Existence of Nearest Neighbor and Variable Range Hopping in Pr$_2$ZnMnO$_6$

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Abstract

A joint investigation of X-ray diffraction (XRD) pattern and Raman spectrum authenticate the double phase monoclinic $P2_1/n$ and cubic $Fd-3m$ structures of polycrystalline Pr$_2$ZnMnO$_6$ (PZM). The existence of two different conduction mechanisms (Nearest neighbor hopping and Mott’s variable range hopping) is observed using a combined study of conductivity, dielectric relaxation and impedance spectra in PZM. This investigation point towards a transition from nearest neighbor hoping to Mott’s variable range hopping mechanism due to lowering activation energy around 580 K. The charge carriers hopping between the localized acceptor states at the grain boundaries (GBs), which dominants conduction mechanism below 580 K. The ac conductivity, dielectric relaxation, Nyquist plot, and electric modulus highlight the blended effect of grains (Gs) and GBs leads to the charge carrier dynamics in PZM. The dielectric relaxation and modulus formalism are analyzed on the basis of empirical Cole-Cole model. The conduction mechanism is found to be highly correlated with the relaxation mechanism and impedance spectroscopy.

1. Introduction

In strongly correlated systems, manganites double perovskite oxides with general formula R$_2$BMnO$_6$ (R = La, Pr, Nd, Sm, and B = Mg, Ni, Cu, Co, Zn) take attention into intense scientific research due to the variety of physical phenomena for over sixty years [1-3]. These type of materials are also important due to their colossal dielectric constant and colossal magneto-resistance property. These type of properties in manganites depends on the basis of Mn$^{3+}$/Mn$^{4+}$ ratio, as reported in previous literature [4,5]. Preliminary literature of Alvarez-Serrano et al. [6] reported that Zn$^{2+}$ doping in the LaMnO$_3$ perovskite leads to Mn$^{3+}$/Mn$^{4+}$ ratio that affects change in the electronic properties of the parent compound [7-9]. The parent material PrMnO$_3$ is also a promising material, which exhibits electrical, magnetic and electrocatalytic properties. The substitution of divalent cation Zn$^{2+}$ at Mn$^{3+}$ site results in an increase in the concentration of Mn$^{4+}$ in PrMnO$_3$ and that also affects John-Teller distortion which results in change Mn–O bond distance and modify Mn$^{3+}$–O–Mn$^{3+}$ bond into
superexchange bond $\text{Mn}^{4+}\text{–O}\text{–Mn}^{4+}$ lead to a decrease in the residual resistivity value and an increase in dielectric constant. R. Martínez-Coronado et al. [10] reported that the coexistence of $\text{Mn}^{3+}$ ion with $\text{Mn}^{4+}$ in $\text{La}_2\text{ZnMnO}_6$ system, which leads a localized site for conduction mechanism. However, La is now being replaced by Pr as the electronic arrangement of Pr matches with that of La and this replacement greatly enhances its electrical properties [11]. Also, the substitution of Pr at La site affects the bond angle $\text{Mn–O–Mn}$ shrinks results in an improvement in carrier confinement and lattice distortions. Substituting La by Pr has improved its working by enhancing its electric conductivity and decreasing its cathodic potential which are basic features of fuel cells [11].

Various hopping models (mobility activated charge carriers) have been presented to report the conduction mechanisms in the various temperature range for this system. Nearest Neighbor hopping is one of the well-known conduction mechanism in various perovskite oxides [12-14]. In this conduction mechanism, the activation energy has a constant single value, which led the charge carriers to hop at the nearest neighbor site from the initial site. Another type of conduction dynamics is the variable range hopping (VRH) mechanism, which led to activation energy to decrease with decreasing temperature [15-19]. This type of carrier dynamics basically occurs at correspondingly low temperatures. However, some literature [20] reported that VRH can also occur at and above room temperature.

Impedance spectroscopy is a powerful technique in solid states due to its capability to recognize the transport behaviors in grains (Gs) and grain boundaries (GBs). The grain and the grain boundaries are two main components that consist the microstructure and the correlation between the grain (G) and grain boundary (GB) are important to understand the overall properties of the materials. No attempt has been made to study the electrical transport properties of the double perovskite oxide (DOP) $\text{Pr}_2\text{ZnMnO}_6$. In this work, we have employed impedance spectroscopy to investigate the electrical transport properties associated with Gs and GBs in $\text{Pr}_2\text{ZnMnO}_6$ (PZM).

