Occurrence of Mixed Phase in $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.9}\text{Cr}_{0.1}\text{O}_3$ bulk sample: Electron Paramagnetic Resonance and Magnetization Studies

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We study the effects of 10% Cr substitution in Mn sites of $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ on the antiferromagnetic (AFM) ($T_N \sim 110$ K) and charge ordering (CO) ($T_{CO} \sim 525$ K) transitions using structural, magnetic and electron paramagnetic resonance (EPR) techniques. Field cooled (FC) and zero field cooled (ZFC) magnetization measurements done from 400 K down to 4 K show that the compound is in the paramagnetic (PM) phase till 50 K where it undergoes a transition to a short range ferromagnetic phase (FM). EPR measurements performed in the temperature range, 300 K till 80 K conform with the magnetization measurements as symmetric signals are observed owing to the PM phase. Below 80 K, signals become asymmetric. EPR Intensity $I \times T$ vs. $T$ plot shows a peak at $\sim 110$ K confirming the presence of AFM. We observe that below 50 K, the sample is in the mixed phase with clusters of AFM and FM coexisting.
I. INTRODUCTION

Manganites of the form $T_{1-x}D_xMnO_3$ (where $T$ is a trivalent rare-earth ion or Bi ion and $D$ is a divalent alkaline earth ion) display competition between ferromagnetic double exchange (Zener exchange) interaction (between $Mn^{3+}$ and $Mn^{4+}$ leading to ferromagnetic metallic (FMM) state) and antiferromagnetic (AFM) super-exchange interaction (between $Mn^{3+}$ ions leading to charge ordering insulating (COI) AFM state)\cite{1-3}. This competition leads to the formation of domains with contrasting properties, i.e. the system stabilizes by breaking into regions with high electron density (this region becomes AFM) and low electronic density (this region becomes FM). This phenomena is called phase separation\cite{4}. Coulomb repulsion between electrons suggests that these regions are of few nanometers. The end members of the phase diagram in these compounds ($TMnO_3$ and $DMnO_3$) are stabilized in AFM state; when the end members are substituted with divalent ions in case of $TMnO_3$ and trivalent ions in $DMnO_3$, FM state starts to build up. This leads to the formation of mixed phase with AFM phase and FM phase existing together. Even in the half doped $T_{0.5}D_{0.5}MnO_3$, COI-AFM state is stabilized due to the presence of equal number of $Mn^{3+}$ and $Mn^{4+}$ ions. Interestingly, it has been found that a few methods like external pressure, magnetic field, reducing the size of the bulk particle to nano and substitution of the Cr ions in sites of Mn ions have resulted in suppression of the CO-AFM phase and enhancement of FMM phase\cite{5-8}. Cr is in trivalent form and it breaks the long range CO state due to its unoccupied $e_g$ orbital, suppressing the AFM phase and enhancing the double exchange interaction resulting in the stabilization of FMM phase.

A few investigations on Cr substituted rare-earth manganites have been reported previously\cite{7,9-11}. Studies done on $Nd_{0.5}Ca_{0.5}Mn_{1-y}Cr_yO_3$ ($y=0.03, 0.05, 0.1$)\cite{7} show that with increasing Cr substitution CO AFM phase diminishes and FMM phase emerges. Studies done on $La_{0.46}Sr_{0.54}Mn_{1-y}Cr_yO_3$ ($0 \leq y \leq 0.08$)\cite{9} show that at $y = 0$ the sample undergoes PM to FM and FM to AFM transitions at 272 K and 190 K respectively. With increasing Cr substitution the FM phase becomes dominant over AFM phase. At $y = 0.08$ AFM phase disappears completely. Studies done on $Nd_{0.6}Ca_{0.4}Mn_{1-y}Cr_yO_3$ system\cite{10} show that, the parent compound which is CO AFM changes to a mixed magnetic state with AFM and magnetic domains coexisting in the region $0.015 \leq y \leq 0.04$ of Cr substitution. In the region $0.04 < y < 0.4$ the sample is in the ferrimagnetic state. Neutron diffraction and magnetization studies done on $Nd_{0.6}Ca_{0.4}Mn_{0.5}Cr_{0.5}O_3$\cite{11} show that manganese and chromium ions order in the lattice in a similar way to $Mn^{3+}$ and $Mn^{4+}$.
ordering in the CO state of $Nd_{0.6}Ca_{0.4}MnO_3$. Below 100 K the magnetic moment increases with decreasing temperature and does not saturate, indicating the presence of FM component. Takuro et al.\cite{12} studied the effects of Cr substitution as an impurity in $Pr_{1-x}Ca_xMn_{0.97}Cr_{0.03}O_3$, $La_{1-x}Ca_xMn_{0.97}Cr_{0.03}O_3$ and $Nd_{1-x}Sr_xMn_{0.97}Cr_{0.03}O_3$. In here just 3% of Cr substitution has induced a short range CO state, but the FM and layered AFM phase remain as long range ordered.

