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Study of structural, electrical and magnetic properties of Zn doped $La_{0.67}Sr_{0.33}MnO_3$

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ABSTRACT

The structural, electrical and magnetic properties have been investigated on $La_{0.67}Sr_{0.33}Mn_{1-x}Zn_xO_3$ ($x = 0.1$ and 0.2) system. The samples have been prepared through the conventional solid-state reaction route. All the prepared samples were found in single phase with orthorhombic crystal structure. The crystallite sizes were estimated through X-ray diffraction (XRD) using the Debye–Scherrer's formula. Temperature dependent resistivity data shows metal to semiconducting (M–S) transition for both samples. Magnetization measurements confirm that the Curie-temperature (T_C) is found to decrease with Zn doping. The reduction in T_C is attributed to the fact that the double-exchange interaction between Mn^{3+}–O^{2-}–Mn^{4+} network has been destroyed by the substitution of Zn at Mn-site.

1. Introduction

The rare-earth doped manganites with the general formula of $R_{1-x}A_xMnO_3$ (R = Rare earth, A = divalent alkaline earth) have attracted much attention in the last decade or so, due to their unique and versatile properties, such as colossal magnetoresistance (CMR) [1,2], gas sensing [3] and fuel cell [4]. Nevertheless, several factors such as the requirement of large magnetic fields, to observe the CMR effect, make the realization of their full potential a rather slow process, and therefore, there are intensive efforts ongoing to optimize the properties of these manganites [5].

The physics of CMR is also closely related to the bad metal features which are ubiquitously observed in the conducting transition metal oxides with strong electron–electron (electron correlation) or electron–lattice interactions. The correlated electrons which are almost localized on the respective atomic sites bear three attributes, namely, charge, spin and orbital degrees of freedom [6,7]. The conduction electrons with an orbital degree of freedom (3d e_g orbitals) are scattered not only by the strong electron-correlation effect but also by the strong electron–lattice coupling termed as Jahn–Teller interaction [8]. The collective or local Jahn–Teller (JT) distortions, as described by the displacement of the oxygen ions surrounding Mn sites, are observed everywhere when the compound shows the dramatic resistive (metal to semiconducting) or magnetic (antiferromagnetic to ferromagnetic) transitions.

The changing Mn^{3+}/Mn^{4+} ratios in the CMR materials are essentially related to the doping mechanism to control the effective Mn valency [9,10]. This is achieved by either substitution and/or by changing overall oxygen contents, which determines the value of metal to semiconducting transition temperature, T_P. In addition, most of these compounds go through a structural phase transition often coupled with the para to ferromagnetic transition and accompanied with a change in sign of charge carriers at T_P [11,12]. The static and dynamic magnetic properties of $LaMnO_{3+\delta}$ bulk and nanocrystalline materials were studied by Chandra et al. [13]. They observed ferromagnetic and antiferromagnetic phases coexisted in these samples. The nature of the ferromagnetic but insulating state for $0.1 < x < 0.17$ in $La_{1-x}Sr_xMnO_3$, and perhaps up to $x \sim 0.3$ for other narrower-W manganites (e.g. $Pr_{1-x}Ca_xMnO_3$), is still puzzling and under investigation. Unlike the other elements, e.g. Fe, Co, Ni and Cu, the mechanism of Zn doping at Mn site is different and only few reports on this system are available about the transport properties of bulk and thin films [14,15]. Some researchers observed the effect of Zn substitution on para to ferromagnetic transition temperature in $La_{0.67}Ca_{0.33}Mn_{1-x}Zn_xO_3$ [16,17]. Whereas, Ghosh et al. [18] studied the effects of transition elements (Cr, Fe, Co, Ni, Cu, Zn) doping in $La_{0.7}Ca_{0.3}MnO_3$ for a fixed (5% at Mn site) dopant concentration. These authors pointed out metal–insulator transition temperature, the Curie temperature, and the maximum value of magnetoresistance (MR), with respect to lattice parameter and the ionic radii of dopants.

