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Colossal magnetoresistance in $La_{0.7}Ca_{0.3-x}Hg_xMnO_3$ ($0\leqslant x\leqslant 0.2$) system over wide temperature range

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ABSTRACT

The divalent substitutions in rare-earth manganites create quenched disorders; those are responsible for the modification of magnetoelectronic properties through competition of two phases. In this regards, the substitution of divalent Hg is rarely studied. Here, we present the results on effect of Hg^{2+} substitution in LCMO manganites. We have synthesized polycrystalline samples with nominal compositions $La_{0.7}Ca_{0.3-x}Hg_xMnO_3$ ($0\leqslant x\leqslant 0.2$) by the standard solid-state reaction method. The X-ray diffraction data revealed monophasic nature without a signature of Hg related or any other impurity phase. The ac susceptibility measurement showed variation in the magnetic transition temperature as well as the transition width. The electrical resistivity measurement showed variation in metal-insulator transition temperature. The magnetoresistance (MR) measurements were carried out at 5 T magnetic field. The samples show varying magnitude of magnetoresistance as high as 74.48%. The distinct feature seen with Hg substitution is the increase in the magnitude of MR and temperature range over which MR value is sustained. It also improves the microstructure of the samples.

1. Introduction

A large body of manganite research has been devoted to divalent cation substitution at 'A' site [1–3]. The composition $La_{0.7}D_{0.3}MnO_3$, where D = divalent element, corresponds to optimum Mn^{3+}/Mn^{4+} ratio. Around this boundary, the double-exchange interaction is enhanced, which is the key parameter for influencing the transport and magnetic properties [4]. In most of the cases, the ground state changes from antiferromagnetic insulator to ferromagnetic metal. This change is associated with appearance of large magnetoresistance (MR) value near the transition temperature. The Ca substitution at La site has attracted more attention due to higher MR value. The composition $La_{0.7}Ca_{0.3}MnO_3$ forms an intermediate bandwidth system with electrical or magnetic transition around 270 K [4,5]. From application point of view, it is desirable to synthesize materials with higher MR value at convenient temperature. It is also expected that the MR value should sustain over a wide temperature range. We pursued this dictum and achieved high MR value over wide temperature range in $La_{0.7}Sr_{0.3-x}Hg_xMnO_3$ system [6]. The Hg-based systems are extensively studied in the context of superconducting cuprates. However, in rare-earth manganate, such substitution is rarely reported [6,7]. Here, we report the synthesis of $La_{0.7}Ca_{0.3-x}Hg_xMnO_3$ ($x\leqslant 0\leqslant 0.2$) system. We investigated the variation of electrical and magnetic properties with composition. We observed decrease in transition temperature and increase in MR value with Hg substitution.

2. Experimental aspects

We synthesized several polycrystalline samples with nominal compositions $La_{0.7}Ca_{0.3-x}Hg_xMnO_3$ ($0\leqslant x\leqslant 0.2$) by standard solid-state reaction method [6]. X-ray diffractometer (Shimadzu, XRD 6000) with CuK_α radiation was employed in the range $15^\circ\leqslant 2\theta\leqslant 70^\circ$ for structural analysis. The magnetic behavior was studied by ac susceptibility measurement. The induction coil method with 1 Oe field at 131.1 Hz was used in the temperature range $80\,K\leqslant T\leqslant 300\,K$. The electrical resistance for 0 and 5 T magnetic field was measured by the standard four-probe method in the temperature range $5\,K\leqslant T\leqslant 300\,K$ using liquid He cryostat. The superconducting magnet (Spectromag 2000) generated the high magnetic field up to 5 T and the sample current was 10 mA during zero and high field-measurement. The MR was defined as $MR=[(R_0-R_H)/R_0]\,100\%$, where R_0 and R_H are resistances without and with magnetic field, respectively.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns for the samples with nominal compositions $La_{0.7}Ca_{0.3-x}Hg_xMnO_3$ ($0\leqslant x\leqslant 0.2$). The prominent peaks are indexed to orthorhombic structure