2. Experiment

PZM in powder form was synthesized through a standard solid-state reaction technique at 1573 K in air for 14 hrs, starting from $\text{Pr}_2\text{O}_3$ (Sigma-Aldrich, 99.9%), $\text{ZnO}$ (Merck, 99%) and $\text{MnO}_2$ (Loba Chemie, 99.99%). The calcined powders added with 5% polyvinyl alcohol were then pressed inside the cylindrical pelletizer and sintered at 1623 K to obtain dense PZM pellets (thickness $= 1$ mm and diameter $= 8$ mm). The crystal structure of PZM was studied using an X-ray powder diffractometer (Rigaku Miniflex II) having Cu-K$_\alpha$ radiation in the 20 range of 20-30.
10° – 80° by scanning rate of 0.02° per step at room temperature. Collected data were refined using the Rietveld method [21] with the FULLPROF program [22]. In the refinement process of XRD pattern, the background was fitted with the 6-coefficient polynomial function and the peak shapes were described by the pseudo-Voigt functions. Scanning electron microscope (SEM) (FEI Quanta 200) was used in order to capture the microstructural image of the prepared sample. Room temperature Raman spectrum of the sample was collected with a LABRAM HR 800 system, which is equipped with a spectrometer of 80 cm focal length, 1800 grooves/mm diffraction grating and a Peltier-cooled charge-coupled device (CCD). A laser of wavelength 488 nm (Ar-ion laser) was used to excite the sample. A 100x objective with NA 0.9 was used to focus the laser beam on the sample. Impedance spectroscopy on the sintered pellet of PZM was performed in the temperature range 300 K to 700 K, using an LCR meter (HIOKI – 3532, Japan). Eurotherm 818p programmable temperature controller was used to control the furnace temperature with an accuracy of ±1 K. This measurement was performed over the frequency range from 45 Hz to 5 MHz at the oscillation voltage of 1.0 V. Before the experiment, the flat surfaces on both sides of the pellets were cleaned properly and contacts were made by thin silver paste. Due to the evaporation effect in silver paste, we have checked both contacts before and after the experiment. The real (ε’) and imaginary (ε’’) part of the complex dielectric constant ε* (= ε’ + jε’’), where ε’ = C_s/C_0 and ε’’= G/ωC_0) were obtained from the capacitance (C_s) and conductance (G), whereas the real (Z’) and imaginary (Z’’) parts of the complex impedance Z* (=Z’ - jZ’’, where Z’= Zcosφ and Z’’ = Zsinφ) were obtained from the impedance (Z) and phase angle (φ), where ω is the angular frequency (ω = 2πν), ν is the measured frequency and j = √(-1). C_0 = ε_0A/d is the empty cell capacitance, where A is the sample area and d is the sample thickness. The ac electrical conductivity σ (= Gd/A) was calculated from the conductance.

3. Result and discussion
a) Structural analysis
The powder XRD profile for PZM is presented in Fig. 1 (a). The Rietveld analysis results confirm that PZM should be refined using a combination of monoclinic P2_1/n and cubic Fd-3m space groups. The presence of the super-lattice diffraction peak (101) at 20 ~ 20° in the XRD pattern indicates in phase tilting of the octahedra with B-site cation ordering, suggest the presence of rock-salt ordered monoclinic P2_1/n space group [23]. On the other side, the peak (111) at 20 ~ 15° confirm the presence of secondary phase distorted cubic Fd-3m in PZM.
reliability factors are found to be $R_{exp} = 6.87$, $R_p = 5.50$, $R_{wp} = 7.05$, and $\chi^2 = 1.05$. The fitting results are $P2_1/n$ (72.28 wt%) with $a = 5.4578 \text{ Å}$, $b = 5.5295 \text{ Å}$, $c = 7.7262 \text{ Å}$ and $\beta = 90.1021^\circ$ and space group $Fd-3m$ (27.72 wt%) with $a = 10.7801 \text{ Å}$. A schematic presentation of the PZM unit cells is shown in Fig. 1 (b) and 1 (c). The distribution of ions at crystallographic positions $4e$ (xyz) for Pr$^{3+}$, $2c$ (00½) for Zn$^{2+}$, $2d$ (½0½) for Mn$^{4+}$ and $4e$ (xyz) for O$^{2-}$, whereas in cubic $Fd-3m$ phase, the crystallographic positions are $16d$ (½1½½) for Pr$^{3+}$, $16c$ (000) for Zn$^{2+}$, $16c$ (000) for Mn$^{4+}$, $8d$ (½½½) and $48f$ (x½½) for O$^{2-}$. Each Ni$^{2+}$ and Ti$^{4+}$ ions surrounded by six O$^{2-}$ ions constitute the NiO$_6$ and TiO$_6$ octahedra, respectively. The difference between the experimental and calculated results was negligible, indicating the good quality of the refinement. The refined parameters are tabulated in Table – 1. The SEM image of PZM pellet, shown in Fig. 1 (d), indicates the high density of the material as well as grains of different sizes and shapes. The average grain size of PZM is found to be $\sim 0.45 \mu m$. The density of PZM is experimentally measured to 6.3 g/cc using Archimedes' principle and was 95% of the theoretical value 6.64 g/cc.

