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Study of coexisting phases in Bi doped $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$

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Abstract

We report the remarkable phase separation behaviour in $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ doped with Bi^{3+} ion at La site. The temperature dependent resistivity and magnetization of $\text{La}_{0.67-x}\text{Bi}_x\text{Sr}_{0.33}\text{MnO}_3$ ($x>0$) show the presence of phase separation of ferromagnetic metallic and charge ordered antiferromagnetic insulating phases. Markedly, the field dependant magnetization studies of $\text{La}_{0.67-x}\text{Bi}_x\text{Sr}_{0.33}\text{MnO}_3$ ($x=0.3$) show the metamagnetic nature of ferromagnetic metallic state implying the competition of coexisting ferromagnetic metallic and charge ordered antiferromagnetic phases. The electron spin resonance and exchange bias studies of $\text{La}_{0.67-x}\text{Bi}_x\text{Sr}_{0.33}\text{MnO}_3$ ($x=0.4$ and 0.5) substantiate the coexistence of ferromagnetic clusters in antiferromagnetic matrix.

Key words: CMR; Manganites; Phase separation; Electron spin resonance

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1. Introduction

The strontium doped lanthanum manganite, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ is one of the colossal magnetoresistance (CMR) oxides, which exhibits a large bandwidth due to the nearly same ionic radii of La^{3+} and Sr^{2+} ions [1, 2]. Nevertheless, this material shows the ground states of spin canted insulator, ferromagnetic (FM) insulator, ferromagnetic metallic (FMM), antiferromagnetic (AFM) insulator and antiferromagnetic metallic behaviours, while paramagnetic insulator and metallic behaviours observed at high temperatures for different Sr doping concentrations [3, 4]. The typical FMM behaviour of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO) is explained by the double exchange mechanism; the ferromagnetism and conductivity are due to the increased exchange of e_g electrons between Mn^{3+} and Mn^{4+} ions, which are strongly Hund's coupled [5]. $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ has been doped with several other ions to study the effect of crystal structure on the electrical and magnetic properties in addition to the induced phases. When doped with elements like, Mo, Co, Zn and Cr at Mn site, the magnetization and conductivity change with doping concentration due to the destruction of Mn-O-Mn network and change of e_g electron density [6-9]. Besides, the rare earth elements like, Pr, Y and Dy doped at La site of LSMO modifies the electrical conductivity and magnetization due to the change of Mn-O-Mn bond angles, Mn-O bond lengths and structural distortions [10-12].

On other hand, Bi doping in manganites is found to be vital in understanding the role of lone pair of electrons in the underlying double exchange and charge ordering mechanisms [13, 14]. The charge ordering occurs in $\text{Bi}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ at above room temperature [15]. The mechanism of charge ordering is possibly related with the highly polarized $6s^2$ lone pair of Bi^{3+} ions in $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$ [15, 16]. Conceivably, the doping of Bi at La site in $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ gives the competition of double exchange and charge ordering effects. We are interested in studying the coexisting phases of ferromagnetic and charge ordering behaviours in Bi doped $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$. Bi^{3+} ion shows an interesting character of two

different ionic radii; 1.24 Å (dominant character) and 1.17 Å (constraint character), while La^{3+} ion has an ionic radius of 1.22 Å [13]. Hence, it is also exciting to study the effect of ionic radius of Bi doped in $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$. Other reports on Bi doping in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ show metamagnetic transitions and coexisting FM and CO/AFM phases [13, 14]. However, the reports on Bi doped $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ [17, 18] provide not enough discussion on these aspects, which made us to explore Bi doped $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ polycrystalline materials to understand the electrical and magnetic interactions as well as coexisting phases.

