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Electron spin resonance and magnetization studies of $Bi_{1-x}Ca_xMnO_3$

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ABSTRACT

The electron spin resonance (ESR) and magnetization measurements were carried out on $Bi_{1-x}Ca_xMnO_3$ ($0.3 \le x \le 0.9$) samples synthesized by sol–gel method. The temperature dependence of inverse of double integrated intensity ($1/DI$), peak to peak linewidth of the ESR signal and magnetization data are used to get information about magnetic interactions. The estimated values of charge ordering temperature (T_{CO}) and long range antiferromagnetic (AFM) ordering i.e., Néel temperature (T_N) are used to construct the magnetic phase diagram of the system. The paramagnetic (PM) to AFM transition at ~150 K co-exists with PM to canted antiferromagnetic (C-AFM) transition at ~120 K for samples with $0.5 \le x \le 0.8$. Whereas only PM to C-AFM transition is observed for samples with $x=0.85$ and 0.90.

1. Introduction

$Bi_{1-x}Ca_xMnO_3$ (BCMO) is an interesting system which exhibits phenomena like charge ordering (CO), orbital ordering (OO) and long range antiferromagnetic (AFM) ordering [1–4]. In this oxide, the Bi cations and oxygen anions stabilize in different magnetic and structural phase as compared to rare earth manganites. The properties of BCMO depend on the behaviour of the highly polarisable $6s^2$ lone pair of Bi^{3+}. The orientation of $6s^2$ lone pair towards a surrounding O^{2-} produces a local distortion or even hybridization between 6s-Bi and 2p-O orbitals. The hybridization may produce a local distortion and reduce the mobility of e_g electrons between Mn^{3+} and Mn^{4+} ions, favouring charge ordering [5,6]. BCMO is insulating over broad composition range [3]. The magnetization studies show that the system behave as ferromagnetic (FM)-spin glass (SG) for $x \ge 0.15$ and spin-glass charge ordered antiferromagnet for $0.25 < x < 0.32$ [7]. High resolution synchrotron X-ray and neutron powder diffraction of $Bi_{1-x}Ca_xMnO_3$ ($x \ge 0.75$) show phase segregation coinciding the electronic localization of the e_g electrons [8]. The system with $x \ge 0.875$ exhibits FM behaviour with reduced resistivity [9].

The electron spin resonance (ESR) is a sensitive technique to understand the short range spin correlations in manganites. We have reported extensive ESR studies on $Bi_{1-x}Ca_xMnO_3$ samples synthesised by solid state reaction for $x \le 0.6$ [1,10] and by sol–gel method for $0.65 \le x \le 0.9$ [11]. The results were interpreted in view of electron phase separation. During the course of our work we have come across ESR and magnetization studies on $Bi_{1-x}Ca_xMnO_3$($x=0.5$, 0.75, 0.8) [12–14] system. The ESR studies along with magnetization measurements can help in constructing the precise magnetic phase diagram of the system. In this work, the extensive ESR and magnetic measurements were carried out to understand the evolution of different magnetic phases in $Bi_{1-x}Ca_xMnO_3$ ($0.3 \le x \le 0.9$) samples synthesised by sol–gel technique.

2. Experimental

The $Bi_{1-x}Ca_xMnO_3$ ($0.3 \le x \le 0.9$) samples were synthesized by sol–gel technique as reported in our earlier work [11]. The X-ray diffraction (XRD) data were obtained by using diffractometer (Bruker D8 Advance) using Cu $K\alpha$ radiation. The temperature (T) dependent ESR spectra were recorded on a JEOL X-band ESR spectrometer in the temperature range 123–453 K. The magnetic measurements were performed in field cooled (FC) and zero field cooled (ZFC) modes in the temperature range 5–350 K in magnetic field of 500 Oe using Quantum Design Physical Properties Measurement System (PPMS).

3. Results and discussions

Fig. 1 shows Rietveld refinement of XRD pattern for $Bi_{0.25}Ca_{0.75}MnO_3$. The XRD data fits to a single phase Pnma space group with orthorhombic structure for all samples except for $x=0.3$. The sample with $x=0.3$ has triclinic (~monoclinic) structure. The estimated average crystallite size is in the range of 22–40 nm.

Fig. 2 shows the Lorentzian fit to the ESR spectra for $x=0.3$, 0.5 and 0.85 samples at 273 K with $g=1.99 \pm 0.01$ [1]. The ESR spectra are similar for other samples in the paramagnetic state.

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It has been pointed that all Mn ions contribute to the ESR signal and the double integrated intensity (*DI*) of the resonance is proportional to the number of ESR centres, which is a measure of ESR susceptibility (χ_{ESR}) [15]. For samples with $0.4 \le x \le 0.8$, $1/DI$ versus (vs) T plots follow same trend i.e., as the temperature decreases from 453 K, $1/DI$ decreases and reaches a minimum at a temperature assigned as the charge ordering temperature (T_{CO}) followed by a sharp increase at a temperature assigned as long range AFM ordering i.e., Néel temperature (T_N). In view of this, the ESR data only for sample with $x=0.5$ is included in Fig. 3(A). $1/DI$ vs T plots for $x=0.3$, 0.5 and 0.85 samples are shown in Fig. 3(A). The solid lines are linear fits as per the Curie–Weiss law (Eq. (1)). For sample with $x=0.3$, the temperature at which deviation from linear fit takes place is taken as T_{CO} and the continuous increasing deviation with decrease in temperature is an indication of strengthening of AFM correlations. T_{CO} is not observed for samples with $x=0.85$ and 0.90.