b) Raman Spectroscopy

Fig. 1 (b) shows the monoclinic $P2_1/n$ structure of PZM, whereas Fig. 1 (c) shows the cubic $Fd-3m$ structure. Basically, these two structures are the three-dimensional network of alternating ZnO$_6$ and MnO$_6$ octahedra. As discussed earlier, PZM crystallizes in a monoclinic structure belonging to $C^5_{2h}$ ($P2_1/n$) space group with two molecules per unit cell (Z = 2), while PZM crystallizes in a cubic structure belonging to $O^7_h$ ($Fd-3m$) space group with Z = 8 formula units. The monoclinic $P2_1/n$ (Glazer’s notation a’a’c’) structure is derived from the cubic prototype $Fm-3m$ (a0a0d0) symmetry by in-phase and anti-phase tilts of BO$_6$ octahedra along the [001] direction. On the other hand, the cubic $Fd-3m$ structure can be driven from the same phase tilts of BO$_6$ octahedra along [001] direction of the cubic cell corresponding to a0a0a0 Glazer’s notation. With the help of factor group analysis, we determine the distribution of zone-center vibrational modes in terms of the respective representations of $C_{2h}$ and $O_h$ point groups and the results are tabulated in Table – 2. There are 24 (12A$_g$ + 12B$_g$) Raman active modes are expected to monoclinic compound [24], while only 6 (A$_{1g}$ + E$_g$ + 4F$_{2g}$) gerade modes are expected for cubic PZM [25]. Fig. 2 represents the room temperature unpolarized Raman Spectrum for PZM. The spectrum shows more pronounced peaks at 94 cm$^{-1}$, 154 cm$^{-1}$, 235 cm$^{-1}$, 429 cm$^{-1}$, 541 cm$^{-1}$, 672 cm$^{-1}$, and 858 cm$^{-1}$ with adscititious comparatively weaker contributions. The spectrum consisting of several phonon modes of both monoclinic and cubic
structure of PZM is fitted utilizing a standard Lorentzian profile. The observed phonon modes and resonance FWHM parameters after deconvolution of the Raman spectrum of PZM are listed in Table 3. The correction between both phases and their prototype phase are shown in Table 4. Where T and L represent the translational and the librational modes of the Pr-cation and ν1, ν2 and ν5 correspond to the totally symmetric stretching, antisymmetric stretching and symmetric bending of BO6 octahedron. Since the monoclinic and cubic structures are a centrosymmetric subgroup of the prototype Fm-3m structure just the Raman active modes of the BO6 octahedron are considered. In this case, the corresponding phonon frequencies are determined by BII-O and BIV-O binding forces. Here BIV-O bond is the strongest bond and also BIV is lighter than BII atom. So the higher frequencies in the spectrum should be assigned to ν1, ν2 and ν5 vibrations of the octahedron with ν1>ν2>ν5. Taking into consideration, the breathing vibrations (A1g and Ag mode) at 858 cm\(^{-1}\) and 797 cm\(^{-1}\) for cubic and monoclinic structures of PZM respectively, are assigned to the symmetric stretching of MnO\(_6\) octahedron is given by ν1 peaks. The antisymmetric stretching of MnO\(_6\) octahedron assigned to A\(_g\) and B\(_g\) (ν2 peaks) modes occurs at 608 cm\(^{-1}\) and 672 cm\(^{-1}\) for monoclinic structure, whereas the peak at 541 cm\(^{-1}\) corresponds to antisymmetric stretching assigned to Eg (ν2) mode of MnO\(_6\) octahedra for the cubic structure of PZM.

