Study of magnetic and electrical properties of Pr$_{0.65}$Ca$_{0.25}$Ba$_{0.1}$MnO$_3$ manganite

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The magnetic properties and magnetocaloric effect (MCE) in Pr$_{0.65}$Ca$_{0.25}$Ba$_{0.1}$MnO$_3$ have been investigated supplemented by electrical data. X-ray diffraction shows that the sample crystallizes in the distorted orthorhombic system with the Pnma space group. Pr$_{0.65}$Ca$_{0.25}$Ba$_{0.1}$MnO$_3$ undergoes paramagnetic–ferromagnetic (PM–FM) phase transition at $T_C \sim 85$ K. For a magnetic field change of 5 T, the maximum value of the magnetic entropy change ($\Delta S_m^{\text{max}}$) is estimated to be 4.4 J kg$^{-1}$ K$^{-1}$ around $T_C$ with a large relative cooling power (RCP) value of 263.5 J kg$^{-1}$. While the modified Arrott plots suggested that the magnetic transition belongs to the second order phase transitions, the universal curves of the rescaled magnetic entropy ($\Delta S_m$) proved the opposite. The electrical properties of Pr$_{0.65}$Ca$_{0.25}$Ba$_{0.1}$MnO$_3$ have been investigated using impedance spectroscopy techniques. The dc-resistivity ($\rho_{dc}$) study shows the presence of semiconductor behavior. Ac-conductivity ($\rho_{ac}$) analysis shows that the conductivity is governed by a hopping process. From the analysis of the alternating regime, the exponent $s$ variation obtained is in good agreement with Mott theory. The impedance spectrum analysis reveals the presence of a relaxation phenomenon. Based on these analyzes, the sample can be modeled by an electrical equivalent circuit.

1. Introduction

Manganese perovskites with the general formula AMnO$_3$, where A = lanthanide or divalent alkaline earth, are of considerable technological importance, particularly with regard to electrical and magnetic properties. The physical properties of these materials can be changed using magnetic or electric fields, which opens up the field to important technological applications. The chemical and physical properties of perovskite oxides vary with composition from dielectric to superconducting, and they find application as magnetic sensors, spintronic devices, catalysts, magnetic recording devices, and magnetoresistive transducers and in magnetic refrigeration systems.

The structural, electrical, and magnetic properties of these compounds are sensitive to both the manganese valence and internal chemical factors, such as the average cationic radius $\langle r_A \rangle$ in the A-site and the A-site cationic disorder. Introducing quenched disorder in manganites as different ions at A-site can lead to a change in structure, which modifies the original system completely. A-site doping can be strongly influenced by the average ionic radius, which exhibits a close relation between the distortion of MnO$_6$ octahedra and the narrowing of the electronic bandwidth.

The low bandwidth manganites Pr$_{1-x}$Ca$_x$MnO$_3$ have been the subject of several studies with calcium concentration due to their diverse physical properties such as charge-ordering (CO), metamagnetic transition, colossal magnetoresistance, and large magnetocaloric effects. In the case of a 35% Ca-doped sample, it undergoes a charge-ordering (CO) transition at about 230 K, an antiferromagnetic (AFM) transition in the vicinity of 160 K. Without applied magnetic field, its electrical conduction shows insulator characteristics. Below the AFM transition temperature, application of a high magnetic field (above $\mu_0H = 4$ T) leads this one to metallic and ferromagnetic (FM) state. In addition, it is worth mentioning for the Pr$_{0.65}$Ca$_{0.35}$Sr$_{0.15}$MnO$_3$ compounds the partial substitution of Sr$^{2+}$ ions for Ca$^{2+}$ ions, having higher ionic radius, shows up many physical interesting phenomena, particularly with $x \approx 0.3$ the charge and orbital ordering appear below 200 K, but above $x \approx 0.3$ collapse into the metallic state has been observed below 100 K. 