2. Experimental

The polycrystalline $\text{La}_{0.67-x}\text{Bi}_x\text{Sr}_{0.33}\text{MnO}_3$ ($x=0, 0.1, 0.2, 0.3, 0.4, 0.5$) samples (indicated as Bi0, Bi1, Bi2, Bi3, Bi4, Bi5 in discussion) were prepared by standard solid state reaction method using high purity La_2O_3 , SrCO_3 , MnO_2 , Bi_2O_3 . The stoichiometric, homogeneously mixed and dried powders were calcined at 700, 800, 900 and 1000 °C for 24 hours to obtain Bi doped manganites without Bi loss [19]. The pellets were sintered at 1000 °C for 72 hrs in air and 800 °C for two hrs in O_2 atmosphere. The X-ray diffraction (XRD) measurements on powders of $\text{La}_{0.67-x}\text{Bi}_x\text{Sr}_{0.33}\text{MnO}_3$ ($x=0, 0.1, 0.2, 0.3, 0.4, 0.5$) were carried out using a Rigaku-SmartLab X-ray diffractometer. The DC electrical resistivity measurements from 10 to 330 K were carried out using a Janis closed cycle refrigerator with the conventional linear four probe method. The magnetic properties were measured by Quantum Design-MPMS-XL SQUID magnetometer. In order to investigate the magnetic interactions and coexisting magnetic phases, we have carried out X-band electron spin resonance (ESR) measurements using Bruker-EMX and JEOL-JES-FA200 ESR spectrometers equipped with low temperature cryostats.

3. Results and discussion

The XRD data of polycrystalline $\text{La}_{0.67-x}\text{Bi}_x\text{Sr}_{0.33}\text{MnO}_3$ samples, in figure 1, show that all the samples exhibit a single phase with no detectable secondary phases. The lattice parameters are calculated using the *FullProf* Rietveld refinement and shown in table 1. For $x \leq 0.3$, the samples show the rhombohedral structure with $R\bar{3}c$ space group and for $x=0.4$ and 0.5 , the samples exhibit orthorhombic structure with *Pbnm* space group. The lattice parameters are found to increase with Bi doping, which indicate the dominant high ionic character of Bi^{3+} ion when doped at La^{3+} site. Such an increase in the volume of unit cell with increase of Bi doping is observed in other reports on $\text{La}_{0.67-x}\text{Bi}_x\text{Sr}_{0.33}\text{MnO}_3$ and $\text{La}_{0.7-x}\text{Bi}_x\text{Sr}_{0.3}\text{MnO}_3$ [17, 18]. In Bi based manganites, the lone pair electrons of Bi^{3+} ion hybridize with oxygen $2p$ orbitals, which in turn reduces the bond length of $\langle\text{Bi-O}\rangle$ and bond angle of $\langle\text{Mn-O-Mn}\rangle$ and increases the bond length of $\langle\text{Mn-O}\rangle$ [19]. Hence, the crystal structure changes from rhombohedral to orthorhombic with increase of Bi doping for $x \geq 0.4$. This implies that in Bi doped $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$, the increase of $\langle\text{Mn-O}\rangle$ bond length and decrease of $\langle\text{Bi-O}\rangle$ bond length and $\langle\text{Mn-O-Mn}\rangle$ bond angle are elucidated. Such structural changes in turn would bring about the changes in electrical and magnetic properties of Bi doped $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$.

Figure 2 shows the resistivity versus temperature of polycrystalline Bi doped $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$. For $x \leq 0.3$, the samples show the metal-insulator behaviour, while $x \geq 0.4$ exhibit the insulator behaviour for the entire range of temperatures. The resistivity increases and the metal-insulator transition temperature, T_{MI} decreases for $x \leq 0.3$. The T_{MI} of undoped $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$, i.e., Bi0 is lower than the other reports which show $T_{MI} > 350$ K under high temperature sintering conditions [20]. However, we have prepared the undoped and doped LSMO samples under the same low temperature sintering conditions to avoid Bi loss. Notably, T_{MI} depends on the sintering and annealing conditions in manganites [21].

Nevertheless, T_M values of doped samples, Bi1, Bi2 and Bi3 are higher than that of other reports, wherein different preparation methods and annealing conditions were used. The low temperature upturn appears below 40 K in Bi0, Bi1, Bi2 and Bi3 samples could be due to the spin polarized transport across the grains and grain boundaries [22]. With increase of Bi doping in $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$, the increased $\langle \text{Mn-O} \rangle$ bond length and decreased $\langle \text{Mn-O-Mn} \rangle$ angle weaken the hopping of e_g electron from Mn^{3+} to Mn^{4+} , thus stabilizing the insulating state down to lower temperatures, leading to decrease of T_M and increase of resistivity. Subsequently, the Bi4 and Bi5 samples show the high resistivity and insulating behaviour in the entire measured range of temperatures. This is due to the possible charge ordering in these samples, as reported in higher doping concentrations of Bi, such as, $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and $\text{La}_{0.7-x}\text{Bi}_x\text{Sr}_{0.3}\text{MnO}_3$ ($x \geq 0.3$) [19, 23]. More light will be thrown on the magnetic state of Bi4 and Bi5 samples in later discussions, using magnetic and electron spin resonance data.

