Crossover between small polaron hopping and Mott’s variable range hopping in Pr$_2$MgTiO$_6$

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Abstract
A combined study of X-ray diffraction (XRD) pattern and Raman spectrum authenticates the lower symmetric orthorhombic $Pnma$ structure for solid-state synthesized Pr$_2$MgTiO$_6$ (PMT). The $A_g$ mode demonstrates itself as a breathing vibration of the TiO$_6$ octahedra. The ac conductivity, dielectric relaxation, and impedance spectra highlight the joint contributions of the grain-boundaries and grain microstructures to the charge carrier dynamics in PMT. The double power-law formalism is accepted to fit ac conductivity spectra. The relaxation spectra has a non-ideal nature with the circulation of relaxation time as observed from the impedance spectroscopic data. An equivalent circuit model has been employed for fitting impedance data using a constant phase element (CPE) model. The dc conductivity investigation points towards a crossover from small polaron hopping to Mott’s variable range hopping due to lowering activation energy. The crossover between two different conduction mechanisms (Mott’s variable range and small polaron hopping) is investigated using a conjunction of thermal varying conductivity, dielectric relaxation and impedance spectrum in polycrystalline PMT.

Keywords Perovskite oxides · Solid state reaction · Electrical Conductivity · Impedance Spectroscopy · Dielectric relaxation

1 Introduction

For further technical advances in the performance and shrinking of capacitive electronic elements, new materials with high dielectric constants ($\varepsilon'$) are immediately desired. Since the first reports of extremely high $\varepsilon'$ colossal values of $\varepsilon'$ in CaCu$_3$Ti$_4$O$_{12}$ [1–3]. Over the last decades, more than a thousand papers have been published on this topic. In the early stages, various intrinsic mechanisms were proposed [2–4]. However, further investigations revealed strong suggestions that the colossal $\varepsilon'$ in CaCu$_3$Ti$_4$O$_{12}$ is of extrinsic (heterogeneous) origin [4–10]. In a pioneering work, we have focused on rare-earth based double perovskite oxide with 4f electronic configuration to achieve high dielectric material with the intrinsic origin. Previous experiments on the R$\text{ETiO}_3$ [RE = rare-earth lanthanides] lanthanide-like perovskites show low-temperature Jahn–Teller cooperative distortions, which are characteristics of localized electrons, can affect both the valences of the cation of Ti as the magnetic response as well as dielectric [11]. The reported value of $\varepsilon'$ is found to be 92 in Pr$_6$NiTiO$_6$[12] at room temperature, where Ni$^{2+}$ and Ni$^{3+}$ mainly contribute to the conduction mechanism. Substitution of single-valent Mg$^{2+}$ instead of multivalent Ni$^{2+}$, opens the Pr$^{3+}$–Ti$^{4+}$ intervalence charge transfer (IVCT) state in the studied compound will have an impact on the electron population of the Pr$^{3+}$ intrinsic 4f electronic configuration and further improve the transport properties of the material. In this work, the correlations between the Pr$^{3+}$ electrical transport properties and structural factors are discussed. With respect to other perovskites [13], La$_2$MgTiO$_6$ is an ideal host material because of its attractive structure characteristics. However, La is now being replaced by Pr as the electronic configuration of Pr matches with that of La and this replacement greatly improves its electrical properties.

The grains and grain-boundaries are the two main components, which institute the microstructures of the material. In this work, we have used alternating current impedance spectroscopy (ACIS) in a variable domain of frequency (42 Hz to 5 MHz) and temperature (300 K to 700 K) to investigate the electrical transport characteristics associated with the grains and grain-boundaries contribution in Pr$_2$MgTiO$_6$ (PMT). Different hopping models (mobility activated charge carriers) have been presented to report the conduction mechanisms for DPO systems. Small polaron hopping is a type of conduction mechanism in which single valued activation energy is involved, which contribute the carriers to hop at the adjacent neighbor site. Another type of conduction mechanism is Mott’s variable range hopping (VRH) mechanism, which occurs at low temperatures due to lowering activation energy with the decrease in temperature [14]. However, it is also reported [12] that VRH can also arise at and above room temperature. No attempt has been made to study the electrical transport properties of the double perovskite oxide (DPO) PMT.