c) Conductivity analysis
The variation of ac conductivity \([\log\sigma_{ac} \text{ vs } \log\omega]\) with frequency at a different temperature is shown in Fig. 3. The value of \(\sigma_{ac}\) increases with the increasing frequency for all measured temperatures, which relates to the trapped charge carriers in the PZM, which results in a thermally activated process [26]. Moreover, the conductivity spectra have been divided into three different distinct regimes. In regime I, the \(\sigma_{ac}\) is independent of frequency suggesting the dc conductivity (\(\sigma_{dc}\)) behavior. In regime II, the \(\sigma_{ac}\) strongly depends on frequency as both increases simultaneously. In regime III, the increase in \(\sigma_{ac}\) with frequency is comparatively lower than that in regime II. The intermediate frequency region (i.e., regime II) is found that the frequency dependence of \(\sigma_{ac}\) can be explained using the Jump relaxation model, which suggest the ionic conduction process in solids on the basis of unsuccessful and successful hopping of charge carriers [27, 28]. A high probability for charge carriers to jump at the nearest neighboring sites and then fort back, which is unsuccessful hop. However, the successful hop described as the neighboring site relaxed with respect to charge carrier's previous position, the charge carriers preferred to stay in the site. In this respect, the conductivity spectra at regime I
is associated with the successful hops. In regime II, the ratio of unsuccessful to successful hops dominating the conduction process, resulting in high dispersion of conductivity value. However, the conductivity spectra show two dispersion regions (regime II & regime III) at each individual temperature. The dependence of ac conductivity on frequency follows the double power law and is given as:

\[
\sigma_{ac} = \sigma_{dc} + A\omega^{k_1} + B\omega^{k_2}
\]  

(1)

In regime II, where exponent \( k_1 \) \((0 < k_1 < 2)\) corresponds to a localized hopping of charge carriers [27]. Whereas, for regime III, the exponent \( k_2 \) \((0 < k_2 < 1)\) corresponds to the translational hopping motion, which can also be defined as short-range hopping. Inset of Fig. 3 shows the variation of \( k_1 \) and \( k_2 \) with the temperature. The value of \( k_1 \) first decreases \((< 580 K)\) and after reaching a minimum value an increase in \( k_1 \) is visible. Hence, in regime II, the conductivity mechanism could be attributed to the localized orientation hopping assisted by both large polaron \((< 580 K)\) and small polaron \((> 580 K)\) hopping mechanism. On the other side, in regime III, the conduction arises due to short-range translational hopping assisted by large polaron hopping mechanism \((< 580 K)\).

The thermal variation of dc conductivity \((\sigma_{dc})\) for PZM is shown in Fig. 4 (a). The values of \( \sigma_{dc} \) are increasing with an increase in temperature suggesting a semiconducting nature of the PZM. The plot shows a sharp change in conductivity slop suggesting the presence of different hopping model in the measured temperature range. To identify the hopping models involved in conductivity mechanism, we have plotted the experimental \( \sigma_{dc} \) using nearest neighbor hopping (NNH) model is shown in Fig. 4 (b) and the equation used is defined as

\[
\sigma_{dc}T = \sigma_\alpha e^{-\left(\frac{E_a}{k_BT}\right)}
\]  

(2)

Here \( \sigma_\alpha \) is the pre-exponential factor, \( E_a \) is the activation energy, \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature. The curve is fitted well at high-temperature regime (above 580 K), where it follows linear NNH model, we have found the value of \( E_a \) is 0.15 eV, which point towards polaronic conduction of charge carriers between two nearest neighboring sites [29]. But, below 580K, the experimental data shows non-linear behavior suggests there is no single activation energy can be extracted, which point towards a different conduction dynamics. The charge carriers hop to a larger distance with different activation energies to locate an energetically favorable site. In this region, the \( E_a \) is calculated using the Eq. and the variation of \( E_a \) with temperature is shown in Fig. 4 (c).

\[
E_a = -\frac{d[\ln(\sigma_{dc})]}{d[1/k_BT]}
\]  

(3)
It is well known that at low temperature the conductivity data for several semiconductors [30] deviates from the linear tendency (i.e., NNH model) and obey the temperature dependency in the form [31-33].

$$\sigma_{dc} = \sigma_0 e^{-[T_0/T]^{\gamma}} \tag{4}$$

where, $\gamma$ is $\frac{1}{4}$, $\frac{1}{5}$, and $\frac{1}{2}$ depends weakly on temperature and other system parameters. Mott [34] reported that at low temperature the hopping length decreases with increasing temperature to present the Mott’s variable range hopping (MVRH) between localized states. In this aspect, we can assume MVRH is present below 580 K, where no single $E_a$ could be extracted. Fig. 4 (d) show the fitting results of experimental data with MVRH formalism using Eq.

