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Transport and magnetoresistance studies on polycrystalline $La_{0.4}Dy_{0.1}Ca_{0.5}MnO_3$: Role of phase separation

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ABSTRACT

Electrical and magnetoresistive response of phase–separated $La_{0.4}Dy_{0.1}Ca_{0.5}MnO_3$ polycrystalline bulk sample has been investigated. The magnetic structure below 25 K is identified as a coexistence of ferromagnetic, strong antiferromagnetic and weak metastable antiferromagnetic domains. The irreversibility in the electrical resistivity with magnetic field cycling is associated to the training effect. The resistivity in the metallic range for $\mu_0 H \leq 4$ T follows Zener polynomial law with unusual values of n exponent due to the high spin fluctuations. Temperature dependence of magnetoresistance (MR) exhibits a plateau–like shape for $\mu_0 H \leq 2$ T. For MR(T), maximum MR ~ 98.8% under 2 T field at 77 K and for MR(H), MR is about 90.5% under 1 T magnetic field at 75 K has been recorded. The colossal values of MR suggest the possibility of using our sample for technological applications. An enhancement of MR(H) at 75 K was observed in the field range 0–2 T due to magnetic field cycling. The spectacular behavior of resistivity for $La_{0.4}Dy_{0.1}Ca_{0.5}MnO_3$ sample is essentially attributed to phase separation phenomenon.

1. Introduction

Half–doped manganites are quite interesting functional oxides, not only because of their potential applications in various fields, but also due to their fascinating and unusual physical properties. The presence of a tight correlation between electrical and magnetic properties of these highly correlated electrons systems stimulates researchers to deeply investigate such correlation, in order to elucidate the factors controlling the evolution of their physical response. Several phenomena like charge ordering (CO), orbital ordering and phase separation are not completely understood in mixed valence manganites. The study of the compound $La_{0.5}Ca_{0.5}MnO_3$ can help in clarifying some points about, both, CO and phase separation. In fact, this half–doped compound presents, when cooled, a paramagnetic (PM)–ferromagnetic (FM) transition in vicinity of $T_C = 220$ K followed by a second transition to the charge–ordered antiferromagnetic (CO–AFM) state around $T_N = 150$ K [1,2]. Below 150 K, the structure is defined as a CO–AFM matrix in which some FM domains are located; this structure testifies the phase separation phenomenon at low temperatures for this compound. Few more reports are available on the investigations on phase separation scenario in $La_{0.5}Ca_{0.5}MnO_3$ compound [3–6]. Awana et al. [3] have studied the CO $La_{0.5}Ca_{0.5}MnO_3$ compound for electrical transport with the thermal hysteresis behavior. They have discussed a large hysteresis in $\rho(T)$ and MR behavior in the context of a complex phase separated magnetic structure of $La_{0.5}Ca_{0.5}MnO_3$ compound. Phase separation and first order magnetostructural phase transition induced anomalous magnetocaloric behavior has been observed in micron and nano sized $La_{0.5}Ca_{0.5}MnO_3$ compounds [4]. Large magnetoresistance (MR) and magnetic field induced modifications in the phase separation scenario have been corrected for $La_{0.5}Ca_{0.5}MnO_3$ compounds [5]. Magnetic field history dependent modifications in the phase fraction of FM and CO–AFM states in citrate–nitrate decomposition method grown polycrystalline $La_{0.5}Ca_{0.5}MnO_3$ compound have been studied [6].

Partial substitution of lanthanum by other rare earths (Eu, Nd, Tb, Sm, etc) in $La_{0.5}Ca_{0.5}MnO_3$ generally generates fascinating physical phenomena [2,7–10]. In fact, such substitution did not affect the amounts of Mn^{3+} and Mn^{4+} ions. However, it induces a decrease in the average ionic radius in A site and enhances structural and magnetic disorder in the lattice. Structural, magnetic and magnetocaloric properties of Eu substituted $La_{0.5}Ca_{0.5}MnO_3$ system