2 Materials and methods

In this section, we have described the materials used, synthesis procedure and the methods adopted for characterizations of PMT.

2.1 Materials
Polycrystalline PMT was synthesized by standard solid state reaction technique. Pr$_2$O$_3$ (Sigma-Aldrich, 99.9%), MgO (Sigma-Aldrich, 99%) and TiO$_2$ (Laboratory Reagent, 98%) were taken as ingredients.

2.2 Synthesis procedure

Stoichiometries amount of powders commixed in agar mortar in the presence of acetone (Merck) for 8 hrs. at periodic intervals. The slurry was dried, ground well, calcined in an alumina crucible at 1473 K for 14 hrs. and brought to room temperature under controlled cooling at a cooling rate of 1 K/min. Due to poor sinterability of PMT, the calcined sample was palletized (thickness, $d = 1$ mm and diameter, $D = 8$ mm) using polyvinyl alcohol (Molecular weight $\approx 115000$, Loba Chemie) as a binder. Finally, the pellets were sintered at 1523 K for 15 hrs. and cooled down to room temperature by controlling cooling at a cooling rate of 1 K/min.

2.3 Characterization techniques

To characterize the structure of the prepared sample, the room temperature X-ray diffraction (XRD) was carried out with the Rigaku Miniflex II diffractometer having Cu Kα radiation ($\lambda = 0.1542$ nm). The detector range is 10° – 150° with a scanning rate of 0.02° per step. Amassed data were refined utilizing the Rietveld method [15] with the FULLPROF program [16]. 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. For SEM analysis, the pellet was kept on the aluminum sample holder by a carbon tape with the gold coating on the crack surface of the pellet. The room temperature Raman spectrum of the sample was collected by 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 PMT was performed in the temperature range 300 K to 700 K, utilizing an LCR meter (HIOKI – 3532, Japan). Eurotherm 818p programmable temperature controller was used to control the furnace temperature with an accuracy of ±1 K. These quantifications were performed over the frequency range from 42 Hz to 5 MHz at the oscillating voltage of 1.0 V. Before the experiment, the flat surfaces on both sides of the pellets were cleaned properly and contacts were made from the thin silver paste. Due to the evaporation effect in the silver paste, we have checked both contacts before and after the experiment. The real ($\varepsilon'$) and imaginary ($\varepsilon''$) part of the complex dielectric constant $\varepsilon^*$ ($= \varepsilon' + j \varepsilon''$, where $\varepsilon' = C/C_0$ and $\varepsilon'' = G/\omega C_0$) were obtained from the capacitance ($C$) and conductance ($G$), whereas the real ($Z$) and imaginary ($Z'$) parts of the complex impedance $Z^*$ ($= Z' - j Z''$, where $Z' = Z \cos \phi$ and $Z'' = Z \sin \phi$) were obtained from the impedance ($Z$) and phase angle ($\phi$), where $\omega$ is the angular frequency ($\omega = 2\pi f$), $f$ is the measured frequency and $j = \sqrt{-1}$, $C_0 = \varepsilon_0 A/d$ is the empty cell capacitance, where $A$ is the sample area and $d$ is the sample thickness. The ac electrical conductivity $\sigma = \varepsilon_0 A/d$ was calculated from the conductance.

3 Results and discussion

3.1 Structural analysis

The room temperature XRD pattern of PMT is displayed in Fig.1 (a), showing a good agreement between the experimental and theoretically simulated patterns. The red circles represent the experimental data and the black solid line represents the calculated diffraction profile obtained by the Rietveld refinement. The green vertical bars denote the Bragg's positions and the blue solid curve at the bottom represent the difference between the theoretical and calculated patterns. The room temperature XRD pattern of PMT is displayed in Fig.1 (a), showing a good agreement between the experimental and theoretically simulated patterns. The red circles represent the experimental data and the black solid line represents the calculated diffraction profile obtained by the Rietveld refinement.
The size of the grains varies from 1.25 μm to 4.7 μm. The density of the pellet is experimentally measured to 5.96 g/cc using Archimedes’ principle and was 95% of the theoretical value 6.275 g/cc.