Bismuth based manganites of the formula $Bi_{1-x}D_xMnO_3$ (where D=Ca,Sr) are different from doped rare-earth manganites due to the presence of highly polarizable $6s^2$ lone pair of electrons present on the Bi ion. It significantly restricts the mobility of $e_g$ electrons and favors charge ordering (CO). Very few investigations have been reported on Cr substituted Bi manganites\cite{8,13}. $Bi_{0.5}Sr_{0.5}MnO_3$ shows $T_{CO} \sim 525$ K and $T_N \sim 110$ K\cite{14,15}. CO in this composition is very robust and this is also followed by the AFM phase. Rao et al.\cite{16} analyzed $Bi_{0.5}Sr_{0.5}MnO_3$ nanoparticles and found that both CO and AFM phases are unaffected unlike the other doped rare-earth manganites\cite{5,6}. Aim of this work is to study if 10% of Cr substitution is sufficient to modify the existing properties and instigate new properties in $Bi_{0.5}Sr_{0.5}MnO_3$ system. We discovered that Cr substitution has led to the formation of AFM phase and creation of short range FM phase which coexist below certain temperature.

II. PREPARATION AND CHARACTERIZATION

Polycrystalline powder of BSMCO bulk sample was prepared via the solid state route. Calculated stoichiometric amounts of 99.9% pure $Bi_2O_3$, $SrCO_3$, $MnCO_3$ and $Cr_2O_3$ were taken and mixed in an agate mortar and ground vigorously for an hour. This powder was then kept in a furnace for sintering at 900°C for 12 hrs. Sintered powder was taken out and ground again for an hour, pelleted and kept in the furnace twice, first at 1100°C and then at 1300°C (with intermediate grinding and pelleting) each for a duration of 24 hrs. The phase purity and the crystal structure of the sample was determined using X-ray diffractometer. Electron probe micro analysis (EPMA) was done to confirm the stoichiometric ratios. Magnetization measurements were done using PPMS facility. EPR measurements were performed using Bruker EMX spectrometer at a nominal frequency of 9.4 GHz.

Room temperature X-ray diffraction pattern for BSMCO is as shown in Figure 1. Rietveld refinement was done on these XRD patterns taking reference data\cite{17} using the GSAS computer program. The sample crystallizes in tetragonal structure with space group P4mm, with cell parameters $a = b = 3.9067\AA$, $c = 3.8010\AA$ $\alpha = \beta = \gamma = 90^\circ$, with $\chi^2 = 8.563$, $Rp = 0.0219$, $wRp =$
FIG. 1. Rietveld refined XRD of BSMCO sample; Here black cross represent experimental data, red circles represent the fit, blue triangle represent background, green line represent the difference between experimental and fitted data, and the vertical bars are the Bragg reflection positions.

0.0509. Stoichiometric ratios calculated using EPMA match to a great extent with the expected values. The calculated stoichiometric ratios for elements are Bi=0.510, Sr=0.489, Mn=0.894, Cr=0.106.

III. MAGNETIZATION STUDIES

The field cooled (FC) and the zero field cooled (ZFC) magnetization curves for BSMCO, measured under 100 Oe field, from 400 K till 4 K are shown in Figure 2. Both FC and ZFC curves conform with each other from 400 K till 50 K indicating the presence of PM phase; at ~ 50 K there is a sharp increase in the FC magnetization curve indicating a building up of FM ordering and at the same temperature ZFC curve undergoes a peak. The large gap between the FC and ZFC
FIG. 2. FC and ZFC magnetization behavior of BSMCO sample, inset shows the dM/dT plot

curve points to short range FM ordering in the system. The Figure 2 shows a plot of dM/dT vs. T on FC curve. Here a sharp dip at 50 K is due to FM transition.