$$\sigma_{dc} = \sigma_0 e^{-[T_0/T]^{\frac{1}{4}}} \tag{5}$$

where $\sigma_0$ is a constant and $T_0$ is the Mott’s characteristic temperature which can be expressed as follows:

$$T_0 = \frac{18\alpha^3}{k_B N(E_F)} \tag{6}$$

Where $N(E_F)$ is the density of states in the vicinity of Fermi energy and $“1/\alpha”$ be the localization length. The value of $T_0$ is extracted from the linear fit in Fig. 4 (d) and is found to be 54171311 K. The hopping energy $E_h(T)$ for a given temperature $T$ follows the following Eq. [35]

$$E_h(T) = \frac{1}{4} k_B T^2 T_0^{\frac{1}{4}} \tag{7}$$

In the inset of Fig. 4 (d) shows the thermal variation of the hopping energy $E_h(T)$ and it can be observed that the hopping energy increases from 0.133 eV to 0.204 eV with an increase in temperature from 300 K to 580 K, suggesting a polaronic MVRH conduction dynamics of PZM. The localization length ($1/\alpha$) is adopted an estimated value of 0.98 Å for manganites based perovskite as reported in previous results [36]. This lower value of “$1/\alpha$” of the charge carriers can be explained by considering the charge carriers hopping between the localized acceptor states at the GBs and it becomes a dominant conduction mechanism at this temperature. Exactly similar behavior is found for many similar materials such as Pr$_{0.8}$Ca$_{0.2}$MnO$_3$ [37,38].

The calculated value of $N (E_F)$ is found to be 4.09687x10$^{21}$ eV$^{-1}$cm$^{-3}$, which implies a high charge concentration in PZM. The higher value of $N (E_F)$ is fortified by many researchers [39].

The mean hopping distance $R_h(T)$ is given by $\frac{3}{8\alpha} \left( \frac{T_0}{T} \right)^{\frac{1}{4}}$ [40]. The value of $R_h(T)$ can also be obtained from the estimated value “$1/\alpha$”. The thermal variation of mean hopping distance $R_h$
(T) (Fig. 7 (d)) shows that the hopping distance decreases from 7.576 Å to 6.425 Å with an increase in temperature from 300 K to 580 K. It is observed that the minimum $R_h(T)$ at 580 K is of the order of the average distance ($d$) of manganese ions at B sites ($d = 6.42$ Å), implying that 580 K marks the maximum temperature corresponding to the shortest hopping distance permitted for VRH to occur [41]. From these results, we can conclude that the $\sigma_{dc}$ point towards a transition from NNH to MVRH around 580 K with decreasing temperature.

d) Impedance analysis

The Nyquist plots for the PZM are shown in Fig. 7 (a) and 7 (b). These plots show two semicircular arcs having center below the X-axis. The red arrow shows the direction of increase, in frequency. The intersection at an X-axis at the low-frequency side gives the total resistance of the system. Each curve passing through the origin, suggesting the contribution of grains in the system. At a particular temperature, the plot shows two semicircular arcs exhibiting the contribution of two types of relaxation process with different relaxation times ($\tau = RC$) in the measured temperature range, which suggest there is another one relaxation process (i.e., grain-boundary) other than grains contribution. Here $\tau$, $R$, and $C$ are the relaxation time, resistance and capacitance of the charge carriers corresponding to each relaxation process, respectively. Basically, GBs are more resistive than Gs. Therefore, the effects of GBs are found on the low-frequency side, where Gs contribution is visible on the high-frequency side.

In order to find the microstructural effect on the electrical transport properties of PZM, we have employed an equivalent circuit model ($(R_g Q_g)(R_{gb} Q_{gb})$) connected in series. For fitting impedance data at each temperature. Here, $R_g$, $R_{gb}$ are the resistances of Gs and GBs, and $Q_g$, $Q_{gb}$ the constant phase element of Gs and GBs, respectively. Here, the constant phase element ($Q$) is used for non-ideal behavior of capacitance and $C = R^{(1-n)/n} Q^{1/n}$ (where $n = 1$ for ideal capacitance). The experimental data are fitted using the Eqs. 8 & 9, considering that PZM consists of GBs and Gs.

$$Z' = Z'_{gb} + Z'_g = \frac{R_{gb}}{1+\left(\frac{1}{\omega Q_{gb} R_{gb}^{n}}\right)^{\frac{1}{n}}} + \frac{R_g}{1+\left(\frac{1}{\omega Q_{gb} R_{gb}^{n}}\right)^{\frac{1}{n}}} \tag{8}$$

and
\[ Z'' = Z''_{gb} + Z''_g = \frac{\frac{1}{\omega Q_{gb}} \frac{1+\eta_{gb}}{R_{gb}}}{1+\left(\frac{\frac{1}{\omega Q_{gb}} \frac{1+\eta_{gb}}{R_{gb}}}{\frac{1}{\omega Q_{gb}} \frac{1+\eta_{gb}}{R_{gb}}}\right)^2} + \frac{\frac{1}{\omega Q_{g}} \frac{1+\eta_{g}}{R_{g}}}{1+\left(\frac{\frac{1}{\omega Q_{g}} \frac{1+\eta_{g}}{R_{g}}}{\frac{1}{\omega Q_{g}} \frac{1+\eta_{g}}{R_{g}}}\right)^2} \]  

where, \( Z' \) and \( Z'' \) are the real and imaginary part of impedance, respectively. The subscript “\( gb \)” and “\( g \)” are indicating the contribution of GB and G respectively. \( \omega \) is the angular frequency, \( R \), \( Q \) and \( n \) are the resistance, constant phase element and the exponent, respectively.

