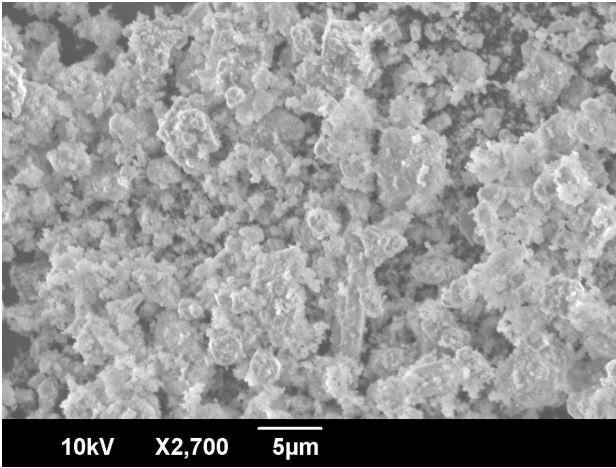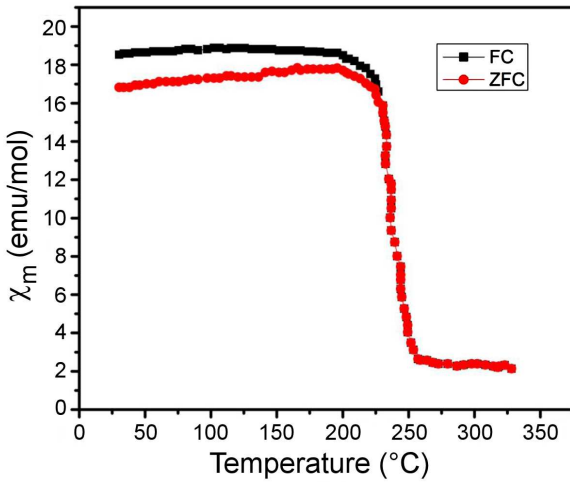
Figure 2. SEM of La$_{0.5}$Nd$_{0.15}$Ca$_{0.35}$MnO$_3$

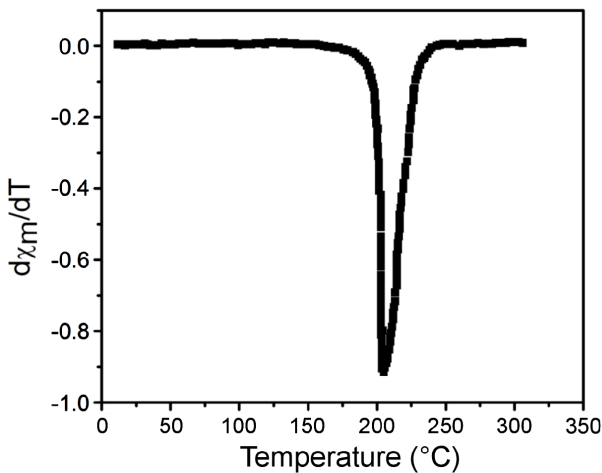**Figure 3. Temperature dependence of susceptibility of La$_{0.5}$Nd$_{0.15}$Ca$_{0.35}$MnO$_3$ in ZFC and FC mode**

Figure 4. Variation of dχ_m/dT with temperature of La$_{0.5}$Nd$_{0.15}$Ca$_{0.35}$MnO$_3$

transition is caused by the mixed valences created in Mn as Mn^{3+}/Mn^{4+} due to cation doping. The replacement of La^{3+} with Ca^{2+}/Nd^{2+}/Nd^{3+} changes the valence of Mn and this in turn changes concentration of Mn^{3+}/Mn^{4+}

which brings changes to transition temperature. The mixed valences of Mn result in double exchange which is probably the reason for ferromagnetism in manganites [29,30]. The Curie temperature can be obtained from the graph of dχ_m/dT vs. temperature shown in Fig. 4 and it is found to be 206.3 K. The observed Curie temperature T_C corresponding to the inflection point in the graph is below that of the parent compound [31] and this result is similar to the one observed for the compound like La$_{0.7}$Sr$_{0.3-x}$Ag$_x$MnO$_3$ [32]. This is due to the superexchange interactions which become dominant over double exchange when Mn^{4+} concentration becomes more than 30% in total value of Mn ions.