We performed a field cooled M vs. H measurement at 5 K in the cooling field of 2 T. The plot is shown in Figure 3. Closer inspection of the hysteresis plot (see the inset of Figure 3) clearly indicates the presence of FM phase. Also note that the magnetization curve does not saturate even till 5T field; indicating the coexistence of non-ferromagnetic clusters in the system, which may be due to either the presence of antiferromagnetically aligned spins or paramagnetically aligned spins.

IV. EPR STUDIES

EPR spectra were recorded using a commercial X-band EPR spectrometer for the sample in the temperature range of 4 K to 300 K. A speck of DPPH was used as a field marker. The signals were fitted to the broad Lorentzian lineshape function in a derivative form.
FIG. 3. M vs. H for BSMCO sample at 5 K cooled in the presence of 2T field; inset of the figure shows an expanded view showing the absence of EB

\[
\frac{dP}{dH} = A \frac{d}{dH} \left( \frac{\Delta H}{4(H - H_r)^2 + (\Delta H)^2} + \frac{\Delta H}{4(H + H_r)^2 + (\Delta H)^2} \right)
\]  (1)

where \( P \) is microwave power absorbed by the sample at resonance, \( \Delta H \) is linewidth, \( A \) is a quantity proportional to the intensity of the signal and \( H_r \) is resonance field to extract the lineshape parameters viz., intensity, g-value and linewidth.

Figure 4 shows the EPR spectra at different temperatures for the BSMCO sample. Here the red line represents the double Lorentzian fit. Below 75 K we could not fit to the double Lorentzian lineshape because the signals were asymmetric owing to the presence of FM phase. But unlike bulk FM, where the signals become stronger here the signals get weaker and weaker with decreasing temperature. This suggests that the FM is not macroscopic but of short range in nature and also there is a competition between the ordered (FM) and disordered state; which conforms with our
magnetization data. The lineshape parameters viz, intensity I, linewidth $\Delta H_{pp} (= \Delta H = \sqrt{3})$ and resonance field ($H_r$) can be extracted from the fitted equation; but only for the symmetric signals. In case of asymmetric signals (given there is no loss of the signal below zero field), one can still measure the resonance field $H_r$ and peak to peak linewidth $\Delta H_{pp}$ and intensity (I) directly from the signal.

The g-value vs. temperature is plotted in the Figure 5. From the plot it is very clear that with decreasing temperature the g-value decreases till 75 K. At $\sim 75$ K, we see a sudden increase in the g-value due to the building up of short range FM ordering. The resonance field $H_r$ vs. temperature for the sample is plotted in the inset of the Figure 5. The resonance field is constant in the paramagnetic region and decreases drastically as it approaches $T_c$. This can be attributed to the local field arising due to the transition.

The EPR linewidth is as shown in Figure 6. As can be seen it increases with decreasing tem-
FIG. 5. Temperature dependence of g-value plot for the BSMCO sample (errors bars are also plotted at selected temperatures); inset shows a plot of resonance field $H_r$ vs. T.

Temperature going from PM phase to FM phase. This is unlike usual manganite systems where the linewidth decreases with decreasing temperature towards $T_c$, reaches a minimum at $T_{min} \sim 1.1 T_c$ and begins to increase again as the temperature is decreased further [20,23]. To understand this atypical behavior better we tried fitting the linewidth variation to different known models [21,22,24,27]. All these fittings resulted in the poor agreement with our data. The minimum in the linewidth observed at $\sim 1.1 T_c$ in many manganites is a consequence of competing effects of spin-phonon interaction and FM/AFM fluctuations which lead to opposite dependence of the linewidth on the temperatures. An absence of an increase in the linewidth with increasing temperature indicates negligible contribution of spin-phonon interaction to the linewidth in our sample.

We then calculated Intensity using the formula [20].
\[ I = (\Delta H_{pp})^2 h \]  

where \( \Delta H_{pp} \) is the peak to peak linewidth and \( h \) is peak to peak height.