The partial substitution of Zn^{2+} at the magnetic sublattice of mixed-valent manganese in $La_{0.6}Sr_{0.4}MnO_3$ induces a random potential fluctuation because the Zn^{2+} ion has the completely filled

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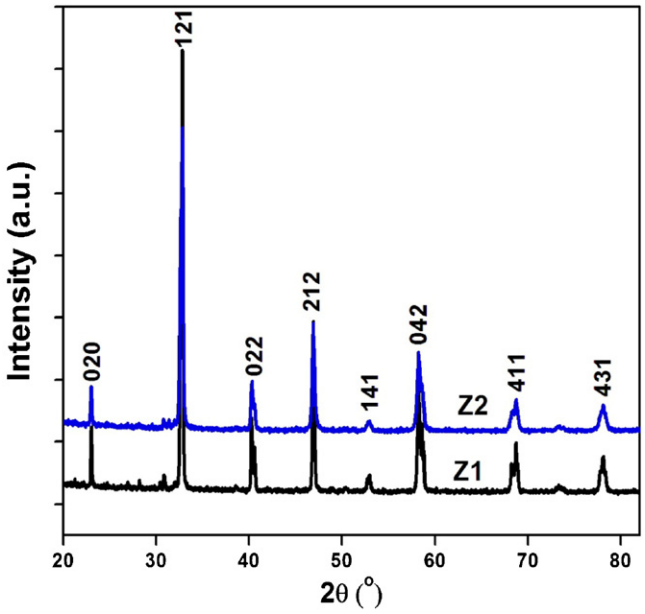

Fig. 1. XRD patterns of Z1 and Z2 samples.

$3d^{10}$ electronic configurations, which is different from those of Mn^{3+} and Mn^{4+} configuration respectively. Secondly, the Zn^{2+} ions do not carry any magnetic moment as they are also expected not to participate in the ferromagnetic (FM) interaction and hence dilute the magnetic sublattice [19]. Keeping this in view, we have aimed to study the structural, electrical and magnetic properties of zinc doped manganites. In this paper, we have carried out the comparative studies of 10 and 20% zinc doping at the Mn site in $La_{0.67}Sr_{0.33}MnO_3$ (LSMO), i.e. $La_{0.67}Sr_{0.33}Mn_{0.9}Zn_{0.1}O_3$ (onwards mentioned as Z1) and $La_{0.67}Sr_{0.33}Mn_{0.8}Zn_{0.2}O_3$ (onwards mentioned as Z2) systems using the resistivity and magnetization measurements. We observed a considerable change in the metal to semiconducting (M–S) transition temperature (T_P) and Curie-temperature (T_C) with Zn doping.

2. Experimental details

The La_2O_3, $SrCO_3$, MnO_2 and ZnO materials were taken as 2.6810, 1.1967, 1.9216 and 0.2007 g respectively for 10% Zn doped sample, while for 20% doped sample these amounts were 2.6868, 1.1993, 1.7117 and 0.4022 g respectively. The polycrystalline bulk samples of $La_{0.67}Sr_{0.33}Mn_{0.9}Zn_{0.1}O_3$ (Z1) and $La_{0.67}Sr_{0.33}Mn_{0.8}Zn_{0.2}O_3$ (Z2) were prepared by mixing and grinding of ingredients La_2O_3, $SrCO_3$, MnO_2 and ZnO powders (all of AR-grade with purity > 99.9% and purchased from CDH) in stoichiometric ratio, heated at 1000 °C for 12 h [7,20]. After this heat treatment samples were ground thoroughly in agate mortar and again heated at 1250 °C for 24 h. For final preparation, samples were ground with polyvinyl alcohol (PVA), pelletized and calcined at 1300 °C for 24 h.

