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Abstract
We report magnetic interactions and electronic transport properties in La0.4Bi0.6Mn0.5Ti0.5O3 perovskite manganite synthesized using solid-state route. After characterizing the samples structurally, the systematic investigations of magnetic and electrical transport behaviors have been undertaken. It has been observed that at low temperatures near TC, the sample is magnetically frustrated leading to the second-order magnetic transition. A justification for the observed magnetic behavior has been explained based on Arrott's plot study. The resistivity as a function of temperature in the absence and the presence of applied magnetic field suggests semiconducting nature of the sample. The conduction of the charge carriers is explained using Shklovskii-Efros-type variable-range-hopping mechanism.

Keywords
Perovskite manganite, Magnetic properties, Arrott Plots, SE-VRH mechanism, Hopping conduction

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Magnetic Interaction and Electronic Transport in La$_{0.4}$Bi$_{0.6}$Mn$_{0.5}$Ti$_{0.5}$O$_3$ Manganite

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Abstract—We report magnetic interactions and electronic transport properties in La$_{0.4}$Bi$_{0.6}$Mn$_{0.5}$Ti$_{0.5}$O$_3$ perovskite manganite synthesized using solid state route. After characterizing the samples structurally, systematic investigations of magnetic and electrical transport behaviors have been undertaken. It has been observed that at low temperatures near $T_c$, the sample is magnetically frustrated leading to second order magnetic transition. A justification for the observed magnetic behaviour has been explained based on Arrott’s plot study. The resistivity as a function of temperature in the absence and presence of applied magnetic field suggests semiconducting nature of the sample. The conduction of the charge carriers is explained using Shklovskii–Efros-type variable range hopping mechanism.

Index Terms - Perovskite manganite; Magnetic properties; Arrott Plots; SE-VRH mechanism; Hopping conduction.

I. INTRODUCTION

In recent years perovskite type manganites with general formula ABO$_3$ have attracted significant deliberation because of their importance both for potential magneto-electronic (ME) applications and fundamental research in condensed matter physics [1, 2]. The properties of these materials such as magnetoresistance (MR %), metal-insulator (M-I) transition, charge and magnetic ordering etc. have attracted significant attention [2]. The substitution of divalent or other trivalent rare earth ions at A-site results in varying the average cationic radii at A-site results in varying the average cationic radii, introducing changes in bond angles and bond lengths. However, the B-site substitution induces local disorder directly into the Mn-O network significantly affecting their magnetism and conductivity [3, 4, 5].

In this paper, we present a study on the nature of the magnetic interactions near the magnetic transition and electronic-transport in a polycrystalline La$_{0.4}$Bi$_{0.6}$Mn$_{0.5}$Ti$_{0.5}$O$_3$. The substitution of non-rare earth ion such as Bi$^{3+}$ (1.24Å) having ionic radii close to La$^{3+}$(1.22Å), has attracted much attention due to their potential application as lead-free magneto-electronic (ME) materials [1, 5]. The presence of the 6S$^2$ lone pair of Bi$^{3+}$ leads to the appreciable ME effects and ferro/antiferromagnetic ordering has been anticipated due to the coupling of the transition metal cation spins. Non-magnetic ions like Ti as a substitute at B site is particularly interesting in order to improve ME behavior [5].

