Magnetic and electron paramagnetic resonance studies of \( \text{Ln}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \) (\( \text{Ln} = \text{Pr, Bi} \)) manganite

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Magnetic and electron paramagnetic resonance studies of Ln$_{0.5}$Ca$_{0.5}$MnO$_3$ (Ln = Pr, Bi) manganite

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ABSTRACT

In this paper we compare the magnetic and electron paramagnetic resonance (EPR) properties of Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ (PCMO) and Bi$_{0.5}$Ca$_{0.5}$MnO$_3$ (BCMO) charge ordered manganites. PCMO and BCMO samples were prepared by solid state reaction method. A commercial SQUID magnetometer was used to study the dc-magnetization in the temperature range of 10-300 K. The EPR experiments were carried out using a commercial X-band (frequency ~ 9.4 GHz) spectrometer in the temperature range 4 K – 300 K. Marked differences are found when the magnetic and EPR properties of rare earth (PCMO) and bismuth based manganites (BCMO) are compared. The temperature dependent resonance fields of PCMO and BCMO samples are seen to be opposite to each other. PCMO shows the resonance field behavior similar to other charge ordered manganites, i.e., decreases with the decrease in temperature whereas the resonance field of BCMO increases with a decrease in temperature. The opposite behavior of resonance field could be due to the different magnetic structures present in the BCMO manganite.

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I. INTRODUCTION

Charge ordering is one of the interesting properties shown by manganites of general formula R$_{1-x}$A$_x$MnO$_3$ (R = rare earth cation such as La$^{3+}$, Pr$^{3+}$, Nd$^{3+}$ Bi$^{3+}$ etc and A = alkaline earth cation such as Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$ etc). In manganites charge ordering results due to the localization of Mn$^{3+}$/Mn$^{4+}$ charges. Coulomb repulsion between the carriers is the reason behind the charge localization and ordering.

The electronic configuration of ‘Bi’ is 6s$^2$6p$^3$ and the trivalent Bi in BiMnO$_3$ contains a lone pair of 6s electrons. When the lone pair character is dominant, Bi$^{3+}$ ion has the same as that of rare earth manganites (⟨rBi⟩ ~1.24 Å). If the lone pair character is not dominant, the ‘Bi’ is more symmetric and its size is reduced (⟨rBi⟩ ~1.16 Å). The crystallization of undoped BiMnO$_3$ take place at high pressure and it exhibits highly distorted perovskite structure.

The undoped parent compounds BiMnO$_3$ and PrMnO$_3$ are showing different magnetic and transport properties in their ground states. The ground state of BiMnO$_3$ is ferromagnetic insulating while the undoped PrMnO$_3$ is anti-ferromagnetic insulator due to a super exchange interaction.$^{1,2}$ There is a covalent bonding between the Bi cations and the oxygen anions in BiMnO$_3$ compound while in rare earth compounds (PrMnO$_3$) the interaction between rare earth ion and oxygen is purely ionic. There is a substantial hybridization between Bi 6p and O 2p orbitals and the conduction electrons partly occupy p-type atomic orbitals while, in rare earth compounds, the conduction band is mainly Mn 3d type. The p-type atomic orbital of bismuth may be the origin for the differences in transport properties of BiMnO$_3$ and rare-earth compounds.

Half doped manganites Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ and Bi$_{0.5}$Ca$_{0.5}$MnO$_3$ are exhibiting different magnetic and electronic properties. Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ is paramagnetic insulator at room temperature, charge ordered phase at temperature T$_{CO}$ = 245 K and antiferromagnetic phase at temperature T$_N$ = 175 K.$^*$ It exhibits insulating behaviour in the temperature range of 4 K to 300 K and show a sharp rise in resistivity at T$_{CO}$. The charge ordering in Bi$_{1-x}$Ca$_x$MnO$_3$ manganite is spread over in much broader range
of ‘x’ than rare earth manganites. Bi$_{0.5}$Ca$_{0.5}$MnO$_3$ is paramagnetic insulator at room temperature, show charge ordered phase at temperature $T_{CO}$ = 325 K.

Bi manganite is less sensitive to the application of the magnetic fields up to 50 T. Magnetic fields of the order of 130 T are needed to completely ‘melt’ the charge order and induce ferromagnetism and metallicity in these Bi$_{0.5}$Ca$_{0.5}$MnO$_3$ manganites. The high charge order stability under the magnetic field may be due to the nature of the bonds of the Bi ions with neighboring oxygens which changes the conduction band.

In Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ below the charge ordering temperature $T_{CO}$ (245K) a CE–type (charge-exchange) magnetic order develops and at a lower temperature the CE-type spin order in the $ab$ planes is formed. The ideal CE-type charge and orbital order implies a FM zigzag arrangement of the ordered eg $(3z^2 - r^2)$ and eg $(3y^2 - r^2)$ orbitals of Mn$^{3+}$ ions in $ab$ plane. The neighboring zigzags are AF coupled; the ordering in the $c$ direction is also AF. This $2$–$r$ insulator at room temperature, show charge ordered phase at $T_{CO}$ and Neél temperature $TN$ respectively while in Bi$_{0.5}$Ca$_{0.5}$MnO$_3$ sample $TN$ was found at 135 K. Due to experimental constraints we could do experiment only in the temperature range of 10–100 K. Therefore CO peak in Bi$_{0.5}$Ca$_{0.5}$MnO$_3$ (at 325 K) is not seen in the figure. From the above magnetic studies it is clear that the charge order temperature of BCMO is larger compared to PCMO system and the antiferromagnetic transition is prominent in BCMO compared to PCMO sample. The inset of Figure 1 shows the temperature variation of the intensity of the electron paramagnetic signals (EPR).

Inset of Figure 2, show the EPR signals from Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ and Bi$_{0.5}$Ca$_{0.5}$MnO$_3$ in the paramagnetic phase at a few selected temperatures respectively. The sharp signal is from DPPH. As can be seen, the signals of the Bi$_{0.5}$Ca$_{0.5}$MnO$_3$ are broader than Pr$_{0.5}$Ca$_{0.5}$MnO$_3$. For both the samples below their $TN$ the EPR signals disappear because in the AFM phase it is difficult to observe EPR signals in X-band region. The signals are fitted to the double Lorentzian line shape function given by the equation,

$$\frac{dP}{dH} = \frac{d}{dH} \left( \frac{\Delta H}{\Delta H^2 + 4(H - H_0)^2} + \frac{\Delta H}{\Delta H^2 + 4(H + H_0)^2} \right)$$  \hspace{1cm} (1)$$

where $H_0$ is the resonance field, $\Delta H$ is the full width at half maximum which when divided by a factor of $\sqrt{3}$ gives peak to peak line width $\Delta H_{PP}$, and $A$ is a quantity proportional to the area under the $\Delta H_{PP}$ curve in the graph.

**II. EXPERIMENTAL DETAILS**

Samples of Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ and Bi$_{0.5}$Ca$_{0.5}$MnO$_3$ were prepared by the standard solid state reaction method. X-ray diffraction (XRD) patterns were recorded using a Philips powder diffractometer (Cu-K$_\alpha$; $\lambda$ = 1.54056 Å$^2$) at room temperature. Composition was checked by EDXA. A commercial SQUID magnetometer was used for the dc-magnetization studies. EPR studies were carried out using an X-band spectrometer (frequency 9.4 GHz). The temperature was varied using an Oxford Instruments continuous helium flow cryostat in the temperature range 10-300 K.

**III. RESULTS AND DISCUSSION**

From X-ray diffraction studies of PCMO is found to crystallize in the orthorhombic structure where as BCMO sample is found to crystallize in the monoclinic structure. The X–ray results are in close agreement with the previous reports.*

Figure 1(a) and 1(b) show the temperature dependent magnetization of PCMO and BCMO respectively under an applied field of 0.1T and 1T. To enable meaningful comparison, reduced temperature ($T/T_{CO}$) is plotted along X-axis.

Two transitions can be observed in the magnetization curve of Pr$_{0.5}$Ca$_{0.5}$MnO$_3$, the first has been found at 245K and the second transition is observed at 170 K which corresponds to charge order temperature $T_{CO}$ and Neél temperature $TN$ respectively while in Bi$_{0.5}$Ca$_{0.5}$MnO$_3$ sample $TN$ was found at 135 K. Due to experimental constraints we could do experiment only in the temperature range of 10–100 K. Therefore CO peak in Bi$_{0.5}$Ca$_{0.5}$MnO$_3$ (at 325 K) is not seen in the figure. From the above magnetic studies it is clear that the charge order temperature of BCMO is larger compared to PCMO system and the antiferromagnetic transition is prominent in BCMO compared to PCMO sample. The inset of Figure 1 shows the temperature variation of the intensity of the Electron paramagnetic signals (EPR).