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were studied [7]. Effect of substitution of La by Nd has been investigated for $La_{0.5-x}Nd_xCa_{0.5}MnO_3$ manganites for their structural and magnetic properties [8]. First order magnetic phase transition has been identified using neutron diffraction and magnetic measurements on Tb doped $La_{0.5}Ca_{0.5}MnO_3$ sample [9]. In addition, recently, charge conduction mechanisms have been studied for the transport properties of $La_{0.4}Sm_{0.1}Ca_{0.5}MnO_3$ manganites [10]. Previously, we have investigated the effect of lanthanum substitution on magnetic and magnetocaloric properties in $La_{0.4}Re_{0.1}Ca_{0.5}MnO_3$ (Re = La, Gd, Eu and Dy) [2]. The study revealed that the CO characterizing the parent compound was not destroyed by substitution and that all the obtained samples are phase−separated.

In the present communication, effect of phase separation and CO on the electrical and the magnetoresistive properties of polycrystalline $La_{0.4}Dy_{0.1}Ca_{0.5}MnO_3$ (henceforth referred as LDCMO) compound has been studied. We have considered this compound for study due to the interesting structural behavior and magnetic ordering [2]. In fact, the substitution of 20% of La^{3+} (r = 1.216 Å) by smaller Dy^{3+} ions (r = 1.083 Å) in $La_{0.5}Ca_{0.5}MnO_3$ leads to a decrease of the unit cell volume from 225.1 to 223.6 $Å^3$ [2]. Moreover, such substitution reduces the average ionic radius at A−site from 1.198 Å to 1.185 Å and highly enhances the cationic mismatch σ^2 from $3.24 \times 10^{-4}Å^2$ to $14.37 \times 10^{-4}Å^2$. Such evolution in the structural parameters will certainly affect the CO of the pristine compound. It is worthy to highlight that Dy^{3+} ions possess a huge magnetic moment ($10.6\mu_B$) compared to other rare earths. Hence, one can expect that the substitution on non−magnetic La^{3+} by Dy^{3+} ions will create additional magnetic interactions inside the structure leading to some modifications in the CO state as well as the volume fractions of the coexistent phases at low temperatures. All these observations indicate that the substitution of La^{3+} by Dy^{3+} ions in $La_{0.5}Ca_{0.5}MnO_3$ will induce a great disorder inside the structure. Thus, it seems quite interesting to check the effect of such disorder on the electrical transport and MR behavior of the sample.

2. Experimental techniques

Single phase polycrystalline LDCMO sample was prepared by using conventional solid state route. The synthesis procedure was previously described elsewhere [2]. Phase purity and homogeneity was verified using powder X−ray diffraction (XRD) followed by a Rietveld refinement using Fullprof code. For XRD data, we have used a Panalytical X'Pert PRO diffractometer with a Philips PW3050/60 X-ray generator. The X-ray generation is controlled by a copper anode (Cu K_α X-ray radiation with a wavelength λ = 1.5418 Å) supplied with 40 kV and a current of 40 mA. The measurement was performed in the range $3° < 2\theta < 81°$ with a step of 0.0167° (0.04 rad Soller slit and 10 mm beam mask). Temperature and magnetic field dependent magnetization, in the temperature range: 10−300 K and field up to 5 T, was recorded using a vibrating sample magnetometer (VSM) (SQUID VSM, Quantum Design). The magnetotransport measurements were performed by using physical property measurement system (PPMS) (Model: 14 T DynaCool, Quantum Design) facility based on the dc four probe technique for a temperature range 2−320 K and for an applied magnetic field reaching 10 T at UGC-DAE CSR, Mumbai Centre.