Study of A-site doped Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ sample would offer a complementary understanding of the structural, magnetic
and electrical properties. To the best of our knowledge, there are no reports on the physical properties of Ba doped Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ compounds. Substitution of calcium by barium is interesting as the difference between ionic sizes of Ca and Ba is significantly large. The selection of Ba as a dopant was inspired by an intention to induce chemical pressure inside the lattice to favor the electron/hole transfer between the neighboring Mn sites. In this context, we report how a direct substitution of barium ion in the A-site affects the physical properties as compared to pure Pr$_{0.65}$Ca$_{0.35}$MnO$_3$. Our results show that at $x = 0.10$ doping level the charge ordering (CO) is destroyed and drastic changes of properties have been observed.

2. Experimental details

Polycrystalline perovskite Pr$_{0.65}$Ca$_{0.25}$Ba$_{0.1}$MnO$_3$ sample was fabricated by standard solid-state reaction method. After thoroughly mixing the stoichiometric reactants of high purity (99.99%) [Aldrich] Pr$_6$O$_{11}$, CaCO$_3$, BaCO$_3$ and MnO$_2$, the sample is fired at 900 °C for 12 h. Then, the mixture was pressed into pellets and sintered at 1000–1200 K for 48 h in air with several intermediate grindings. The powder X-ray diffractometer (“Panalytical X pert Pro” diffractometer with Cu-Kα radiation ($\lambda = 1.5406 \text{ Å}$) was employed to identify the phase purity and crystalline structure at room temperature. The unit cell parameters were refined using the Rietveld analysis of the X-ray powder diffraction data with the help of FULLPROF software.$^{15}$ The static magnetic measurements were carried out in magnetic fields up to 5 T at temperatures between 5 and 285 K on a BS2 magnetometer equipped with a super conducting coil and developed at Neel Institute. On the both side of the pellet, we deposited a thin aluminum film through a circular mask of 6 mm of diameter. Then, we obtained a configuration of a plate capacitor used to measure both the capacitance and the conductance. The sample is mounted in a cryostat which allows the variation of temperature from 80 to 300 K. Conductance and capacitance measurement are performed using an Agilent 4294A analyzer.

3. Results and discussion

(a) X-ray diffraction

In order to determine the crystalline structure of Pr$_{0.65}$Ca$_{0.25}$Ba$_{0.1}$MnO$_3$, room temperature powder X-ray diffraction (XRD) pattern was collected. The XRD pattern of Pr$_{0.65}$Ca$_{0.25}$Ba$_{0.1}$MnO$_3$ sample is shown in Fig. 1. It is seen from the results that all peaks can be indexed according to a perovskite structure with orthorhombic $Pnma$ symmetry. Rietveld refinement confirms that there are no detectable impurities in this compound. From the XRD pattern lattice parameters obtained from refinements are: $a = 5.4565(3) \text{ Å}$, $b = 7.7240(4) \text{ Å}$ and $c = 5.4519(5) \text{ Å}$.

(b) Magnetic and magnetocaloric effect

The temperature dependence of the magnetization, $M(T)$, measured via field-cooled (FC) protocol at 0.05 T applied magnetic field is shown in Fig. 2(a). With decreasing

Fig. 1 Rietveld refined powder XRD patterns of the Pr$_{0.65}$Ca$_{0.25}$Ba$_{0.1}$MnO$_3$ compound.