3.2 Raman Spectroscopy

The Raman spectrum for PMT is displayed in Fig. 2. The spectrum has ascended contributed from the bands at 162, 262, 377, 466, 370 and 594 cm\(^{-1}\) with additional reasonable weaker contributions (Table 2). The spectrum consisting of a number of phonon modes is fitted using a standard Lorentzian profile. PMT unit cell (Inset of Fig. 1 (a)) consists of a three-dimensional network of MgO\(_6\) and TiO\(_6\) octahedra, whereas Pr atom occupies the interstitial position. From Rietveld analysis of XRD pattern, we have found that the PMT crystalize in an orthorhombic \(Pnma\) structure. The orthorhombic \(Pnma\) (Point group: \(D_{2h}\)) symmetry is derived from the cubic prototype \(Fm\overline{3}m\) symmetry by the in-phase and anti-phase tilting of the MgO\(_6\) and TiO\(_6\) octahedra corresponding to the Glazer notation \(a'\overline{b}b\)\(^{-}\). From the group-theoretical analysis, the zone center vibrational modes are present in terms of the illustration of the \(D_{2h}\) point group and the corresponding results are tabulated in Table 3. The structure of PMT, which consists of strongly (Ti\(^{4+}\)) and weakly (Mg\(^{2+}\)) bonded octahedra, only the internal modes of the TiO\(_6\) octahedron may be considered. The total number of atoms in the \(Pnma\) unit cell is 20 resulting in a total of 60 modes out of which 3 are acoustic (\(\Gamma_{\text{acoustic}}\)), 8 are inactive (\(\Gamma_{\text{inactive}}\)), 24 are Raman active (\(\Gamma_{\text{Raman}}\)) and 25 are IR active (\(\Gamma_{\text{IR}}\)) [19].

Other peaks are assigned as: 107 (\(B_{1g}\)), 162 (\(B_{1g}\)), 262 (\(A_{1g}\)), 319 (\(B_{2g}\)), 377 (\(B_{2g}\)), 466 (\(B_{2g}\)), 594 (\(A_{2g}\)), 675 (Overtone) and 709 (Overtone) cm\(^{-1}\). Along with them, peaks at 92 (\(A_{1g}\)) and 453 (\(A_{1g}\)) cm\(^{-1}\) are also present, which are not deconvoluted with the Lorentzian profile as their position are close to other strong peaks. So, a combined study of X-ray diffraction (XRD) pattern and Raman spectrum authenticates the lower symmetric orthorhombic \(Pnma\) structure of PMT.

3.3 Conductivity analysis

In order to understand the charge carrier dynamics, the ac conductivity investigation was framed in a temperature interval of 300 K to 700 K. The frequency dependent ac conductivity at various temperatures are shown in Fig. 3 (a). The measured frequency window is characterized by four distinct regions: two plateau and two dispersion domains, indicating the effects of grain-boundaries and grains [20]. The value of “\(\sigma_{dc}\)” can be calculated by extrapolating conductivity value to the zero applied frequency (\(\nu = 0\)). For temperature 700 K, we have named these four distinct regions into two parts as region I and region II (Fig. 3 (a)), where each region contains one plateau and one dispersion. In the region I (i.e., \(<10^4\) Hz), the plateau represents the total conductivity followed by a dispersion region in which the grain boundary contribution relaxes. In region II (i.e., \(>10^4\) Hz) the plateau represents the grain contribution to the total conductivity. With the decrease in temperature, the frequency dispersion region gradually moves towards the low-frequency region. The presence of multiple plateaux and dispersion regions can be explained by a power law formation with each plateau and dispersion region being explained by a separate power function. In order to fully characterize the conductivity spectra for PMT, a double power-law formalism is adopted given by Eq. (1), highlighting the contributions of grain-boundaries and grains [20],

\[
\sigma(\omega) = \sigma_0 + A\omega^{k1} + B\omega^{k2}
\]  

where \(\sigma_{dc}\) is the frequency independent conductivity, i.e., dc conductivity, the coefficients \(A, B,\) and the exponents \(k_1, k_2\) are the temperature and material geometry-dependent parameters. The experimental conductivity data are fitted by Eq. 1 for the temperature of 700 K as shown in Fig. 3 (a). The values of the fitted parameters are listed in Table 4.