The peak-to-peak ESR linewidth (Fig. 3(B)) decreases linearly as temperature decreases from 453 K to T_{CO} for samples with $0.3 \le x \le 0.8$. The linewidth variation with temperature is strongly dependent on x value and the temperature range. This has been discussed in view of competing FM and AFM correlations in our earlier work [1,11]. Using Huber et al. [16] approach, the Curie–Weiss temperature (θ) estimated from linewidth plots are listed in Table 1.

Fig. 4(A) shows magnetization (M) vs T for $x=0.3$, 0.5 and 0.85 samples. For samples with $0.30 \le x \le 0.80$, M vs T plots show same

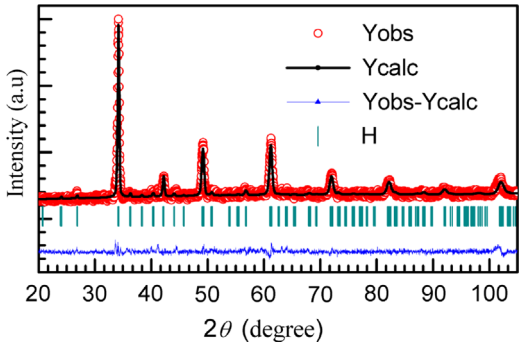

Fig. 1. Rietveld fit for the XRD pattern of $Bi_{0.25}Ca_{0.75}MnO_3$.

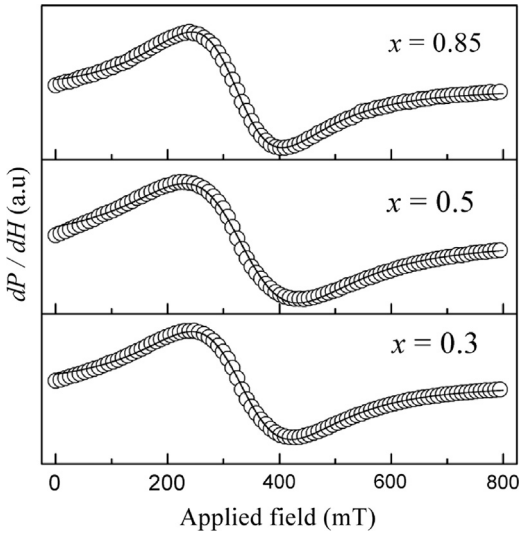

Fig. 2. Lorentzian fit (solid line) to the ESR spectra (open circles) of $Bi_{1-x}Ca_xMnO_3$ at 273 K.

Table 1
Parameters estimated from ESR and magnetization data.

x	ESR θ (K)	Magnetization θ (K)	μ_{eff}^{exp} (μ_B)	μ_{eff}^{th} (μ_B)
0.30	102	95	5.65	4.58
0.40	140	138	5.92	4.48
0.50	134	127	5.59	4.38
0.60	141	121	5.10	4.29
0.65	109	90	5.06	4.23
0.70	75	69	5.17	4.18
0.75	61	76	4.92	4.13
0.80	57	48	4.90	4.07
0.85	−14	−44	4.76	4.02
0.90	−156	−159	5.41	3.97

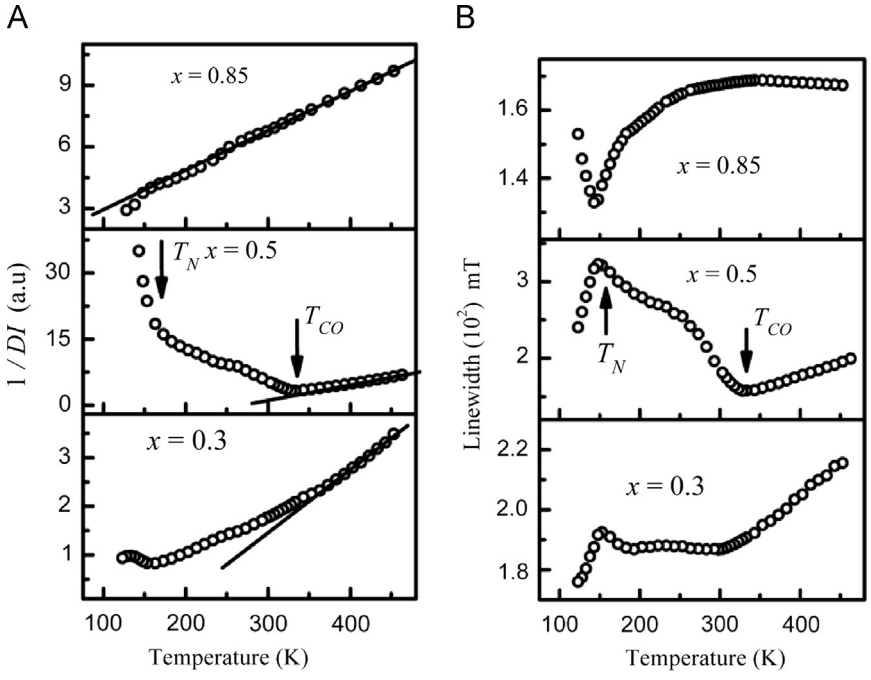

Fig. 3. (A) $1/DI$ vs T and (B) linewidth vs T for $Bi_{1-x}Ca_xMnO_3$.

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