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(Pbnm space group). The samples are mostly monophasic with no signature of unreacted oxides or any other impurity. There is slight shifting of peaks towards lower 2θ values for $x\neq0$ samples indicating rise in interplanar spacing (d values). The corresponding lattice parameters for all the samples are given in Table 1. The lattice parameters a, b, c and unit cell volume V show systematic increase with x values. In fact, a compression of unit cell is expected for higher values of x. However, the expansion of unit cell can occur as a result of higher cationic disorder [8,9]. The likely origins of these disorders are intra and inter octahedral distortions of MnO_6 ligand. Recently, we have reported a detailed structural analysis and refined stoichiometry of Hg-substituted manganite system using neutron diffraction technique [10]. The Hg substitution occurs with lower stoichiometric value as a result of partial escape of Hg at reaction temperature. Therefore, such system will have cationic vacancies at ‘A’ site within tolerance limit.

Fig. 2 shows the variations of normalized ac susceptibility with temperature for these samples. All the samples exhibited paramagnetic–ferromagnetic transition at variant temperatures. We determined three parameters from these plots. The $T_{c\ onset}$ is the temperature of commencement of paramagnetic to ferromagnetic transition; $T_{c\ mid}$ corresponds to the minimum in the temperature dependence of the derivative of susceptibility ($d\chi/dT$) and ΔT_c is the difference between these two characteristic temperatures. The observed values of all these three parameters are included in Table 1. There is clear trend of decrease in $T_{c\ onset}$ and $T_{c\ mid}$ values with increasing x. On the other hand, the value of ΔT_c increases with x.

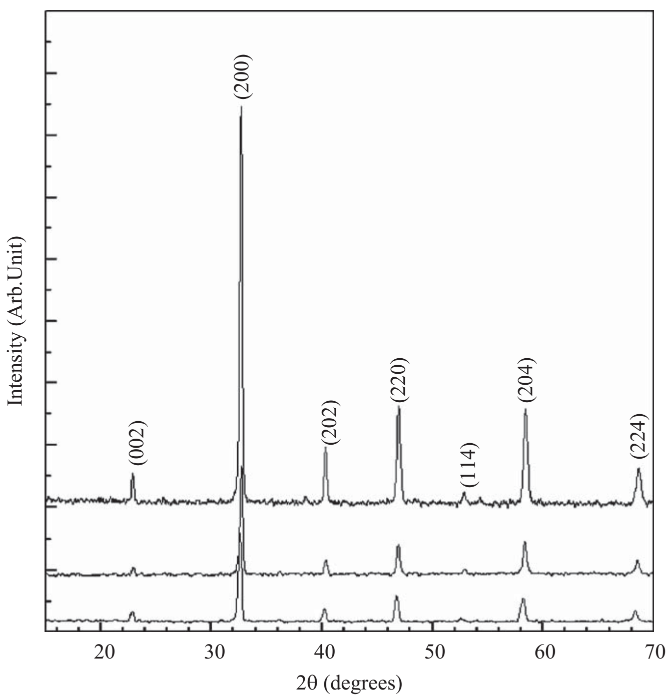

Fig. 1. X-ray diffraction patterns for the samples with nominal compositions $La_{0.7}Ca_{0.3-x}Hg_xMnO_3$ ($x=0.0$, 0.1, 0.2) from bottom to top.

Table 1
The lattice parameters, electrical and magnetic transition temperatures and maximum MR values for $La_{0.7}Ca_{0.3-x}Hg_xMnO_3$ ($x=0.0$, 0.1, 0.2) samples.