Fig. 2  (a) Temperature dependence of FC magnetization measured at a field of 0.05 T, the inset shows the derivative of magnetization with respect to temperature ($dM/dT$ vs. $T$). (b) Inverse susceptibility versus temperature plot for Pr$_{0.65}$Ca$_{0.25}$Ba$_{0.1}$MnO$_3$ bulk.
temperature the Pr$_{0.65}$Ca$_{0.35}$Ba$_{0.1}$MnO$_3$ compound displays a typical paramagnetic–ferromagnetic (PM–FM) transition. The Curie temperature ($T_C$), corresponding to the minimum in $dM/dT$ curve (see inset of Fig. 2(a)), is determined to be 85 K. Apparently, as compared to Pr$_{0.65}$Ca$_{0.35}$MnO$_3$, a 10% barium substitution at the A-site destroys the charge ordering (CO) in the pristine compound. Because the larger ionic size of Ba$^{2+}$ compared to that of Ca$^{2+}$, the destruction of CO state can be attributed to the increase of the average ionic radius of the A-site ($r_A$) which leads to the increase of $e_g$ bandwidth, favors the electrons movement through the lattice and promotes the FM metallic state. The isoelectronic A-site substitution controls the structure by the distortion of MnO$_6$ octahedra, i.e., tilting and rotation of the MnO$_6$ octahedra, which modifies local structural parameters such as the Mn–O bond distance and Mn–O–Mn bond angle, and then directly influence the case of electron hopping between Mn ions. Several works on manganites show that the FM state as well as the CO are affected due to the chemical pressure at A-site.$^{16-20}$

In Fig. 2(b) we have reported the inverse susceptibility $1/\chi$ as a function of temperature for Pr$_{0.65}$Ca$_{0.25}$Ba$_{0.1}$MnO$_3$. A deviation has been observed which starts around 225 K far above $T_C$, which may be due to growth of short range magnetic interactions in the compound.$^{17,18}$ However, the curve in PM regime from 230 to 285 K obeys the Curie–Weiss (CW) formula $\chi = C/(T - \theta_B)$, where $C$ is the Curie constant and $\theta_B$ is the PM Curie temperature. The fitting of the linear region to the CW law yields positive $\theta_B$, $\theta_B = 66.5$ K, indicating dominant FM interactions. On another hand, the detailed calculation of the theoretical effective moment ($\mu_{\text{eff}}$) can be found elsewhere.$^{21}$ Moreover, the experimental effective moment is found to be $\mu_{\text{exp}} = 14.5 \mu_B$, which is much larger than its theoretical counterpart $\mu_{\text{theo}} = 5.53 \mu_B$, confirming clearly the magnetic inhomogeneity of our sample. This behavior can be explained in terms of the presence of FM clusters of Mn$^{3+}$, Mn$^{4+}$ double exchange pairs together in the PM region.$^{22}$

Fig. 3(a) shows the evolution of isothermal magnetization as a function of the magnetic applied field, $M(H)$, for Pr$_{0.65}$Ca$_{0.25}$Ba$_{0.1}$MnO$_3$ sample. At low temperature, we can see that the magnetization increases linearly with increasing magnetic field. Therefore the magnetization $M(H)$ increases monotonically with increasing magnetic field change. In addition, we can see in Fig. 4(a) the presence of a transition temperature shift induced by the applied magnetic field. Therefore, the $-\Delta S_M$ is maximized around $T_C$ and its maximum values ($-\Delta S_M^{\text{max}}$) are found to be approximately 2.5 and 4.4 J kg$^{-1}$ K$^{-1}$ under a magnetic field changes of 2 and 5 T. Other important parameter of refrigerant materials is the relative cooling power (RCP) which is defined by the product of the peak entropy change and the full width at half maximum of the peak, i.e., $\text{RCP} = -\Delta S_M^{\text{max}} \delta_{\text{TPWHM}}$ (where $\delta_{\text{TPWHM}}$ is the full width at half-maximum of $\Delta S_M(T)$). Thus, the resulting RCP values are found to be 104.2 and 263.5 J kg$^{-1}$ under a magnetic field changes of 2 and 5 T, respectively. The obtained values are
comparable with those of several manganite systems with a large MCE, suggesting that our compound may be suitable candidate for magnetic refrigeration. The large MCE in Pr_{0.65}Ca_{0.25}Ba_{0.1}MnO_{3} can be understood by its sharp magnetization change at the FM–PM transition and its high magnetization saturation.