The black solid lines in Fig. 7 (a) and 7 (b) represent the fitting to the electrical equivalent circuit and the fitted parameter are tabulated in Table. Fig. 7(c) and inset of Fig. 7(c) shows the fitted GB resistance and G resistance against temperature, which is obtained from the previous figures [Fig. 7(a) and 7 (b)]. These two figures show that the values of \( R_{gb} \) and \( R_g \) are decreases with increasing temperature, suggesting thermal activation of the localized charges. Similarly, Fig. 7(d) and inset of Fig. 7(d) show the variation of \( n_{gb} \) and \( n_g \) with the temperature, respectively. It has been observed that the values of \( n_{gb} \) and \( n_g \) are increases with increasing temperature. The value of \( n_{gb} \) varies from 0.956 at 300K to 0.975 at 700K, whereas, the value of \( n_g \) varies from 0.77 at 300K to 0.845 at 700K. This suggests that both GB capacitance and G capacitance move towards the ideal behavior. This is due to the vanishing of defects such as trapped charge at GBs and removes electronic or ionic defects in grain interior with increasing temperature. But, the value of \( n_g \) (0.845) at 700K is also suggested that there is still some electronic or ionic defects presence.

In order to correlate the conduction mechanism through impedance spectroscopy, we have plotted the previous fitting parameters \( R_g \) and \( R_{gb} \) using the NNH model (Eq.) as shown in Fig. 9 (a) and 9 (c), respectively.

\[ \frac{R}{R_0} = R_{\alpha} e^{\left(\frac{E_a}{k_B T}\right)} \]  

where “\( R_{\alpha} \)” is the pre-exponential term, “\( k_B \)” is the Boltzmann constant, and “\( E_a \)” is the activation energy of the carriers for conduction. The linear trend shows a reasonably good fit for the NNH model above 580 K with corresponding activation energies 0.15 eV and 0.18 eV for the grains and grain-boundaries, respectively. Below 580 K, the trends show non-linear behavior, which suggests the presence of another conduction model in PZM. In this region, the charge carriers prefer to hop between the sites lying within a certain range of energies. By employing MVRH, the impedance data are fitted well using

\[ \ln\left(\frac{R}{R_0}\right) = \left(\frac{T}{T_0}\right)^{\frac{1}{4}} \]  

(11)
where $R_0$ is the pre-exponential factor and $T_0$ is the characteristic temperature. Insets of Fig. 9 (a) and 9 (c) show a good agreement between the experimental data and MVRH. The calculated values of $T_0$ are K and K for Gs and GBs, respectively.

e) Dielectric relaxation

Fig. 5 (a) and 5 (c) show the frequency dependence behavior of the dielectric constant ($\varepsilon'$) and loss tangent (tan$\delta$) for PZM at various temperatures, respectively. It is observed that the value of $\varepsilon'$ decreases with increasing frequency. In the measured frequency range, two dielectric dispersion in $\varepsilon'$ and corresponding two peaks (one at low frequency and another one at high frequency) in tan$\delta$, are observed, suggesting the presence of two types of the relaxation process. At low frequency, the dielectric dispersion and the corresponding peak at tan$\delta$ are due to the presence of GBs in the system, whereas at high frequency, that is due to the presence of Gs. These two dispersions in $\varepsilon'$ and corresponding two peaks in the tan$\delta$ move towards a high-frequency region with the increase in temperature, suggests thermally activated relaxation process. In the measured frequency window, it is seen that the dispersion in $\varepsilon'$ and corresponding larger peak in tan$\delta$ due to GBs enters from the low-frequency side, on the other hand, the dispersion in $\varepsilon'$ and the corresponding smaller peak in tan$\delta$, which is due to Gs gradually vanishes on the high frequency side with increasing temperature. With the increasing frequency, after a certain value of frequency, the dipoles lag behind the applied field and do not respond with the field, resulting in a sudden drop in the value of $\varepsilon'$. The maximum value of tan$\delta$ is around 0.4 – 0.5 for GBs and 0.2 – 0.25 for Gs, as described by other researchers [20, 42]. The $\varepsilon'$ depends on the frequency can be explained by the empirical Cole-Cole equation [43, 44]:

$$
\varepsilon^* = \varepsilon' + j\varepsilon'' = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)}{1 + (j\omega \tau)^{1-\alpha}} \tag{12}
$$

$$
\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)(1 + (\omega \tau)^{1-\alpha} \sin(\alpha \pi/2))}{[1 + 2(\omega \tau)^{1-\alpha} \sin(\alpha \pi/2) + (\omega \tau)^2]^{(1-\alpha)}} \tag{13}
$$