We measured \( \Delta H_{pp} \) and \( h \) directly from the signal and calculated the intensity down to 50 K. Figure 7 shows the intensity plot against temperature. The EPR intensity is usually proportional to the DC susceptibility. Intensity vs. temperature is plotted and it is observed that intensity increases with decreasing temperature, closely resembling the FC magnetization trend as can be seen in the main Figure 2. Intensity plot distinctly shows that as the temperature decreases intensity increases gradually peaking at around \( \sim 110 \) K. This peak is very close to the AFM ordering temperature in an undoped system which is at \( \sim 110 \) K. Earlier reports have shown that a peak is observed in an intensity plot if there exists an AFM ordering in the system. Normalized ‘\( I \times T \) vs. \( T \)’ is plotted in the inset of Figure 7. As pointed in the figure there is a prominent peak.
FIG. 7. Temperature dependence of normalized Intensity $I_N$; inset to the figure normalized $I \times T$ vs. $T$ plot

at $\sim 110$ K, which confirms the existence of AFM phase.

V. DISCUSSION

10% Cr ion substitution has resulted in considerable changes in the system. $Cr^{3+}$ is the main driving force behind the appearance of FM phase as well as weakening of AFM phase in our system. We observe that our results are in agreement with earlier reports on Cr doped rare-earth manganites\textsuperscript{7,9–12} as well as Bi manganites\textsuperscript{8,13}. Below we discuss the results of earlier reports on Cr substituted Bi manganite systems in comparison with our system.

According to Yamada et al.\textsuperscript{13} in $Bi_{1-x}Sr_xMn_{1-y}Cr_yO_3$ where $x=0.25$, 0.3, 0.4 and $0 \leq y \leq 0.1$, for all the samples Curie temperature is positive suggesting ferromagnetic interaction between Mn spin moments. The magnetization in the AFM phase increases with Cr doping upto 10% and
$T_N$ disappears for $y=0.1$. Thus the degree of AFM state by Cr doping decreases with increasing $x$. Authors also observe that upon Cr substitution the AFM phase in the system transforms into PM state rather than FM state. According to Xiong et al. in $Bi_{0.5}Ca_{0.5}Mn_{1-y}Cr_yO_3$ where $0 \leq y \leq 0.15$ with increasing Cr content; here for $y=0$, $T_N \sim 130$ K. With increasing Cr content, AFM ordering shifts slightly to lower temperature but it is unaffected till $y \leq 0.24$. Above this there is a depression in the AFM ordering. The reciprocal susceptibilities of all the samples show positive $\Theta_{cw}$ (curie constant) value, indicating the presence of local FM correlation and weakening of AFM ordering. Our results are in agreement with earlier reports as in our sample we observe the weakening of AFM phase, emergence of FM phase, and below certain temperature both FM and AFM coexist together. According to magnetization short range FM ordering takes place below 50 K. EPR signals become asymmetric below 80 K indicating the presence of local field arising due to the presence of FM ordering, which is reflected in g-value plot. These asymmetric signals becoming weaker with decreasing temperature and absence of the minimum at $\sim 1.1T_c$ in the linewidth plot confirms the very nature of FM being short range. Magnetization does not display the presence of AFM phase but peak in the EPR intensity at $\sim 110$ K exhibits the presence of AFM in the system.

We infer that at higher temperatures the sample is in the PM phase, as the temperature decreases the sample undergoes a transition to a AFM phase at $\sim 110$ K due to the interaction between Mn ion moments. Further down the temperature at $\sim 50$ K, FM clusters are formed due to the interaction between Cr ion moments leading to the formation of mixed phase. This causes increase in the magnetization. In this work we observe that 10% of Cr substitution has instigated the emergence of short range FM phase and weakening of AFM phase.

VI. CONCLUSION

In summary, we prepared $Bi_{0.5}Sr_{0.5}Mn_{0.9}Cr_{0.1}O_3$ bulk sample and performed magnetization and EPR measurements. The FC and ZFC magnetization measurements show that the sample undergoes transition to a short range FM phase at 50 K. The EPR data complies with the magnetization data by indicating the presence of short range FM. Further EPR intensity gives the evidence of the presence of AFM below 110 K. We observe that the sample is in the mixed phase with the coexistence of FM and AFM clusters.

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