3.3. Magnetoresistance

The resistivity of the La$_{0.5}$Nd$_{0.15}$Ca$_{0.35}$MnO$_3$ sample measured against temperature in FC and ZFC conditions is shown in Fig. 5. The resistivity measurement between 10 and 300 K gives good evidence of metal to semiconductor transition. The sample has a metallic behaviour
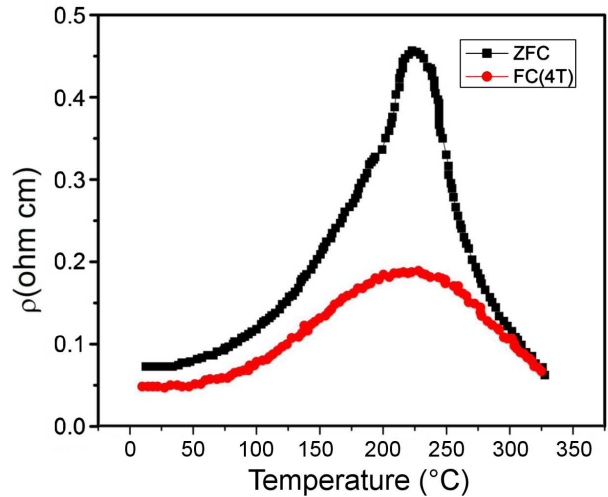

Figure 5. Resistivity versus temperature curve of La$_{0.5}$Nd$_{0.15}$Ca$_{0.35}$MnO$_3$

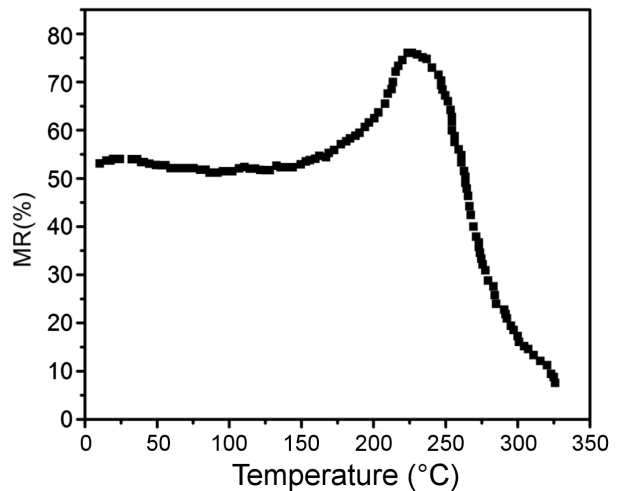**Figure 6. Magnetoresistance versus temperature curve of La$_{0.5}$Nd$_{0.15}$Ca$_{0.35}$MnO$_3$**

at lower temperatures, below T_{MS} (metal to semiconductor transition temperature) and semiconductor behaviour at temperatures above T_{MS}. The close resemblance of T_{MS} and T_C reveals the simultaneous occurrence of both ferromagnetic to paramagnetic and metallic to semiconductor transitions, which is an indication of the strong correlation between electric and magnetic properties [32,33]. A decrease in the resistance is also observed in the vicinity of T_{MS} for an increase in the magnetic field. It may be due to the local ordering of spins in the presence of a magnetic field. The spin ordering may cause less scattering by the increase of exchange interaction which intern results in a drop in resistivity and large magnetoresistance [34–37]. The coexistence of ferromagnetism and metallic behaviour produces a comparatively larger magnetoresistance which is indicated in Fig. 6.

IV. Conclusions

The cation doped sample $La_{0.5}Nd_{0.15}Ca_{0.35}MnO_3$ is prepared by a conventional solid state reaction method. The XRD result revealed the formation orthorhombic perovskite sample with *Pbnm* space group symmetry. The AC susceptibility and resistivity measurements demonstrate the existence of both metal to semiconductor ($T > T_{MS}$) and ferromagnetic to paramagnetic ($T > T_C$) transitions. The sample also possesses high magnetoresistance.

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