Here, $\varepsilon_s$ is the static dielectric constant, $\varepsilon_\infty$ is the value of $\varepsilon'$ at infinite frequency, $\tau$ is the mean relaxation time, $\alpha$ is the degree of the distribution of relaxation time and $\omega$ is the angular frequency. The black solid lines in Fig. 5 (a) represents the fitting to the experimental data with the Eq. 13 at three different temperatures 300K, 500K, and 700 K and the fitted parameters are shown in Table - 6. The value of $\alpha > 0$, which suggests a broader peak than that in a Debye relaxation (where $\alpha = 0$). The values of relaxation times ($\tau$) decrease with increasing temperature, which suggests an increase in the dipole density and expeditious polarization rate
in PZM. The variation of the relaxation times corresponding to the GBs and Gs are shown in Fig. 6 (a) and 6 (b) by utilizing the NNH model with Eq. 14.

\[ \tau = \tau_0 e^{\frac{E_a}{k_B T}} \]  
\[ \tau = \tau_a e^{\left(\frac{T_0}{T}\right)^{\frac{1}{4}}} \]  

Here, \( \tau_0 \) is the pre-exponential constant, \( k_B \) is the Boltzmann constant, \( E_a \) is the activation energy and \( T \) is the absolute temperature. It is observed that the temperature dependence of \( \tau_g \) (Fig. 6(a)) and \( \tau_{gb} \) (Fig. 6(b)) follow the NNH model using the Eq. 14 for the temperature above 580K. The values of \( E_a \) are found to 0.15eV and 0.15eV for Gs and GBs, respectively. This result indicates the change in the relaxation mechanism at 580K. Fig. 6(c) shows the variation of \( \tau_g \) with temperature using MVRH model (Eq. 15). Good agreement between the experimental data and MVRH is obtained. The small differences in the activation energies for the conduction and relaxation process because only the hopping energy of the charge carriers between localized states are responsible for relaxation process, whereas the hopping energy as well as disorder and binding energy of polarons are involved in conduction mechanism [45-47]. From this results we can conclude that same type of charge carriers are responsible for both the conduction and relaxation process.

The variation of \( \varepsilon' \) with the temperature at various frequencies is shown in Fig. 5 (b). This spectrum shows the increase in \( \varepsilon' \) with the temperature and no relaxor-like behavior is found. As the number of charge carriers increases with increasing temperature, so the polarization increases as results \( \varepsilon' \) increases. With the further increase in temperature, the material exhibits colossal dielectric behavior similar to that reported in CaCu$_3$Ti$_4$O$_{12}$ [48]. However, in the measured temperature range, the increase in \( \varepsilon' \) is a step-like, which shifts towards high temperature with increasing frequency. This type of behavior is observed due to the presence of two different types of relaxation mechanism, which can be described by two parallel RC circuit connected in series with different RC value as described in Sec. 3 (d). Here the values of R and C for GBs are much higher than that of Gs, which creates a high resistive thin layer that effects in \( \varepsilon' \). This layer distributes a high capacitance by offering strong dislike to flow of charges, results in high \( \varepsilon' \) at low frequency and high temperature.

The dependence of tan\( \delta \) on temperature is shown in Fig. 5 (d). This graph shows two sets of peaks in tan\( \delta \). With the increasing frequency, the positions of observed two set of peaks shift to high temperature, suggesting the presence of two thermally activated relaxation in PZM. The tan\( \delta \) peaks depend on the mobility of the charge carriers and temperature. With the increase in
temperature, the mobility of charge carriers increases and commence relaxing at the comparatively high-temperature side results in tanδ peaks move towards the high-temperature side with increasing frequency.