Figure 3 shows the temperature dependence of magnetization (M - T) of Bi doped $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ samples from 10 to 390 K with applied field of 10 mT in field cooled mode. The undoped $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ shows the ferromagnetic transition temperature, T_C at about 375 K which is comparable to the previous reports [24, 25]. The M - T data shows a two step transition behaviour with Bi doping for $x > 0$. This indicates that Bi doped LSMO samples undergo an intermediate magnetic state across the transition. The transition temperatures, T_{CH} and T_{CL} are high moment and low moment magnetic transitions respectively. The stepwise magnetization is a remarkable behaviour in our Bi doped $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$. Notably, the stepwise magnetization behaviour is reported only in low bandwidth manganites such as, $\text{La}_{0.67-x}\text{Nd}_x\text{Ca}_{0.33}\text{MnO}_3$, $\text{La}_{0.625-x}\text{Pr}_x\text{Ca}_{0.375}\text{MnO}_3$, and $\text{La}_{0.67-x}\text{Bi}_x\text{Ca}_{0.33}\text{MnO}_3$ [26-29]. T_{CL} is almost constant for all the doped samples except $x=0.3$. T_{CH} decreases monotonously with increasing Bi doping up to $x=0.3$. Bi4 and Bi5 samples do not show the transition to high moment state. Nevertheless, a spin flip transition is observed at 42 K. In order to verify the

stability of intermediate magnetic states, we have applied high magnetic field of 1 T and measured the temperature dependence of magnetization. As shown in figure 4, with higher applied field the stepwise magnetization behaviour has suppressed and gives the single magnetic transition temperature, T_C for Bi0, Bi1, Bi2 and Bi3 samples. In Bi0, Bi1, and Bi2 (for doping concentrations of $x=0, 0.1$ and 0.2), a clear paramagnetic to ferromagnetic transition is observed. Whereas, Bi3, Bi4 and Bi5 samples ($x=0.3, 0.4$ and 0.5) show the antiferromagnetic Néel temperature, T_N at about 269, 185 and 170 K respectively. The low temperature transition observed for Bi4 and Bi5 samples is attributed to spin flip transitions. The T_N is found to decrease with increase of Bi doping for $x \geq 0.3$. The magnetic states of Bi3, Bi4 and Bi5 samples could be assigned to antiferromagnetic states based on other reports of Bi doped manganites [16, 17]. Nevertheless, we have not observed transitions related to charge ordering state in $M-T$ data of Bi3, Bi4 and Bi5 samples with applied field of 1 T. The charge ordered transitions in Bi3, Bi4 and Bi5 samples could possibly be above 390 K [24, 29]. Notably, the magnetization systematically increases with Bi doping from $x=0$ to 0.2 below the transition temperature, but it decreases for $x=0.3$ to 0.5. We have further studied the field dependant magnetization and electron spin resonance of these samples to establish the precise magnetic state of these samples.

The field dependant magnetization, $M-H$ data in figure 5 shows that Bi0, Bi1 and Bi2 samples exhibit ferromagnetic hysteresis loops below the magnetic transition temperature (T_C) and the magnetization is found to be saturated below 1 T. The Bi4 and Bi5 samples show the hysteresis loops which are not saturated up to 5 T. Interestingly for Bi3 sample, we have observed unsaturated magnetization at high temperature, hysteresis loops with metamagnetic behaviour in the temperature range from 100 to 200 K and saturated loops at low temperatures. From the resistivity and magnetization data, we have ascertained the ferromagnetic metallic nature of polycrystalline $\text{La}_{0.37}\text{Bi}_{0.3}\text{Sr}_{0.33}\text{MnO}_3$. In spite of the