Additionally, a phenomenological universal curve for DS_{M}(T) in the vicinity of a second-order phase transition has been theoretically established and successfully applied to several families of magnetic material, which can be used as a further criterion to reveal the order of the magnetic phase transition. In addition, this scaling can be particularly helpful for investigating the refrigerant capacity of a similar material. However, a breakdown of the universal curve can be attributed to inhomogeneity within the material.

The temperature axis was transformed according to the relation:

\[
\theta = \begin{cases} 
-(T - T_1)/(T_1 - T_c) & T \leq T_c \\
(T - T_c)/(T_2 - T_c) & T > T_c
\end{cases}
\]

where T_{1} and T_{2} are the temperature of the two reference points. For present study, T_{1} and T_{2} are chosen such that DS_{M}(T_{1})/DS_{M}^{\text{max}} = 0.5. The rescaled DS_{M}(T) curves for different maximum applied magnetic fields ranging from 1 up to 5 T with increments of 1 T are shown in Fig. 4(b). It has been reported that the essential region for collapse to determine the order of the transition is \theta < -1 (T < T_c). However, the deviation of collapse for first-order phase transition may not be obvious around -1 < \theta < 0. The divergence of the curves is clear in the Pr_{0.65}Ca_{0.25}Ba_{0.1}MnO_{3} compound, particularly far above and below the T_{c}, indicating clearly that this compound does not follows an universal curve and the magnetic phase transition is first order. Thus, we conclude that there is not perfect agreement of the rescaled curves below T_{c}, however a check of the Arrott plots [M^2(H/M)] constructions suggested the second order quality of the transition in our sample.

(c) DC-resistivity study

The variation of the dc-resistivity (\rho) as a function of temperature of Pr_{0.65}Ca_{0.25}Ba_{0.1}MnO_{3} is represented schematically in Fig. 5. Across all the studied temperature ranges, the \rho decreases by increasing temperature which indicates that this compound exhibits a semiconductor behavior. The decrease in \rho when the temperature increases could be due to the increase the density of free carriers that acquire a sufficient thermal energy thermal to easily cross the barriers encountered.

(d) AC-conductivity study

The inset of Fig. 5 shows the frequency dependence of conductivity (\sigma) at different temperatures for Pr_{0.65}Ca_{0.25}Ba_{0.1}MnO_{3}. As we can observe, ac-conductivity (\sigma_{ac}) spectrum exhibits the presence of several behaviors. At low frequency (f < 10^4 Hz), a large plateau, corresponds to dc-conductivity (\sigma_{dc}), appears and the \sigma increases by increasing temperature. Such behavior indicates that conduction process is thermally activated by increasing the density of free carriers in the structure. Above 10^5 Hz and for T > 180 K, a metallic behavior appears.

\[
\Delta S_{M}^{\text{max}} = \Delta S_{M}(T_{2})/\Delta S_{M}^{\text{max}} = 0.5.
\]
accompanied by a decrease in $\sigma$. However, for $T < 180$ K the $\sigma$ monotonically increases with increasing frequency, indicating a superposition of different relaxation processes. The range of temperature, where $\sigma$ monotonically increases, could be described by the law of Jonscher:

$$A = \omega^s$$

where $A$ is a constant determining the strength of polarizability and $s$ is the frequency exponent representing the degree of interaction between mobile charge and the lattices around them. To get an information about the conduction mechanism in our sample, we will study the variation of the exponent $s$ depending on the temperature. From the region where the $\sigma$ is proportional to $\omega^s$ the value of the exponent $s$ is determined from the slope of the linear parts of $\sigma$ versus frequency. As shown in Fig. 6(a), the exponent $s$ decreases by increasing temperature. The result are in good agreement with a hopping mechanism in disordered material and confirm that conduction process is thermally activated. Such behavior is observed in different oxides and amorphous compounds and is discussed using Pike model. 