The value of dc conductivity is collected from the previous fitted value (\(\sigma_{dc}\)) of the ac conductivity spectra. Fig. 3 (b) shows the temperature dependent dc conductivity for PMT, showing the semiconducting nature of the material. In Fig. 3 (c), the experimental data are fitted using the small polaron hopping (SPH) model, defined as,

\[
\sigma_{dc} = \sigma_a \exp \left( \frac{-E_a}{k_B T} \right)
\]

where \(k_B\) is the Boltzmann constant, \(\sigma_a\) is the pre-exponential factor, \(E_a\) is the activation energy, and \(T\) is the absolute temperature. The high-temperature region is well fitted by Eq. 2, whereas a linear deviation is obtained in the case of the low-temperature region below 400 K, showing the presence of another conduction. The activation energy (\(E_a = 0.33\) eV) extracted from the high-temperature region suggesting polaronic conduction of
carrier between nearest neighboring sites [21]. However below 400 K, the non-linear behavior of the experimental data indicating a conduction dynamics with a different origin.

The activation energy ($E_a$) in this region is calculated using the relation $E_a = -d[ln \sigma]/d[1/k_B T] [22]$ and the temperature dependent $E_a$ is shown in the inset of Fig. 3 (c). The value of $E_a$ decreases from 0.33 eV to 0.275 eV with decreasing temperature suggested that at low temperatures, the range of hopping is greater than the distance between the neighboring equivalent sites due to the lower activation energy involved. In this aspect, the experimental data in the low-temperature range are fitted with the Mott’s variable-range hopping (VRH) formation, which is defined as [23, 24]

$$\sigma_{dc} = \sigma_0 \exp \left(-\frac{E_a}{k_B T}\right)^{\frac{3}{2}}$$  \tag{3}

where $\sigma_0$ is a constant and $T_0$ is the Mott’s characteristic temperature, which can be expressed in terms of the density of states in the vicinity of the Fermi energy, $N(E_F)$, and the localization length “$\xi$” as follows:

$$T_0 = \frac{18}{k_B N(E_F) \xi^3}$$  \tag{4}

Fig. 3 (d) displays the variation of $ln \sigma$ with $1/T^{1/4}$. The fitted parameter $T_0$ is extracted from the linear fit is found to be 669348164 K. The hopping energy $E_h$ follows the following Eq. [25]

$$E_h = \frac{1}{4} k_B T^4 T_0^{\frac{1}{2}}$$  \tag{5}

In the inset of Fig. 3 (d) shows the temperature dependent hopping energy $E_h$ and it can be detected that the hopping energy increases from 0.25 eV to 0.31 eV with increase in temperature from 300 K to 400 K, suggesting a polaronic VRH conduction of the PMT. The mean hopping distance $R_0$ is given by $\frac{3}{4} \xi (\frac{k_B T}{\hbar})^{\frac{1}{2}}$ [26]. By adopting a projected value of 2.2 Å for $\xi$ [25], the calculated value of $N(E_F)$ is found to be 2.93x10^{-23} eV^{-1}m^{-3}, which implies a high charge concentration in PMT. The higher value of $N(E_F)$ is found by other researchers [27]. The hopping distance $R_h$ can also be obtained from the estimated value $\xi$. The value of mean hopping distance $R_h$ shows that the hopping distance decreases from 3.188 nm to 2.967 nm with increasing temperature from 300 K to 400 K. It is observed that the minimum $R_h$ at 400 K marks the maximum temperature corresponding to the shortest hopping distance permitted for VRH to occur [28]. This result shows a crossover between small polaron hopping (SPH) and Mott’s variable range hopping (VRH) around 400 K.