Inset of Figure 2, show the EPR signals from Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ and Bi$_{0.5}$Ca$_{0.5}$MnO$_3$ in the paramagnetic phase at a few selected temperatures respectively. The sharp signal is from DPPH. As can be seen, the signals of the Bi$_{0.5}$Ca$_{0.5}$MnO$_3$ are broader than Pr$_{0.5}$Ca$_{0.5}$MnO$_3$. For both the samples below their $TN$ the EPR signals disappear because in the AFM phase it is difficult to observe EPR signals in X-band region. The signals are fitted to the double Lorentzian line shape function given by the equation, $\frac{dP}{dH} = \frac{d}{dH} \left( \frac{\Delta H}{\Delta H^2 + 4(H - H_0)^2} + \frac{\Delta H}{\Delta H^2 + 4(H + H_0)^2} \right)$.  \hspace{1cm} (1)$$

where $H_0$ is the resonance field, $\Delta H$ is the full width at half maximum which when divided by a factor of $\sqrt{3}$ gives peak to peak line width $\Delta H_{PP}$, and $A$ is a quantity proportional to the area under the $\Delta H_{PP}$ curve in the graph.

![Figure 1. Temperature dependent magnetization for (a) Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ and (b) Bi$_{0.5}$Ca$_{0.5}$MnO$_3$. Inset shows the temperature variation of the intensity of the electron paramagnetic (EPR) signals to be next discussed in the text.](image)
FIG. 2. In the inset are presented EPR signals of (a) Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ and (b) Bi$_{0.5}$Ca$_{0.5}$MnO$_3$ at different temperatures. The sharp line is the DPPH signal. The continues lines indicate the experimental data and the dots show the fits to Lorentzian equation. The main panel presents temperature dependence of the linewidth for (a) PCMO and BCMO respectively extracted from the fits as described in the text.

curve. EPR parameters intensity, line width and resonance field were extracted from the fits and temperature dependence of EPR parameters have been studied. To enable meaningful comparison, reduced temperature (T/T$_{CO}$) is plotted along X-axis.

Inset of Figure 1 show the temperature dependence of the EPR intensity of PCMO and BCMO samples respectively. The intensity plot of PCMO and BCMO samples roughly follows the susceptibility behavior.

Figure 2 shows the temperature dependence of the peak to peak line width in the PCMO and BCMO sample respectively. Line widths of BCMO are larger than PCMO system. Qualitatively we can say that larger line widths of BCMO may be due to its robust charge ordering compared to PCMO sample.

Figure 3 show the temperature dependence of the resonance field in the PCMO and BCMO sample respectively. Interestingly the resonance field behavior of PCMO and BCMO samples are exactly opposite to each other. PCMO sample shows the resonance field behavior similar to other charge ordered manganites, decreases with decrease in temperature where as the resonance field of BCMO increases with decrease in temperature.

Now we will address the possible reason for the different resonance field behavior of BCMO sample compared to PCMO sample. As is well known, the resonance field in magnetic systems is the sum of the externally applied magnetic field and the local field. The local field in turn is a sum of the anisotropy field and the demagnetization field. We note that even though the samples are in the paramagnetic state, they are subject to an average local field while approaching TN due to the AF fluctuations. Assuming the demagnetization field to be negligible for the powder samples, the anisotropy field is behind the shift of the resonance field. The important point to consider here that not only the magnitude of the anisotropy field but also its sign is important. If the magnetocrystalline anisotropy (MA) is of negative sign, then decreasing temperature has the effect of decreasing the overall magnetic field experienced by the resonating species, thus requiring an increasing applied field to observe resonance. We propose that BCMO has an effectively negative MA leading to increasing resonance field with the decrease in temperature. While it is reasonable to expect PCMO and BCMO to have MA of opposite signs in view of their different types of CO, more studies are needed to confirm this proposal.

IV. CONCLUSIONS

In summary, we have compared the magnetic and electron paramagnetic resonance properties of Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ and Bi$_{0.5}$Ca$_{0.5}$MnO$_3$ manganites. Marked differences were found in their magnetic properties. The charge ordering temperature of Bi$_{0.5}$Ca$_{0.5}$MnO$_3$ is large compared to Pr$_{0.5}$Ca$_{0.5}$MnO$_3$. From the EPR measurements it is clear that the line width is large for the BCMO sample. Interestingly the resonance field behaviour of the BCMO sample is entirely different compared to the PCMO sample. We attribute resonance field behaviour to opposite temperature dependences of the anisotropy fields in the two samples.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.
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