ferromagnetic metallic state, the metamagnetic behaviour is observed in $\text{La}_{0.37}\text{Bi}_{0.3}\text{Sr}_{0.33}\text{MnO}_3$. The metamagnetic behaviour with saturated M - H loops was observed earlier in the insulating $\text{La}_{0.4}\text{Bi}_{0.3}\text{Sr}_{0.3}\text{MnO}_3$ [23], $\text{Nd}_{0.8}\text{Na}_{0.2}\text{MnO}_3$ [30] and $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ [31] compositions. From the observation of metallic resistivity and magnetization hysteresis loops, we believe that there is a phase competition in Bi3 sample; the ferromagnetic metallic phase coexists with antiferromagnetic charge ordered phase. In Bi4 and Bi5, the hysteresis loops are non linear below 1 T and the loops are linearly increasing with increase of field above 1 T. The M - H loops around the zero field opens when the temperature decreases, which indicates the coexisting ferromagnetic phase in these samples. We reckon that the ferromagnetic clusters coexisting in the antiferromagnetic matrix exhibit the unsaturated magnetization curves up to 5 T. Hence, from the M - H loops, we have established that the Bi4 and Bi5 samples are of dominant antiferromagnetic nature with coexisting ferromagnetic clusters.

The electron spin resonance spectra of polycrystalline $\text{La}_{0.67-x}\text{Bi}_x\text{Sr}_{0.33}\text{MnO}_3$ samples from 300 K to low temperatures are shown in figure 6. The ESR measurements on the magnetic samples show resonance absorption at low fields due to the internal field added with applied magnetic field. The resonance field (H_0) is sum of the external applied field (H_{ex}) and internal field (H_i) of the material, i.e., $H_0 = H_{ex} + H_i$. In paramagnetic state, the internal field, $H_i = 0$, the resonance occurs at ~ 3200 G in X-band (9.2 GHz) ESR measurements. The room temperature ESR data of Bi0, Bi1 and Bi2 samples show the resonance peak at lower fields of 1550, 1363 and 1814 G respectively. The low field ferromagnetic resonance observed up to room temperature supports the ferromagnetic nature of Bi0, Bi1 and Bi2 samples as observed from magnetic studies.

The ferromagnetic resonance field shifts towards lower fields with decreasing temperature for Bi0, Bi1 and B2 samples. This indicates the increase of internal field with

decrease of temperature, as supported by magnetization data. Notably, we have also found broad and low intensity resonance line at ~ 3200 G for Bi0, Bi1 and Bi2 samples. The high field resonance line exists below the transition temperature in polycrystalline manganites, which possibly arises from the ferromagnetic clusters of different mobility [32]. Moreover, the multiple low field resonance lines observed at intermediate temperatures could be due to the roughness of polycrystalline grains, which leads to random anisotropy field [33].

The ESR data of Bi3, Bi4 and Bi5 samples show the high field resonance line at ~ 3200 G at room temperature and the low field resonance lines appear when the temperature decreases below the transition temperatures, which is the evidence of coexisting magnetic phases. The Bi3 sample shows the shoulder corresponding to the ordered magnetic state at 300 K at 2529 G. Upon decreasing the temperature, the intensity of low field resonance increases and shifts to lower fields, while the high field resonance peak is suppressed below 250 K. Similarly, Bi4 and Bi5 samples show the low field shoulder appearing at 440 G at 243 K and 432 G at 200 K respectively. Furthermore, the intensity of low field resonance increases with decrease of temperature and high field resonance suppresses at low temperatures. Remarkably, the resonance fields corresponding to low field line increase with decrease of temperature for both Bi4 and Bi5 samples. The increase in resonance field of low field line with decreasing temperature indicates the increasing negative internal fields which oppose the applied field in Bi4 and Bi5 samples.

We have analyzed the ESR data using asymmetric Lorentzian line shape [34].

$$\frac{dP}{dH} \propto \frac{d}{dH} \left[\frac{\Delta H + a(H - H_0)}{(H - H_0)^2 + \Delta H^2} \right] \quad (1)$$

Here H_0 and ΔH are the resonance field and line width respectively and ' a ' is the asymmetry parameter, denoting the dispersion to absorption ratio. The asymmetry is due to the skin depth effect arising out of conductivity of the samples.