II. EXPERIMENTAL PROCEDURE

Polycrystalline La$_{0.4}$Bi$_{0.6}$Mn$_{0.5}$Ti$_{0.5}$O$_3$ perovskite manganite has been synthesized using conventional solid state reaction method [5]. High purity powder oxides La$_2$O$_3$ (99.99 %), Bi$_2$O$_3$ (99.9 %), MnO$_2$ (99.9 %) and TiO$_2$ (99.9 %) (Sigma Aldrich & Co) weighed in stoichiometric ratios have been used in sample synthesis. Due to volatile nature of Bi, we have followed low temperature synthesis procedure for the formation of perovskite structure. The phase purity has been verified by X-ray diffraction (XRD) using Cobalt source at room temperature. The field emission scanning electron microscope (FE-SEM) spectrometer equipped with Electron dispersion X-ray spectroscopy (EDS) has been used for the microscopic and elemental compositional analysis. Electrical resistivity measurements as a function of temperature and magnetic field have been carried out using standard four probe setup. For in-field measurements magnetic field has been applied parallel to the direction of current, built-in with Oxford spectromag 10T superconducting magnet at University Grant Commission-Department of Atomic Energy, Consortium for Scientific Research (UGC-DAE CSR), Indore. DC magnetization as a function of magnetic field and temperature were carried out using Superconducting Quantum Interference Device-Magnetic Properties Measurements Systems (Quantum Design SQUID- MPMS XL 5).

III. RESULTS AND DISCUSSIONS

Fig. 1 shows the low intense X-Ray Diffraction (XRD) pattern of the sample with small amount (<10%) of un-reacted Bi$_2$O$_3$ impurity peaks which arises due to the low temperature synthesizing process.

![Fig. 1](image-url)

Fig. 1 display XRD pattern for the studied sample. Asterisk is impurity peaks due to un-reacted Bi$_2$O$_3$.
The Rietveld refinement on the XRD pattern yields tetragonal perovskite structure indexed using 14/mcm space group. The lattice parameters have been found to be, a=5.432 Å, b=5.432 Å and c=7.716 Å with cell volume V=227.67 Å³.

In Fig. 2 EDS pattern shows the presence of elements in the sample close to their chemical compositions. Inset of Fig.2 we show micro-structural morphology of the studied sample using FE-SEM. The grains show distinct shape with well-defined grain boundaries. But the uniformity of the grain shapes is not homogeneous and also form agglomeration (dark patches) attributed due to the strain produced by Ti ions on the lattice arrangements [6, 7] or may be due to visco-elastic character of the sintered samples.

In Fig. 3 we show MT plot at constant magnetic field H=500 Oe measured both in field cooled cooling (FCC) and field cooled warming (FCW) conditions. The MT plot doesn’t show thermal hysteresis between FCC and FCW which confirms the paramagnetic (PM) to frustrated ferromagnetic (FM) phase transition at $T_c=40$ K is of second order type. The magnetic $T_c$ is obtained from $dM_{FCW}/dT$ plot as shown in Fig. 3. The unsaturated FM behavior at low temperature indicates critical behavior around $T_c$ arising due to magnetic inhomogeneities of Ti substitution [5].

In order to understand this critical nature we have analyzed the DC susceptibility obtained from MT plot using critical scaling hypothesis. While approaching magnetic transition temperature, $T_c$ from the PM side, DC susceptibility, $\chi$ (T) is expected to follow the scaling law [8] given as $\chi (T) \sim (T/T_c-1)^{\gamma} \sim \tau^{\gamma}$. The scaling equation is modified accordingly as, $\chi_{C}^{-1} \approx \tau^{\gamma}$, where $\chi_{C} = \chi(T_c)$, $\tau = T/T_c-1$ and $\gamma$ is critical exponent. The plot of $\ln (\chi_{C}^{-1}/\tau^{\gamma})$ vs. $\ln (T/T_c-1)$ is shown in inset of Fig.3 for the studied sample. Linear fitting the above plot yields the value of slope ($\gamma$) =0.92 which deviates from unity suggesting that the sample doesn’t possess long range FM interaction below $T_c$.

In Fig. 4 we show magnetization (M) vs. magnetic field (H) isotherms measured in the temperature (T) range of $10 \leq T \leq 60$ K exhibits critical behavior around $T_c$. At 10 K, magnetization rises sharply with the increase in applied magnetic field and shows no evidence of saturation up to 5T. The linear variation of M vs. H at high field as expected for an antiferromagnet (AFM) can be observed for other measured temperatures also, which implies that the compound exhibits magnetic frustration near $T_c$. The closer magnetization measurements in the temperature range 30-40K have been carried up to 2.5 T, which also shows no evidence of saturation. And at 300K the sample shows proper PM nature.

