Electron spin resonance and AC susceptibility studies on La$_{0.9}$Pb$_{0.1}$MnO$_3$ single crystals

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1. Introduction

Last two decade, there has been a great interest in the properties of rare-earth manganese perovskite R$_1$−$_A$MnO$_3$, where R is a rare-earth element such as La, Pr, Nd or Y, and A is one of the divalent alkali earth ions including Sr, Ca, Ba and Pb [1]. The reason is not only the colossal magnetoresistance (CMR) that occurs in these systems, but also a rich variety of the physical phenomena including intrinsically inhomogeneous ground states, phase separation, charge/orbital ordering [2]. The competing interactions in the manganite showing CMR are mainly the Jahn–Teller interaction favoring insulating behavior and the double exchange (DE) favoring the ferromagnetic metallic state [3]. The properties of R$_1$−$_A$MnO$_3$ are sensitive to the hole-doping level x and the average A-site radius, which determines the effective one electron bandwidth (W) or the equivalent Mn 3d $e_g$-electron transfer interaction (t).

Nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) are excellent tools for detecting changes in the local electronic properties, especially the local magnetic anisotropy of various electronic sub-phases in colossal magneto-resistance manganites. The most common Mn ion that is measured via ESR is Mn$^{2+}$ which is generally accepted as not being present in these compounds. Careful ESR measurements on doped manganites by Causa et al [4] and Lofland et al [5] show that both Mn$^{3+}$ and Mn$^{4+}$ contribute to the ESR signal. The bottleneck model used by Shengelaya et al [6] shows that the ESR intensity is proportional to the total susceptibility of Mn$^{4+}$ and Mn$^{3+}$ spins. Composition dependent $T_C$ and Mn valance of LPMO material reported in the literature [7], La$_1$−$_x$Pb$_x$MnO$_3$ (0.1 ≤ x ≤ 0.5) compounds with their $T_C$ values around 300 K could be potential materials for room temperature applications and with relatively low-doping level (x = 0.1) possess large CMR value. Early ESR studies on the La$_1$−$_x$Pb$_x$MnO$_3$ system were performed in single crystals [8] and poly crystals [9]. The aim of this paper is to report on the experimental investigation which reveals some of the specific features of magnetic properties of La$_{0.9}$Pb$_{0.1}$MnO$_3$ single crystals and provides experimental evidence for phase separation. The experiments involved measurements of AC magnetization at various frequencies and Electron spin resonance below and above the transition temperature ($T_C$).

2. Experimental procedure

The LPMO crystals were grown in high temperature solution growth method using PbO–PbF$_2$ as flux. The charge-flux ratio and PbO–PbF$_2$ ratios are 1:6 and 1:1.15 respectively. The starting materials La$_2$O$_3$, PbO and MnO$_2$ were taken in a stoichiometric ratio of La$_{0.9}$Pb$_{0.1}$MnO$_3$ and the ratio between flux and the crystallizing compound was approximately 6:1. The experimental procedure has been described elsewhere [10]. The structure and phase purity of the samples were examined by powder X-ray diffraction using CuKα radiation at room temperature. All the measurements were done in the easy axis of magnetization along the ab plane. The temperature variation of linear AC susceptibility (χ'') was measured at different frequencies using Quantum Design Physical Property Measurements system (PPMS) from 10 K to 300 K. The ESR measurements at 9.5 GHz (X band) were taken in a JEOL ESR spectrometer.

3. Results and discussion

From the powder X-ray diffraction studies it was confirmed that the LPMO crystal belongs to the trigonal crystal system with space

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measured in easy axis ab plane with an alternating field of 10 Oe and frequencies $f = 500$, 1000 and 10,000 Hz.

group R$\bar{3}c$ and the lattice parameters are $a = 5.5285(1)$ Å, $c = 13.4180(3)$ Å. The composition of the crystals measured using EDX was found to be $La_{0.91}Pb_{0.09}Mn_{1}$ ($\pm 5\%$). Fig. 1 shows the temperature dependence of the ZFC out of phase ($χ''$) and in phase ($χ'$) susceptibility for the single crystals of $La_{0.9}Pb_{0.1}MnO_3$. AC susceptibility was measured with an alternating field of $h_{ac} = 10$ Oe with different frequencies viz. 500, 1000 and 10,000 Hz. At about 254 K, both susceptibilities abruptly decrease to zero, exhibiting the ferromagnetic-paramagnetic phase transition. The frequency dependent maxima in the $χ'$ susceptibility at low temperature. Below $T_c$, the material shows the magnetic inhomogeneity. The Assymetric Parameter ($AP$) serves as a clue to determine the homogeneity in the sample [13]. The lower value of $AP$ corresponds to the inhomogeneous local field distribution. The $g$-value of LPMO single crystal showed less than that of the free electron ($g_e = 2.0023$) value which is shown in Fig. 4. The ferromagnetic material shows the $g$ value more than free electron $g$ value [9] and the lower value may be due to the magnetic inhomogeneity. The Assymetric Parameter ($AP$) serves as a clue to determine the homogeneity in the sample [13]. The lower value of $AP$ corresponds to the inhomogeneous local field distribution.

The linear $χ''(T)$ and $χ'(T)$ AC susceptibility shows frequency dependence in the ferromagnetic region and may be due to cluster glass property. Unusual dynamics and frequency-dependant phenomena are common features of this magnetically inhomogeneous phase, which is normally quoted as a cluster-glass or SG like behaviour.

Fig. 1. Real and imaginary parts of the AC susceptibility of $La_{0.9}Pb_{0.1}MnO_3$ single crystals measured in easy axis ab plane with an alternating field $h_{ac} = 10$ Oe and frequencies $f = 500$, 1000 and 10,000 Hz.

Fig. 2. Temperature dependence of ESR line below and above Curie temperature of $La_{0.9}Pb_{0.1}MnO_3$ single crystals measured in easy axis ab plane.

Fig. 3. Temperature dependence of $H_r$ and $ΔH_{pp}$ below and above Curie temperature. Inset shows the double integrated intensity.

Fig. 4. Temperature dependence of $g_{eff}$ and $AP$ (asymmetry parameter) below and above the Curie temperature.
Increase of line width below $T_c$ due to the local magnetic inhomogeneity and an increase with the decreasing temperature can be attributed to the random shape and distribution [15]. The splitting of the ESR line below and above the Curie temperature region due to some of the Mn$^{3+}$ ions which may surrounded by Mn$^{4+}$ to form spin clusters and associated local distortion below the paramagnetic to ferromagnetic phase transition temperature. The interaction between the localized magnetic moments becomes more significant which contributes to the broadening of the resonance line [16]. Glassy magnetism in LPMO material is reported in the literature [12,17] and consistent with our experimental investigations.

4. Conclusions

In summary, we have studied the nature of spin systems in a La$_{0.9}$Pb$_{0.1}$MnO$_3$ crystal undergoing the CMR by means of the ESR and AC susceptibility measurements. Both AC and ESR measurements confirm the phase separated magnetic structure of the crystals which may be due to the ferromagnetic micro regions surrounded by the insulating regions below the $T_c$. Frequency dependence of peak temperature and the splitting of ESR lines provide experimental microscopic evidence for phase separation and the cluster glass state.

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References