Parameters	$x=0$	$x=0.1$	$x=0.2$
Lattice parameter a (Å)	5.440	5.475	5.523
Lattice parameter b (Å)	5.466	5.478	5.518
Lattice parameter c (Å)	7.701	7.740	7.788
Unit cell volume V (Å^3)	229.07	232.15	237.42
$T_{c\ onset}$ (K)	289.31	264.30	254.28
$T_{c\ mid}$ (K)	271.32	246.29	226.28
ΔT_c (K)	17.99	18.01	28.00
T_{MI} (K)	220.35[a]	254.121	232.163
Max. MR (%)	58.64	67.70	74.48

[a] A cusp in ρ–T curve is seen at 276.60 K.

In general, the magnetic transition in manganites is governed by the double-exchange interaction. It is believed that for lower values of average ‘A’ site ionic radius $\langle r_A \rangle$, the MnO_6 octahedral tilting is more, which reduces the overlap of 3d–2p orbitals of Mn–O linkage. As a result, T_c values decrease gradually with $\langle r_A \rangle$ [11]. The variation of T_c in our sample is consistent with this argument as the average ionic radii reduces with increasing x values. In addition, ionic radii mismatch or variance σ^2 also cause linear depression in T_c values [8,12]. Another distinct feature of our samples is the broadening of magnetic transition or higher values of ΔT_c. The lowering of T_c may be attributed to the weakening of double exchange, while the broadening may be associated with large distribution of T_c values [13]. Gutierrez et al. provided direct evidence by polarized neutron diffraction for the coexistence of nanometer-sized FM and AF regions [14]. They argued that short-range-ordered magnetic regions persist at temperatures well above ordering temperature and the PM–FM transition is mediated by percolation-like process.

The variations of zero-field and high-field (5 T) electrical resistivities with temperature for all the samples are depicted in Fig. 3. The values of metal–insulator transition temperature (T_{MI}) determined from the slope of ρ–T curves are included in Table 1. The samples showed a trend of decrease in T_{MI} with increasing x. All the samples exhibited large suppression of resistivity on application of high magnetic field. This change in resistance, quantified as magnetoresistance is also shown as a function of temperature in Fig. 3. The maximum MR values for $x=0$ samples are 58.6%. A significant enhancement in the MR values is seen

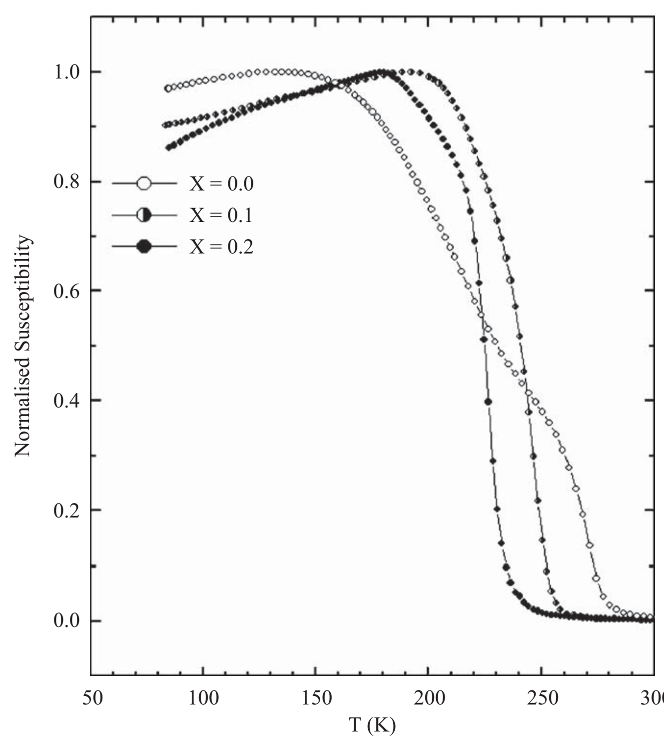

Fig. 2. The variation of normalized ac susceptibility as a function of temperature for the $La_{0.7}Ca_{0.3-x}Hg_xMnO_3$ ($x=0.0$, 0.1, 0.2) samples.