The low field ESR lines of Bi0, Bi1 and Bi2 samples are fitted with single asymmetric

Lorentzian line shape. The temperature dependence of the resonance fields of Bi0, Bi1 and Bi2 samples in figure 7 shows that the resonance fields of low field line decrease monotonously with decreasing temperature and almost constant at low temperatures. Notably, the behaviours of resonance fields of Bi0, Bi1 and Bi2 samples mirror the temperature dependence of magnetization data with applied field of 1 T.

On the other hand, the ESR data of Bi3, Bi4 and Bi5 samples show two absorption lines, which we have fitted with two asymmetric Lorentzian line shapes. The obtained resonance fields are shown in figure 8. For Bi3 sample, resonance field of low field line decreases monotonously with decrease of temperature and that of high field resonance is almost constant from 300 to 250 K. On the other hand, the resonance fields of high field lines of Bi4 and Bi5 samples decrease slightly with decrease of temperatures from 300 to 200 K and from 300 to 100 K respectively. The observed high field resonance and the decrease of resonance fields with decrease of temperature could be in the same way attributed to the spin clusters of different mobility and the orbital ordering [35-38]. Remarkably, the resonance fields of low field lines of Bi4 and Bi5 samples increase with decrease of temperature. Though, the *M-H* loops of Bi4 and Bi5 samples show antiferromagnetic behaviour, the antiferromagnetic resonance would not be observed using X-band ESR measurements. Indisputably, the low field resonance lines of Bi4 and Bi5 samples arise from the ferromagnetic phase. A similar high field shifts of low field resonance line in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, $\text{Pr}_{0.65}\text{Ca}_{0.25}\text{Sr}_{0.10}\text{MnO}_3$ and $\text{Nd}_{0.52}\text{Sr}_{0.48}\text{MnO}_3$ were attributed to the coexistence of ferromagnetic clusters in antiferromagnetic matrix; the negative field due to large anisotropy of the antiferromagnetic phase shifts FM resonance line upwards [39-42]. The low field resonance lines appear at the magnetic transition temperature, T_N of Bi4 and Bi5 samples. It corroborates that the ferromagnetic clusters emerge with the antiferromagnetic phase of these samples. The line widths of Bi doped LSMO samples

increase with decrease of temperature, which is due to the demagnetizing field from the defects between the grains and surface granularity in the polycrystalline materials. Similar line width behaviour is commonly observed in manganites [43, 44].

In spite of the ferromagnetic ground state of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$, when doped with Bi ions, it converts into charge ordered antiferromagnet. $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$ is known to exhibit a high temperature charge ordered state and the antiferromagnetic structure appears at low temperatures [14, 45]. When Bi^{3+} ion is doped at La site of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$, the charge ordered phase is induced. We reckon that the charge ordered phase grows as Bi concentration increases and consequently Bi doped $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ samples become phase separated. Hence, the step wise behaviour observed in magnetization data of $\text{La}_{0.67-x}\text{Bi}_x\text{Sr}_{0.33}\text{MnO}_3$ ($x > 0$) samples is due to the coexistence of ferromagnetic and antiferromagnetic charge ordered phases. The disappearance of stepwise behaviour in high field (1 T) magnetization data shows the weak nature of charge ordering effect in Bi1 and Bi2 samples. This implies that the higher applied field induces the ferromagnetic polarization along the percolation path in these phase separated compounds. However, Bi4 and Bi5 samples show antiferromagnetism associated with charge ordering from the magnetic studies, implying the dominant charge ordered antiferromagnetic ground state. Remarkably, the low temperature electrical resistivity and magnetic measurements confirm the dominant ferromagnetic metallic ground state of Bi1 and Bi2 samples and charge ordered insulating and antiferromagnetic nature of Bi4 and Bi5 samples over the entire temperature range. Interestingly, Bi3 sample shows the metamagnetic behaviour in the ferromagnetic metallic region of temperatures from 100 to 200 K. This indicates that there is a phase competition of ferromagnetic and charge ordered antiferromagnetic ground states in Bi3 sample. Akimoto *et al* reported the antiferromagnetic metallic ground state in doped manganites [46]. We have observed the metallic behaviour from electrical studies and antiferromagnetic Néel temperature from the high field

magnetization data for Bi3 sample. We reckon that Bi3 sample also has the antiferromagnetic metallic ground state. However, the ESR measurements show an apparent ferromagnetic behaviour for Bi3 sample. Hence, we believe that there is a phase competition of ferromagnetic metallic and antiferromagnetic charge ordered states in Bi3, i.e., $\text{La}_{0.37}\text{Bi}_{0.3}\text{Sr}_{0.33}\text{MnO}_3$.