Further we have fitted the M-H isotherm to understand the magnetic interaction at $T_c=40$ K (inset of Fig.4) using critical scaling equation, $M=DH^{1/\delta}$ [9], where D is critical amplitude and $\delta$ is critical magnetization exponent. The best fit value of $\delta$ obtained using above equation is found to be $<2.0$. This is less than the value of 3 (for ideal long range) further confirms the absence of long range FM interaction around $T_c$ [9].

This nature of absence of long range FM interactions around magnetic $T_c$ likely leads to a phenomenon called Griffith’s phase [4, 10]. This is shown by the evidence of the downturn deviation from the characteristic Curie–Weiss linear law and
the formation of FM clusters embedded in host PM matrix which is already been reported by us for the aforesaid and similar kind of sample [4, 10].

The regular Arrott plot shown in Fig. 5 as $M_1^2$ vs. $M_2^2$ relationship is based on the mean-field (MF) model of critical exponent $\beta = 0.5$ and $\gamma = 1.0$. Thus $M_2^2$ vs. $M_2$ curves reveal the magnetic nature around $T_C$ and the extrapolation of the fitted line on magnetization data at $T = T_C$ should pass through the origin. According to the criterion proposed by Banerjee et al. [11], the order of magnetic transition can be determined from the slope of these straight lines. In the present study, the Arrott plot $M_2^2$ vs. $M_2$ displays the positive slope of the curves at all temperatures studied. This specifies that a transition between the magnetically ordered and the PM phases is of the second order. The critical temperature of magnetic transition could not be evaluated from Arrott plots as the high magnetic field plot extrapolation did not reach origin. This suggested that the competition amongst the FM and AFM interactions lead magnetic transition is spread broadly both in temperature and in magnetic field. The broadening effect may be understood due to the substitution of non-magnetic Ti ions at Mn site which leads to the destruction of $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{3+}$ network replaced by $\text{Mn}^{3+}-\text{O}^{2-}-\text{Ti}^{4+}$ network [6, 8].

![Resistivity vs. Temperature](image)

**Fig. 5** $M_2^2$ vs. $H/M$ (Arrott plots) is displayed at constant temperatures. Inset we display $M_2^2$ vs. $H/M$ (Arrott plots) at constant temperature measured up to 2.5T. Solid lines are linear fits to the experimental data.

In Fig. 6 we show electrical resistivity ($\rho$) vs. temperature ($T$) at $H=0$ and 5T for the studied sample. The application of magnetic field (5T) has no effect on resistivity, since both the resistivity data overlap on one another as shown in Fig. 6 with different scales. The sample exhibit semiconducting nature measured throughout the temperature range ($180 \, K < T < 300 \, K$) without any phase transition. The resistivity measurements below 180 K was not possible due to the instrumental limitation as $\rho>1 \, \Omega$. This robust insulating behavior indicates the localization (ascribed to $6s^2$ lone pair of $\text{Bi}^{3+}$) of the charge carriers which is common in $\text{Bi}$ based samples. However, the substitution of $\text{Ti}^{4+}$ at Mn sites could not produce metallic behavior in the sample [6, 8].

The electrical transport of the charge carriers in the sample exhibiting semiconducting nature is generally governed by Variable Range Hopping (VRH) mechanism [6, 8, 10]. It is widely believed that these charge carriers form small polaron connected to local Jahn-Teller (JT) distortions [12] which facilitate the transport by hopping.

The electrical resistivity arising from hopping mechanism follows Arrhenius like equation [6, 8] given by,

$$\rho(T) = \rho_0(T) \exp(T_0/T)^{\gamma}$$

Where $T_0$ is a characteristic VRH temperature and characteristic exponent $\gamma=1$, $\frac{1}{4}$ and $\frac{1}{2}$ for hopping over the nearest sites (NSH), Mott’s VRH and Shklovskii-Efros (SE-VRH) mechanisms respectively [5, 8].