All the samples were characterized by X-ray diffraction (XRD) (Bruker D8 Advance) using Cu-K_α radiation ($\lambda \sim 1.5406$ Å) in the 2θ range 20–80° with scan speed 0.2°/min and step size is 0.02°. The resistivity of samples was measured by using standard four-probe technique in the temperature range 5–300 K in a cryostat assembly (VTI or magnet system). Four contacts of indium were made on a well sintered pellet using conductive solder of low melting point. Fine enameled copper wires were used to pass the constant current of the order of few microamperes through the outer two leads using a constant current source (KEITHLY, Model-2400). The voltage developed across the two inner leads was measured using the sensitive digital multimeter (KEITHLY, Model-182) as a function of temperature. The temperature was controlled using the temperature controller (Lakeshore-DRC-93CA). The magnetization measurements were carried out using Vibrating Sample Magnetometer (VSM, Model-MTS-XL) in the temperature range 100–400 K.

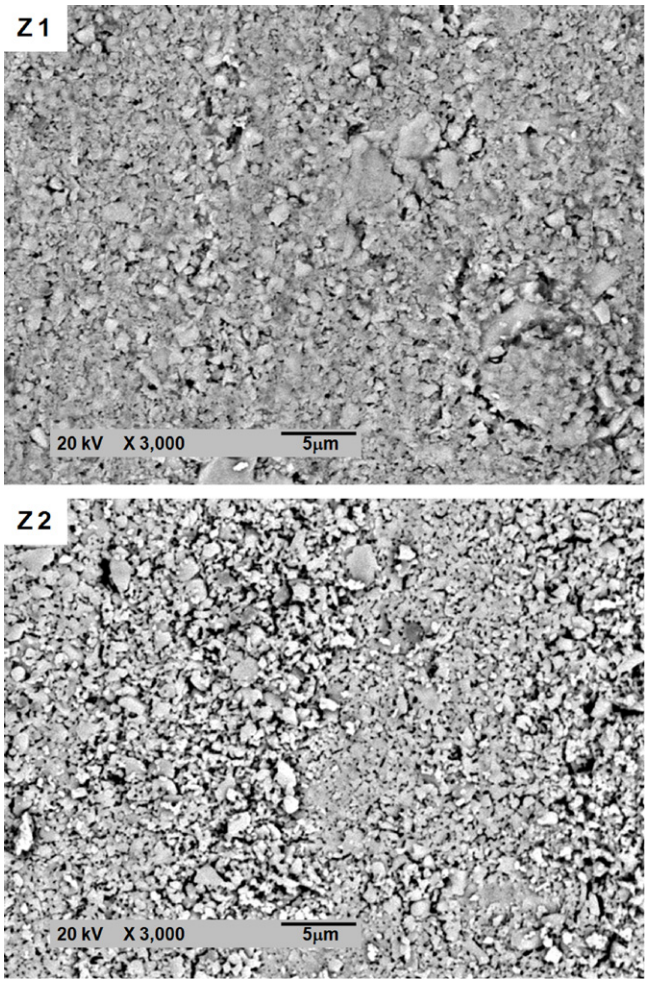

Fig. 2. SEM micrographs of Z1 and Z2 samples.

3. Results and discussion

3.1. Surface and morphological studies

The representative XRD patterns of Z1 and Z2 are shown in Fig. 1. At room temperature, the XRD patterns show that both the samples are formed in a single phase with orthorhombic crystal symmetry with *Pnma* space group.

Average crystallite size using most intense peak (1 2 1) has been determined from XRD patterns by using Debye–Scherrer's formula [21,22]. The unit cell volume increases with increase in Zn concentration, since the ionic radius of Zn^{2+} is larger than that of Mn^{3+}, so the Zn substitution can of course make the volume larger as the doping level goes from 10% to 20%. The lattice parameters, unit cell volumes and the crystallite size have been tabulated in Table 1. The lattice parameters changed considerably as compared to parent compound LSMO. The as-obtained crystallite sizes (D) are 27.48 nm and 24.32 nm for the samples Z1 and Z2 respectively.

SEM micrographs for Z1 and Z2 samples are displayed in Fig. 2. The particles can be clearly distinguished and all the observed particles connect with each other. The particles of the sample Z2 are in better and clear shape than those of the Z1 sample, revealing that increase in Zn doping could improve the crystallization of the sample. In addition, the particle sizes for the two samples are comparable, which are estimated to be mostly within 200 nm range. Obviously, the particle sizes observed by SEM are several times larger than the crystallite sizes calculated by XRD [23].