In ESR data of Bi0, Bi1, Bi2 and Bi3 samples, a decrease of resonance field of low field line with decrease of the temperature is observed. This indicates the dominant ferromagnetic ground state in these samples. However in Bi4 and Bi5 samples, resonance field of low field line increases with decrease of temperature. The increasing resonance field with decreasing temperature indicates the role of anisotropy on the ferromagnetic resonance in these samples. The ferromagnetic resonance arising from the ferromagnetic phase of these samples is influenced by the dominant charge ordered coexisting phase which exhibits strong anisotropy under the applied field. The charge ordering phase exhibits the CE-type antiferromagnetism which gives rise to the induced anisotropy opposing the applied field [45, 47].

The magnetic and ESR studies suggest that Bi4 and Bi5 samples show the ferromagnetic clusters coexist in antiferromagnetic matrix. Usually, in systems having a ferromagnetic and antiferromagnetic interface, the intrinsic exchange bias effect is observed [48, 49]. In order to verify the coexistence of ferromagnetic clusters in antiferromagnetic matrix in higher Bi doped LSMO samples, we have measured M - H hysteresis loops of Bi4 and Bi5 samples at 10 K after field cooling at 5 T. Remarkably, we have observed the exchange bias effect in these samples; the M - H loops shift towards the negative field axis as shown in figure 9. The antiferromagnetic interface provides a higher opposing anisotropy field acting on the ferromagnetic clusters, which in turn require large field to saturate in the negative field direction. Nevertheless, the observed exchange bias effect in Bi4 and Bi5

samples confirms that there exists intrinsic ferromagnetic and antiferromagnetic interface. The intrinsic exchange bias effect was observed in several ferromagnetic/antiferromagnetic core/shell structured particles [49, 50], in addition to phase separated [51] and nanocrystalline manganites [52]. The intrinsic exchange bias effect thus clearly shows the ferromagnetic clusters in antiferromagnetic matrix as perceived from the magnetic and ESR measurements of $\text{La}_{0.67-x}\text{Bi}_x\text{Sr}_{0.33}\text{MnO}_3$ for $x \geq 0.4$.

Conclusions

Bi doping in $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ shows the transition from rhombohedral ($0 \leq x \leq 0.3$) to orthorhombic structures ($0.4 \leq x \leq 0.5$) accompanied by the transition from ferromagnetic metallic to antiferromagnetic insulating states. The metal-insulator transition and ferromagnetic to paramagnetic transition temperatures are found to decrease with increase of Bi doping. The metamagnetic behaviour of $\text{La}_{0.37}\text{Bi}_{0.3}\text{Sr}_{0.33}\text{MnO}_3$ shows the competition of coexisting ferromagnetic metallic and charge ordered antiferromagnetic insulating phases. The ESR study confirm that $\text{La}_{0.27}\text{Bi}_{0.4}\text{Sr}_{0.33}\text{MnO}_3$ and $\text{La}_{0.17}\text{Bi}_{0.5}\text{Sr}_{0.33}\text{MnO}_3$ samples show the dominant charge ordered antiferromagnetic phase coexisting with ferromagnetic clusters. Remarkably, the electrical transport and magnetic studies along with the ESR study help to ascertain the coexisting phases in polycrystalline Bi doped $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ samples.

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Figure captions

Figure 1. Room temperature XRD data of polycrystalline $\text{La}_{0.67-x}\text{Bi}_x\text{Sr}_{0.33}\text{MnO}_3$ ($x=0, 0.1, 0.2, 0.3, 0.4$ and 0.5), i.e., Bi0, Bi1, Bi2, Bi3, Bi4 and Bi5.

Figure 2. Temperature dependence of resistivity of polycrystalline Bi doped $\text{La}_{0.67-x}\text{Sr}_{0.33}\text{MnO}_3$ ($x=0, 0.1, 0.2, 0.3, 0.4$ and 0.5), i.e., Bi0, Bi1, Bi2, Bi3, Bi4 and Bi5.