f) Electric modulus formalism

The electrical modulus formalism is an important tool, which provides us a piece of useful information about the charge transport mechanism, such as electrical transport and conductivity relaxation. It is also a useful tool to differentiate the localized dielectric relaxation processes from the short or long-range polaron hopping and long-range conduction [49]. Fig. 8 (a) and 8 (b) show the real (M') and the imaginary (M'') part of the electric modulus (M*) are plotted against the frequency, respectively. It is observed that the value of M' increases with increasing frequency and there is two step-like increase is found in the measured frequency range. The step-like increase in M' is due to the scarcity of polarization of dipole towards the applied electric field. These two step-like increase in M' corresponding two peaks displays in M'' also. This behavior suggests the presence of two types of polarization effects. The first peak in M'' and corresponding first step-like increase in M' at low frequency is due to GB contribution and similarly the second peak in M'' and corresponding second step-like increase in M' at high frequency is the effect of Gs contribution. With the increase in temperature, the value of M' decreases and corresponding peaks in M'' shift towards high-frequency range suggesting thermally activated process and indicating a correlation between the motion of mobile charge carriers. The low frequency (< 10^2 Hz) peak in M'' suggest the charge carriers undergoes long ranged hopping from one site to the neighboring sites. In the other side, the peak in M'' at high frequency due to the charge carriers which are confined to trapping center and their mobility is restricted to short distances. The frequency dependence of M' and M'' can be explained by the empirical Cole-Cole equation [43, 44]:

\[
M' = \frac{M_s M_\infty [M_s A + (M_\infty - M_s) \cos \varphi] A}{M_s^2 A^2 + 2 A (M_\infty - M_s) M_s \cos \varphi + (M_\infty - M_s)^2}
\]

\[
M'' = \frac{M_s M_\infty [(M_\infty - M_s) \sin \varphi] A}{M_s^2 A^2 + 2 A (M_\infty - M_s) M_s \cos \varphi + (M_\infty - M_s)^2}
\]

where \( \varphi = \tan^{-1}\left[\frac{(\omega t^M)^{1-\alpha} \cos(\frac{\alpha \pi}{2})}{1 + (\omega t^M)^{1-\alpha} \sin(\frac{\alpha \pi}{2})}\right] \), and \( 0 < \alpha < 1 \).

Here, \( M_\infty \) and \( M_s \) are the value of electric modulus (M') at infinite and zero frequency, respectively. \( \omega \) is the angular frequency, \( t^M \) is the relaxation time corresponds to M'' peak, \( \alpha \) and \( \alpha \) are the relaxation parameters.
is the degree of the distribution of relaxation time. A good agreement is found between the experimental data and theoretical fitting using Eq. 16. The fitted parameters are listed in Table -6. The relaxation time \( \tau^M \) is corresponding to \( M'' \) peak is same as the relaxation time \( \tau \) corresponds to \( \tan\delta \) peak, because the electrical modulus \( M^* \) is calculated from the reciprocal of \( \varepsilon^* \).

Fig. 10 shows the frequency dependence of combined plot of imaginary parts of impedance and modulus at different temperatures 300 K (a), 500 K (b), 600 K (c) and 700 K (d). This figures may help us to investigate the type of charge carrier's movement in the relaxation process. The position of two peaks \( Z'' \) and \( M'' \) will separate from each other for the small-range movement of charge carriers. In fig. 10 (a), we cannot define the type of movement as the peaks are not in the measured frequency range at 300 K, so it may be long-range or short-range hopping. In Fig. 10 (c) and 10 (d), the difference in peak frequencies \( Z'' \) and \( M'' \) indicates that the charge carriers are localized and differs from an ideal Debye type behavior, also suggesting the relaxation process is dominated by the short-range movement of charge carriers [49]. The presence of two peaks suggests that the conduction process comes from the contribution of both Gs and GBs, whereas at room temperature (300 K), the main contribution comes from Gs and at the high temperature (700 K), the major effect is due to the GBs. The intermediate temperature shows the contribution of both Gs and GBs.

4. Conclusions
A combined study of X-ray diffraction (XRD) and Raman spectrum of PZM authenticate the double phase structure. The presence of super-lattice peaks (101) and (111) in the XRD pattern indicate the corresponding tilting of \( \text{MnO}_6 \) octahedra for monoclinic and cubic symmetry, respectively. Also, \( A_g \) and \( A_{1g} \) mode manifest the breathing vibration of the \( \text{MnO}_6 \) octahedra in both phases. The ac conductivity, dielectric relaxation, Nyquist plot, and electric modulus highlight the blended effect of grains (Gs) and GBs leads to the charge carrier dynamics in PZM. The existence of two different conduction mechanisms (Nearest neighbor hopping and Mott’s variable range hopping) is observed using a combined study of conductivity, dielectric relaxation and impedance spectra in PZM. This investigation point towards a transition from nearest neighbor hoping to Mott’s variable range hopping mechanism due to lowering activation energy around 580 K. The charge carriers hopping between the localized acceptor states at the grain boundaries (GBs), which dominants conduction mechanism below 580 K. The dielectric relaxation and modulus formalism are analyzed on the basis of empirical Cole-
Cole model. The conduction mechanism is found to be highly correlated with the relaxation mechanism and impedance spectroscopy.

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