### 3.4 Dielectric relaxation

Fig. 4 (a) shows the variation of dielectric constant ($\varepsilon'$) with the frequency in the temperature range 300 K to 700 K. These plots show that there is only one Debye-like dispersive region. With the increase of temperature, all these dispersions move towards higher frequencies. Fig. 4 (c) shows the frequency dependence of tanδ plot. It is found that only one relaxation peak is observed in the measured frequency range, which is due to the presence of grains, whereas at low frequency, the tail of another relaxation process is observed due to grain-boundary contribution except for room temperature data at 300 K. This suggest only one relaxation process is involved at the lower activation energy. This type of behavior in $\varepsilon'$ shows a step-like increase with increasing temperature, which shifts to a higher temperature with increasing frequency. This type of behavior in $\varepsilon'$ is very similar in high dielectric constant materials [31-36]. This type of behavior is caused by an equivalent circuit consisting of the grain contribution, which is connected in series with grain boundary contribution, where R and C are much higher than that of grain. The highly resistive layers that generate this equivalent circuit due to and
grain boundaries. This layer distributes a high capacitance by offering aversion to further flow of charges which result in high dielectric constant at low frequencies and high temperatures [37, 38].

We have studied the temperature-dependent relaxation time (τ) corresponding to the visible peak position in Fig. 4 (c). Temperature-dependent relaxation time (τ) corresponding to the grains is plotted in Fig. 4 (d) by utilizing the SPH model.

\[
\tau = \tau_o \exp \left( \frac{E_a}{k_BT} \right)
\]

(6)

Here, \(\tau_o\) is the pre-exponential factor, \(k_B\) is the Boltzmann constant, \(E_a\) is the activation energy and \(T\) is the absolute temperature. It is observed that the value of \(\tau\) decreases with increasing temperature and their temperature dependence follow the Arrhenius law (Eq. 6) for higher temperatures from and above 400 K and found the value of \(E_a\) is 0.25 eV. This is in accordance with our conductivity analysis results in Sec. 3.3, which also suggests that the relaxation mechanism changes at 400 K. Inset of Fig. 4 (d) show the evolution of relaxation time (τ) with temperature using Mott’s variable range hopping (VRH) model utilizing Eq. 7.

\[
\tau = \tau_o \exp \left[ \frac{(T/T_0)^{\frac{1}{4}}}{k_B T} \right]
\]

(7)

Here, \(\tau_o\) is a constant, \(T_0\) is the Mott’s characteristic temperature. From the figure, we observed that a good agreement between the experimental data and VRH fitting were obtained. This result correlates with the conduction mechanism in PMT.

### 3.5 Impedance analysis

Fig. 5 (a)-(c) show the experimental (points) and fitted (solid lines) complex impedance plane plot (Z-plot) for PMT at different temperatures. At each temperature, the Z-plot shows one depressing semicircular arc with the tails of another semicircular arc exhibiting the contribution of two different types of relaxation process to the charge carrier dynamics of the PMT. Due to the non-ideal behavior of capacitance, the center of the semicircle is found below the real axis with a spike-like nature in the low-frequency region. The decrease in the diameter of the semicircular arc with the increasing temperature points towards the thermally activated conduction mechanism in PMT in the grain interiors [38]. In perovskite oxides, the grains are less insulating than grain-boundaries, due to the presence of dangling bonds and non-stoichiometries distribution of oxygen at the grain-boundaries, and can act as carrier traps and form a Schottky barrier for charge transport. The capacitance of this layer is proportional to the reciprocal of the thickness of the layer (\(C \propto \frac{1}{d}\), \(d\) is the thickness of the layer). The rejoinder of grain-boundaries lies at lower frequencies than that of grains, due to their higher capacitance and resistance [39]. Consequently, we assign the more minute (at higher frequencies) and larger (at lower frequencies) arcs to the grains and grain boundaries.