Figure 3. The temperature dependence of magnetization of $\text{La}_{0.67-x}\text{Bi}_x\text{Sr}_{0.33}\text{MnO}_3$ ($x=0, 0.1, 0.2, 0.3, 0.4$ and 0.5), i.e., Bi0, Bi1, Bi2, Bi3, Bi4 and Bi5 for applied magnetic field of $H=10$ mT with field cooling mode.

Figure 4. Temperature dependence of magnetization of $\text{La}_{0.67-x}\text{Bi}_x\text{Sr}_{0.33}\text{MnO}_3$ ($x=0, 0.1, 0.2, 0.3, 0.4$ and 0.5), i.e., Bi0, Bi1, Bi2, Bi3, Bi4 and Bi5 with applied field of 1 T in field cooling mode.

Figure 5. Magnetization versus magnetic field at different temperatures for $\text{La}_{0.67-x}\text{Bi}_x\text{Sr}_{0.33}\text{MnO}_3$ ($x=0, 0.1, 0.2, 0.3, 0.4$ and 0.5), i.e., Bi0, Bi1, Bi2, Bi3, Bi4 and Bi5.

Figure 6. Electron spin resonance data of the $\text{La}_{0.67-x}\text{Bi}_x\text{Sr}_{0.33}\text{MnO}_3$ ($x=0, 0.1, 0.2, 0.3, 0.4$ and 0.5), i.e., Bi0, Bi1, Bi2, Bi3, Bi4 and Bi5 at different temperatures. The dotted lines showing the low field resonance peak positions are guide to eye.

Figure 7. Temperature dependence of the low field resonance lines of $\text{La}_{0.67-x}\text{Bi}_x\text{Sr}_{0.33}\text{MnO}_3$ for $x=0, 0.1$, and 0.2 , i.e., Bi0, Bi1 and Bi2.

Figure 8. Temperature dependence of the high and low field resonance lines of $\text{La}_{0.67-x}\text{Bi}_x\text{Sr}_{0.33}\text{MnO}_3$ for $x=0.3, 0.4$ and 0.5 i.e., Bi3, Bi4 and Bi5. The open and closed symbols are resonance fields corresponding to low and high field lines respectively.

Figure 9. Magnetization versus magnetic field at 10 K for $\text{La}_{0.27}\text{Bi}_{0.4}\text{Sr}_{0.33}\text{MnO}_3$ (Bi4) and $\text{La}_{0.17}\text{Bi}_{0.5}\text{Sr}_{0.33}\text{MnO}_3$ (Bi5). The samples were field cooled at 5 T.

Table captions

Table 1. Lattice and structural parameters of $\text{La}_{0.67-x}\text{Bi}_x\text{Sr}_{0.33}\text{MnO}_3$ ($x=0, 0.1, 0.2, 0.3, 0.4$ and 0.5), i.e., Bi0, Bi1, Bi2, Bi3, Bi4 and Bi5.

Sample	Structure	Space group	a (Å)	b (Å)	c (Å)
Bi0	Rhombohedral	$R\bar{3}c$	5.491(3)	5.491(3)	13.327(2)
Bi1	Rhombohedral	$R\bar{3}c$	5.501(2)	5.501(2)	13.370(3)
Bi2	Rhombohedral	$R\bar{3}c$	5.509(9)	5.509(9)	13.410(7)
Bi3	Rhombohedral	$R\bar{3}c$	5.507(1)	5.507(1)	13.423(6)
Bi4	Orthorhombic	$Pbnm$	5.769(1)	5.482(9)	14.023(8)
Bi5	Orthorhombic	$Pbnm$	5.768(6)	5.491(1)	14.027(2)

$\text{La}_{0.67-x}\text{Bi}_x\text{Sr}_{0.33}\text{MnO}_3$ show the transition from rhombohedral to orthorhombic structure

Resistivity and magnetization for $x>0$ show phase separation of FMM and AFI phases

$\text{La}_{0.37}\text{Bi}_{0.3}\text{Sr}_{0.33}\text{MnO}_3$ exhibits a competition of FMM and AFI phases

Magnetization and ESR illustrate coexisting FM clusters in AFM matrix for $x=0.4, 0.5$

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9