$$\sigma = \sigma_0 T \exp(-E_{ac}/k_B T)$$

where $\sigma_0$ is a pre-exponential factor, $T$ is the absolute temperature, $E_{ac}$ represents the activation energy of conduction mechanism and $k_B$ is the Boltzmann constant. It is clear, at high temperatures, that $\sigma$ follows this equation, suggesting that the electronic conduction is dominated by thermally activated hopping of small polaron (SPH). From this figure, it is found that activation energy decreases when increasing frequency (see the inset of Fig. 6(b)). This can be explained by the fact that the charge carriers choose the easiest path between sites. Therefore, the hops become only between closer sites and the activation energy decreases with frequency.

(e) Complex impedance analysis

The complex impedance $Z^*$ of the network is defined as:

$$Z^* = Z'(\omega) + jZ''(\omega)$$

where $Z'$ is the real part and $Z''$ the imaginary part of the complex impedance. Fig. 7(a) displays the evolution of $Z'$ with frequency at different temperatures for Pr$_{0.65}$Ca$_{0.25}$Ba$_{0.1}$MnO$_3$. At low frequencies, the spectrum of $Z'$ has higher values. Such behavior is widely observed in perovskite systems. At higher frequencies, however, the value of $Z'$ merges for all temperatures. Such observation indicates the presence of space charge polarization, which is released at high temperatures. At low frequencies and when temperature increases, $Z'$ decreases. This behavior can be related mainly to the lowering in the density of trapped charges and then a rise in the mobility of charges carriers. The behavior of $Z'$ observed for this compound at lower and higher frequencies is in good agreement with the reported results in the literature. The variation of $Z''$ as a function of frequency and temperature is shown in Fig. 7(b). This spectrum is characterized by the presence of a peak at a specific frequency, which is conventionally known as the “relaxation frequency” $\bar{f}_r$. When the temperature increases, the relaxation frequency shifts to the higher frequency region (see inset of Fig. 7(b)). This evolution indicated the presence of...
a relaxation phenomenon in the studied compound. In addition, it is noticed that the center of each peak, i.e., at the maximum of $Z''$, does not lie at the identical frequency indicating a deviation from the typical Debye’s model in the material. Also, it indicates that the peak intensity of $Z''$ decreases with temperature, confirming the semiconductor in this compound.46 By determining the value of the relaxation frequency, which determined for the low frequency peak centered at $f_r$ and using the following relation: $2\pi f_r \tau = 1$, the relaxation time ($\tau$) can be calculated. Using Arrhenius model, the inset of Fig. 6(a) exhibits the variation of log $\tau$ versus 1000/$T$. It is observed that the value of $\tau$ decreases by increasing the temperature, which indicate a thermally activated process. This result shows the presence of one conduction mechanism where the slope does not changes across all the studied temperature ranges.

Fig. 8 shows the Nyquist diagram of the system Pr$_{0.65}$Ca$_{0.25}$Ba$_{0.1}$MnO$_3$ obtained at $T = 80$ K. The spectrum is characterized by the appearance of a semicircle arc. To connect the microstructure of the compound with its electrical response, an equivalent electrical circuit can be established by modelling the impedance data using Zview software. As can be seen in Fig. 8, the agreement between the experimental and theoretical data is satisfactory. Then, the equivalent configuration is of the type $([R_p/ZCPE_3] + [R_d/ZCPE_2] + [R_s/ZCPE_1])$ as shown in the inset of Fig. 8.