3. Results and discussions

Fig. 1 shows the refinement of the XRD pattern for LDCMO sample. The refinement using standard Rietveld technique has shown that the sample crystallizes in orthorhombic *Pnma* space group (no. 62) with cell parameters a = 5.410 Å, b = 7.632 Å and c = 5.416 Å, with the absence of any secondary phase [1]. The

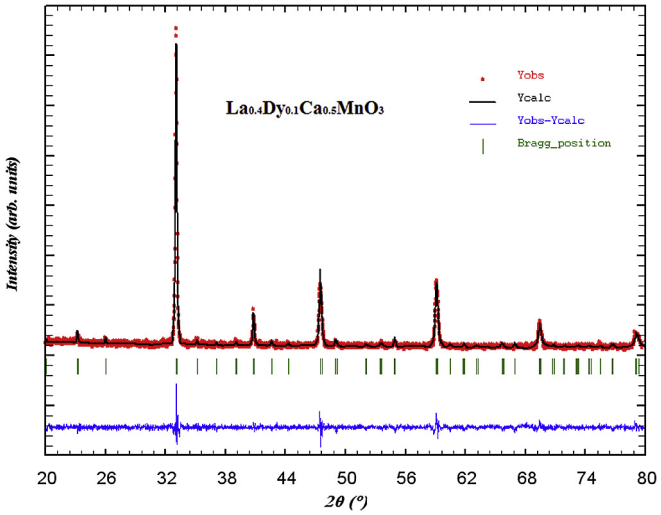

Fig. 1. Rietveld refined XRD pattern of LDCMO sample [2].

reliability factors are $\chi^2 = 2.69$ (goodness of fit with Bragg contribution) and $R_p = 4.79\%$, which testifies the quality of the refinement. Fig. 2 depicts the temperature (cooling and heating cycles) dependence of electrical resistivity under 0 T applied magnetic field for LDCMO sample. It is clear that with decreasing temperature (cooling cycle), LDCMO sample undergoes an insulator−metal transition at temperature T_ρ ~ 58 K while during heating cycle, it shifts towards higher temperature ~ 77 K. In a previous study, $La_{0.375}Tb_{0.125}Ca_{0.5}MnO_3$ compound did not exhibit such transition under zero applied magnetic field [5] while $La_{0.4}Sm_{0.1}Ca_{0.5}MnO_3$ compound shows transition at 123 K [6]. This suggests that the occurrence of such phase transition depends on substituent nature (particularly cationic size) and structural disorder. Presently studied LDCMO compound possesses larger A−site structural disorder ($\sigma_A^2 = 14.37 \times 10^{-4}Å^2$) as compared to that for earlier reported $La_{0.4}Sm_{0.1}Ca_{0.5}MnO_3$ compound ($\sigma_A^2 = 8.08 \times 10^{-4}Å^2$) which results in comparatively lower value of T_ρ ~ 77 K. The lower inset of Fig. 2 shows the evolution of magnetization as a function of temperature under an applied field of 0.05 T. The magnetization curve shows a unique transition from PM to FM state with decreasing temperature at T_C = 70 K detected by the minimum of dM/dT as function of temperature. The T_C value is very close to (in between) both the T_ρ values, which suggests the presence of some correlation between electrical and magnetic properties inside our studied sample. Also, the PM−AFM transition, taking place at temperature T_{CO}, cannot be detected in this curve (Fig. 2). Occasionally, this is the situation for CO manganites where, T_{CO} cannot be seen in the $\rho(T)$ plot [11,12]. This can be correlated with the well known fact that CO manganites possess a strong coexistence of FM and CO phases. However, for $La_{0.5}Ca_{0.5}MnO_3$, T_{CO} = 150 K [1,2] and for $Dy_{0.5}Ca_{0.5}MnO_3$, the CO transition is located near T_{CO} = 300 K [13]. Since our sample have a medium composition between these two compounds, we expect to have 150 K < T_{CO} < 300 K for our specimen which indicates the presence of some CO−AFM domains in the PM phase. This observation will be confirmed later by the isothermal magnetization as a function of the applied magnetic field. In addition, it is clear that the resistivity curves recorded during cooling and warming sequences exhibit a bifurcation at 90 K. Resistivity demonstrates a hysteretic behavior between the bifurcation temperature (~90 K) and low temperature ~ 25 K. We believe that the phase separation phenomenon is responsible for the observed thermal hysteresis. In fact, we have previously proved that this sample is a mixture of FM and AFM domains at very low temperatures with the persistence of CO