Effect of Cr-doping on magnetic phase separation in 
Bi_{0.5}Ca_{0.5}MnO_{3}

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Abstract. The effect of Cr doping on the magnetic phase separation in Bi_{0.5}Ca_{0.5}Mn_{1-x}Cr_{x}O_{3} (x = 0-0.05) was explored by temperature dependent Electron Spin Resonance (ESR) studies. The volume fraction of ferromagnetic (FM) domains increase at the expense of antiferromagnetic (AFM) domains and the Charge Ordering (CO) is suppressed with the increase in Cr content. With increase in Cr content the CO transition is smeared and it almost disappears at x = 0.05. The CO temperature, T_{CO}, decreases from 317K to 278K as x increases from 0 to 0.05. The Neel temperature T_{N}, is ~160K for the x = 0 and 0.01 samples and it decreases to ~ 120 K for sample with x = 0.05. A strong competition between the FM and AFM correlations is observed as a function of composition and temperature in the temperature range T_{N} < T < T_{CO}.

1. Introduction

The effect of doping at the Mn-site by other transition metals such as Cr and Co on charge-ordering (CO) in perovskite manganites of Ln_{0.5}A_{0.5}MnO_{3} (Ln = rare earth, A = alkaline earths) has been reported in the past few years. The Bi(Ca, Sr)MnO_{3} manganites are semiconductors and exhibit high charge ordering temperature (T_{CO}) [1-4]. The behavior of the Bi-manganites and their comparison with Lanthanide manganites has been studied in the recent years. Substitution of Mn by 3d transition metal (TM) ions can affect the stability of CO phase. The phenomenon of phase separation (PS) i.e. coexistence of CO and ferromagnetic (FM) phases has been reported by several groups [5-8]. There have been some reports of magnetization and transport studies on Cr doped Bi-manganites [9-11]. ESR is known to be a powerful technique for understanding the spin structure and its dynamics. The high sensitivity of the technique enables the detection of changes in short-range magnetic interactions and formation of micro magnetic phases. We have reported in our earlier work ESR studies on Bi_{0.5}Ca_{0.5}MnO_{3} [12, 13]. In this paper work we report temperature dependent ESR study on Cr – doping at Mn site in Bi_{0.5}Ca_{0.5}MnO_{3}.

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2. Experiments

The samples of Bi$_{0.5}$Ca$_{0.5}$Mn$_{(1-x)}$Cr$_x$O$_3$ (x = 0, 0.01, 0.03, 0.05) were prepared using the solid-state reaction method by grinding stoichiometric amounts of Bi$_2$O$_3$, MnO$_2$, CaCO$_3$ and Cr$_2$O$_3$ for the required compositions. The samples were calcined in air at temperatures of 600°C to 900°C for several hours with intermediate grinding. An extra amount of Bi$_2$O$_3$ was added to compensate the loss during calcination. The XRD plots were recorded to check the phase formation.

The ESR spectra of the samples were recorded on a JEOL X-Band ESR spectrometer fitted with a temperature controller and continuous gas-flow cryostat for liquid nitrogen in the temperature range 100–480K (±0.5 K). In order to eliminate the size effect and cavity overloading, powder (grain size ~1μm) samples of 1–5 mg were placed at the bottom of quartz tube centered in microwave rectangular cavity. The ESR spectra were recorded within the linear response regime at microwave power of 1mW.

3. Results and discussion

The ESR spectra of all the compositions consist of broad resonance lines, which can be fitted by a Lorentzian line shape. The spectra are almost symmetric with respect to the resonance field as the temperature increases confirming the absence of skin depth effect. The $g$ values estimated from the resonance field of all the compositions are ~2. The ESR signal observed in manganites is assigned to some combination or clusters of Mn$^{3+}$–Mn$^{4+}$ ions coupled by a strong short-range FM double exchange (DE) interactions [14, 15]. All Mn ions are assumed to contribute to the ESR signal and the double integrated (DI) line intensity therefore should be proportional to the number of ESR centres and is a measure of $\chi_{ESR}$ [16].
Figure 1 depicts the $1/D_I$ v temperature plots of $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{Mn}(1-x)\text{Cr}_x\text{O}_3$. The charge ordering temperature, $T_{\text{CO}}$, and antiferromagnetic onset temperature, $T_O$, are indicated on the plots. The linear fits as per Curie-Weiss law are obtained in the high temperature region till $T_G$. As $x$ increases $T_G$ decreases and the Curie-Weiss behaviour extends to a broader temperature range. The deviation from Curie–Weiss law and the high positive value of the Curie-Weiss temperature, $\theta$, indicates strong FM interactions at high temperatures [12]. In the temperature range $T_{\text{CO}} > T > T_N$, which is the paramagnetic (PM) + CO phase, the linear fits with lesser slopes are obtained. The small yet positive $\theta$ values indicate weaker FM interactions in the PM + CO state.

The $T_{\text{CO}}$ decreases from 317K to 278K as $x$ increases from 0 to 0.03 and it almost disappears at $x = 0.05$. The Neel temperature $T_N$, is ~160K for the $x = 0$ and 0.01 samples and it decreases to ~ 120 K for sample with $x = 0.05$. The collapse of CO state with Cr doping has been reported earlier from magnetization measurements [9-11, 17-19]. Cr$^{3+}$ doping at the Mn site gives rise to Mn$^{3+}$ - O – Cr$^{3+}$ SE FM correlations along with existing Mn$^{3+}$ - O – Mn$^{4+}$ FM correlations. As the net FM contributions increase, the strength of the AFM correlations leading to the CO state gets suppressed. Xiong et al [9] articulates that the ‘melting’ of the CO state is due to the deviation of the Mn$^{4+}$/Mn$^{3+}$ ratio from 1:1, which proves inexpedient to the coherence of the CO state and to the ‘microregions’ of FM domains in the CO matrix due to the FM coupling between Cr$^{3+}$ and Mn$^{4+}$. Doping Cr$^{3+}$, which is a smaller ion, at the Mn site changes the Mn – O bond length and the Mn – O – Mn bond angle which can act against the FM correlations.