(f) Dielectric properties

The study of the dielectric properties is another important source of information regarding the conduction process. The complex dielectric permittivity according to the Mott’s theory is defined as:

$$\varepsilon' = \varepsilon'(\omega) - je''(\omega)$$

where $\varepsilon'$ and $\varepsilon''$ are the real and imaginary parts of $\varepsilon^*$, respectively. $\varepsilon'$ describes the stored energy and $\varepsilon''$ describes the dissipated energy in the dielectric material, due to the presence of an applied electric field. The dissipation factor ($D$) and the capacitance ($C$) of the compound are measured over a wide frequency range (40 Hz to 10 MHz). Thus, $\varepsilon'$ and $\varepsilon''$ can be determined using the following expressions: $\varepsilon' = Ct(\varepsilon_0 A)$ and $\varepsilon'' = \varepsilon D$, where $\varepsilon_0$ is the free space permittivity, $t$ is the thickness of the sample and $A$ is the area of the electrodes. The evolution of $\varepsilon'$ and $\varepsilon''$ with frequency in the temperature range 80–160 K for Pr$_{0.65}$Ca$_{0.25}$Ba$_{0.1}$MnO$_3$ are shown in Fig. 9(a and b). As can be seen, at low frequencies, $\varepsilon'$ has higher values which can be related to the presence of space charge produced via the electrode-sample contact and interface between the grain and their boundaries.56 According to Singh et al.57 and Kar et al.58 such behavior can be attributed to the presence of several parameters of polarizations such as dipolar, atomic, ionic, interfacial and electronic polarization in the compound. Therefore, under the applied alternative electric field all electric dipole moments will be oriented in his direction. Then, all the polarization mechanisms can participate to polarization of the system. At higher frequencies, the decrease in the permittivity $\varepsilon'$
could be explained that the heavy particles cannot follow the applied electric field and then dipole response is weak, inducing a reduction of ionic and dipolar polarization contributions. Such behavior is observed when the charge carrier hopping cannot follow the alternating current beyond a certain frequency, which decreases the probability of electrons reaching the grain boundary and as a result, polarization decreases. However, at high frequencies, \( \varepsilon' \) remains important which may be due to a localized accumulation of charges involving the presence of interfacial polarization.\(^7\)

Fig. 9(b) clearly shown that \( \varepsilon'' \) decreases with increasing the frequency and no peak is observed, confirming that the polarization phenomenon in this sample is governed by a hopping process.\(^6\) This result may be due to space charge polarization and interface effects.\(^6\) At low frequencies, \( \varepsilon'' \) has higher values, suggesting the contribution of all polarization effects particularly the interfacial/space polarization due to an inhomogeneous dielectric structure. At high frequencies, where the electric dipoles cannot follow the applied electric field, the low value attained may be due to the gradual decrease of the dielectric loss. On another hand, the variation of \( \tan(\delta) = \varepsilon''/\varepsilon' \) as a function of frequency is shown in Fig. 9(c). At constant frequency the dielectric loss increases by increasing temperature which may be due to the increase in conductivity. However, by increasing frequency, the loss tangent first decreases and then increases. Since the charge carriers cannot follow the electric field, at higher frequencies, the value of \( \tan(\delta) \) remains low.

4. Conclusion

Structural, magnetic and electrical properties of Pr\(_{0.65}\)Ca\(_{0.25}\)Ba\(_{0.1}\)MnO\(_3\) manganite were investigated. A Rietveld analysis shows that the sample crystallizes in the orthorhombic structure with \textit{Pnma} space group. Magnetic measurements show a sharp paramagnetic to ferromagnetic transition around Curie temperature \( T_C \). A large maximum of magnetic entropy change \((-\Delta S^\text{max}_M)\) value has been found with a large relative cooling power (RCP) value. The variation of resistivity as a function of the temperature shows the presence of a semiconductor behavior. The ac-conductivity study is obeyed to the Jonscher law. The dominance of hopping mechanism was confirmed by the variation of the exponent \( s \). Complex impedance analysis permits to model the sample by an electrical equivalent circuit and displays the presence of a relaxation phenomenon. The dielectric study shows the contribution of different types of polarization.

Conflicts of interest

There are no conflicts to declare.

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