![Resistivity vs. Temperature](image)

**Fig. 6** Resistivity ($\Omega cm$) vs. Temperature ($K$) at applied magnetic field 0T and 5T for the sample. Inset $\ln(\rho/T^\gamma)$ vs. $T^{-1/2}$ with linear fitting is displayed for both 0T and 5T.

The later mechanism is being used to analyze the transport behavior in the sample which depends on the Coulomb Gap (CG) in the vicinity of the localized density of states (DOS). It is further understood that this model well describes the transport mechanism in the sample, where the DOS near Femi energy ($E_F$) is not constant but vanishes linearly with energy [5, 8]. This vanishing DOS, results in the temperature dependence of resistivity which still describes eq (1) but with $\gamma=\frac{1}{2}$ in all dimensions. In SE-VRH regime the pre-factor $\rho_0$ ($T$) can be written as $\rho_0(T) = CT^n$ in eq. (1), where $C$ is constant and $n$ is 9/2 or 5/2. The values 9/2 or 5/2 assigned for ‘n’ depends on wave function of the localized charge carriers [8]. Then eq. (1) in logarithmic form is plotted as $\ln(\rho/T^n)$ vs. $T^{-1/2}$, where $n$ and $q$ are chosen to be 9/2 and 1/2 respectively. By linear fits for these plots as shown in inset of Fig. 6 yields the values of $T_0 = 2.239x10^7$ K for $H=0T$ and $2.226x10^7$ K for $H=5T$. It can be observed that the value of $T_0$ varies only at second decimal point with the application of magnetic field which is influenced by the width ($\Delta$) of CG [8]. The $\Delta$ is found to be 0.556 eV for $H=0T$ and 0.554 eV for $H=5T$. These values are estimated using the equation, $\Delta=K_B(T_{V})^{1/2}$ [8], where $T_V$ ($\sim$186 K) is onset of VRH temperature. The obtained values infer that application of the magnetic field has no effect in reducing the ‘$\Delta$’ between the Mn hopping sites.
We have also verified the values chosen for ‘n’ and ‘q’ by presenting the local activation energy ($E_{ac}$) model. The $E_{ac}=d\ln(p)/d(1/K_BT)$ [5, 8] as shown in Fig. 6 for both H=0T and 5T nearly matches and found to increase with temperatures. Further from $E_{ac}$ and eq (1) we get,

$$\ln\left[E_{ac}/(K_BT)^n\right]=\ln q + q \ln T_0 + q \ln(1/T) \quad (2)$$

If $T_0$ is independent of temperature then ‘n’ varies within some arbitrary interval and ‘q’ can be obtained from the slope by fitting $\ln\left[E_{ac}/(K_BT)^n\right]$ vs. $\ln(1/T)$ as shown in inset of Fig. 7. The obtained best fit value of $q \approx 0.51$ suggests that assigned value of n=9/2 and the transport of charge carriers via hopping is in good agreement with SE-VRH mechanism [5, 8].

**Fig. 7 Local activation energy ($E_{ac}$) vs. temperature at applied magnetic field 0T and 5T for the sample. Inset $\ln\left[E_{ac}/(K_BT)^n\right]$ vs. $\ln(1/T)$ at H=0T with least square fitting (LSF) to find the values of characteristic exponent ‘q’ is displayed.**

**IV. Conclusions**

In summary, we have reported on magnetic interactions and electronic transport properties in La$_{0.6}$Bi$_{0.4}$Mn$_{0.5}$Ti$_{0.5}$O$_3$ perovskite manganite. The magnetic properties of the sample indicate the absence of true long range FM interaction due to criticality in their magnetic spin arrangements in temperature region nearby $T_C$. The exhibited behavior is consistent with the non-magnetic nature of Ti substitution at Mn site. The hopping transport of the charge carriers is due to SE-VRH mechanism which is usually observed for those samples with magnetic inhomogeneities and disorder in their local lattice ordering. However the applied magnetic field is also not sufficient to remove this degeneracy in conduction process.

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