According to magnetic cluster model DI varies as $DI = I_0 \exp( E/k_B T)$, where $E$ is the activation energy. The linear behaviour of $\ln DI$ v 1000/T plots (figure 2) in the high temperature region indicates the existence of short range FM correlations within the bulk PM phase mediated through the activated hopping of Mn$^{3+}$ - Mn$^{4+}$ small polaron. A deviation from linearity is seen before the onset of CO. In the temperature range $T_{\text{CO}} > T > T_N$ the slope of the linear fits decrease. This indicates the weakening of FM correlations and the emergence of AFM correlations which are favored by CO, in the PM + CO phase. The slopes increase with increasing $x$, indicative of stronger FM correlations with increasing $x$ both above and below $T_{\text{CO}}$. Below $T_O$, for the samples $x = 0$, 0.01 and 0.03, $\ln DI$ drops rapidly but does not show any sign of ceasing due to the presence of FM inhomogeneities in the long range AFM ordered matrix.

For the sample $x = 0.05$, it is observed that the plots show a linear fit in the high temperature range. Below ~340K the slope changes continuously (evidenced as multiple kinks), indicating contributions of emerging AFM ordered domains. The continuous fluctuations in 1/DI in the temperature range ~240K – 340K is a signature of competition between the FM and AFM correlated domains. It is difficult to determine if the sample exhibits CO which can be assigned to a single magnetic entity in this temperature range.

The concept of Griffiths phase (GP) physics is used to explain the ESR data [20-22]. According to the Griffiths theory [20], there is always a finite probability of finding FM clusters for a system with randomly distributed spins in the temperature range of $T_C(p) < T < T_G$ between the random transition temperature $T_C(p)$ and the pure transition temperature $T_G$. The phase between $T_C(p)$ and $T_G$ called as GP. GP is thus characterized by the formation of FM clusters below $T_G$. The susceptibility increases with decreasing temperature for all samples due to the formation of short range FM clusters which are segregated within the PM matrix in the range $T > T_{\text{CO}}$. Higher values of Curie-Weiss temperature $\theta$ are obtained as these FM clusters have larger spins (and hence larger susceptibilities) compared to that of individual magnetic ions. CO favours AFM ordering. This abates the DE interaction, destroying the FM order and this is seen as a minima in the 1/DI versus T plots, designated as $T_{\text{CO}}$. This explains the deviation from linearity of 1/DI in the high temperature PM region. In the PM + CO phase orbital ordering sets in progressively, which leads to long range AFM ordering at ~ 175K – 195K. It is apparent that the FM and AFM clusters coexist in the temperature range below $T_{\text{CO}}$. There have been
previous reports of the existence of FM domains in the CO state in Cr doped manganites [23]. There are also reports of large FM clusters formed above T_C and smaller clusters found in an AFM background with decreasing temperature [24]. In this system larger FM clusters are formed in the PM phase while smaller ones in the range T_CO > T > T_N. These small FM clusters persist even at low temperatures indicated by the temperature independent ln(DI) below T_O in the ln(DI) v 1000/T plots. The FM correlated domains in the T_CO > T > T_N range are either more in number or have larger sizes, evident from the increasing slope with increasing Cr in the 1/DI v T plots.

For x = 0.05 the FM domains dominate for a broader range of temperatures. It is evident that the change of slope in the plots indicates the evolution of AFM clusters. Below ~ 240K the linear dependence with a lesser slope confirms the presence of growing AFM clusters with decreasing temperature. The slopes of the fits for x = 0.05 are greater than that obtained in the similar temperature ranges for the samples with lesser Cr content, indicating stronger FM correlations in this sample. The concept of biphasic domains can be applied to the present system too as a PM phase is observed at high temperatures and FM correlated domains emerge with decreasing temperature; the presence of FM clusters in an AFM matrix too quantifies to make these samples behave similar as systems with biphasic domains [10].

The variation of peak to peak linewidth (ΔH) with temperature was studied for all the samples. For the undoped sample the data is reported in our earlier work [13]. In the temperature range T > T_CO, ΔH increases from a value of 155 ± 5 mT linearly with increase in temperature at a rate of ~ 0.25 mT / K. In the charge-ordered state, T_N < T < T_CO, the (ΔH) first increases, remains constant over a temperature range and then again increases with decrease in temperature. The (ΔH) decreases sharply below T_N. The magnitude and temperature dependence of (ΔH) for T > T_CO is independent of Cr content. However, in the charge-ordered state, T_N < T < T_CO the peak in (ΔH) shifts progressively to lower temperature with increase in Cr content.

4. Conclusions
The effect of Cr doping on the magnetic phase separation in Bi_{0.5}Ca_{0.5}Mn_{1-x}Cr_xO_3 (x = 0-0.05) is explored by temperature dependent ESR studies. The volume fraction of ferromagnetic domains increase at the expense of antiferromagnetic domains and the charge ordering is suppressed with increase in Cr content. With increase in x the CO transition is smeared and it almost disappears at x = 0.05. The T_CO and T_N decrease from 317K to 278K and from ~ 160K to ~ 120K respectively as x increases from 0 to 0.05. A strong competition between the FM and AFM correlations is observed as a function of composition and temperature in the temperature range T_N < T < T_CO. The GP physics model can be used to explain the temperature dependent ESR studies of this system.
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