In order to understand the contribution of the microstructure to the electrical transport properties of PMT, an equivalent circuit model (Inset of Fig. 5 (a)) has been employed for fitting impedance data at different temperatures. The constant phase element (Q) is used for the deviation of capacitance from its ideal behavior, which may be due to the presence of more than one relaxation. The capacitance of CPE can be designated as \(C_{CPE} = Q^{\alpha} \exp\left(\frac{k_BT}{\theta}\right)^{\alpha}\), where \(n\) estimates the non-ideal behavior. The value of \(n\) is zero for the ideal resistance and unity for the ideal capacitance. Here \(R\) and \(Q\) are the resistance and constant phase element of grains (g). The solid lines in Fig. 5 (a) and 5(b) represent the fitting to the electrical equivalent circuit and the fitted parameter \(R\) and \(n\) were obtained for various different temperatures. The inset of Fig. 5 (b) shows the variation of \(n\) with the temperature. It is observed that \(n\) has an increasing tendency (from 0.96 to 0.995) in the measured temperature range. This suggests that the grain capacitance approaches to ideal behavior with increasing temperature. The value of fitted grain resistance \(R\) decreases with increasing temperature, suggesting the thermal activation of the localized charges. In order to correlate the conduction mechanism through impedance spectroscopy, we have plotted the previous fitting parameter \(R\) using the SPH model (Eq. 8) as shown in Fig. 5 (c).

\[
R = R_a e^{\left(\frac{E_a}{K_B T}\right)}
\]

(8)

where \(R_a\) is the pre-exponential term, \(k_B\) is the Boltzmann constant, and \(E_a\) is the activation energy. The linear behavior shows a reasonably good fit for the SPH model above 400 K with corresponding activation energy 0.235 eV for the grains. The small differences in the activation energies for the conduction, relaxation, and impedance because only the hopping energy of the charge carriers between localized states are responsible for relaxation and impedance, whereas the hopping energy, as well as disorder and binding energy of polaron, are involved in conduction mechanism [39-41]. From these results, we can conclude that the same type of charge carriers are responsible for the conduction, relaxation and impedance process.

Below 400 K, this behavior shows non-linear behavior, which suggests the presence of another conduction model in PMT. In this region, we have employed VRH (Fig. 5 (d)), the impedance data are fitted well using
\[ \ln(R/R_0) = (T/T_0)^{\frac{1}{2}} \]  

where \( R_0 \) is the pre-exponential factor and \( T_0 \) is the characteristic temperature. Fig. 5 (d) shows a good agreement between the experimental data and VRH. These results correlate with the conduction mechanism and dielectric relaxation in PMT.

4 Conclusions

In this work, the electrical transport properties of polycrystalline PMT synthesized by solid-state reaction technique. A combination of XRD and Raman spectroscopic investigations confirms the lower symmetric orthorhombic \( Pnma \) structure for PMT. The \( A_2 \) mode demonstrates itself as a breathing vibration of the TiO\(_6\) octahedra. The conductivity, relaxation and impedance spectra highlight the combined contributions of the grain-boundaries and grain microstructures to the carrier dynamics in PMT. The double power-law formalism is accepted to fit ac conductivity spectra. The relaxation spectra has a non-ideal nature with the circulation of relaxation times as observed from the impedance spectroscopic data. An equivalent circuit model has been employed for fitting impedance data using a constant phase element (CPE) model. The dc resistivity investigation points towards a transition in the conduction mechanism showing a gradual crossover at temperature 400 K, from SPH to Mott’s VRH due to lowering activation energy. The conduction mechanism is shown to be highly correlated to the relaxation mechanism and impedance spectra.

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**Figures:**

![a](image1.png) ![b](image2.png)

Fig. 1: (a) The X-ray diffraction pattern of PMT at room temperature, (b) The SEM micrograph of PMT.
Fig. 2: Raman spectrum of PMT at room temperature. (Experimental data are red open circles, while the solid line represents phonon modes adjusted by Lorentzian curves).

Fig. 3: (a) Frequency dependence of the ac conductivity at various temperatures. (b) The thermal variation of dc resistivity for PZM; The dc resistivity of PZM describes the conduction process using (c) small polaron hopping model, (d) Mott’s variable range hopping model; The insets show the hopping energy (d) as a function of temperature; (c) Variation of activation energy with the temperature below 500 K.
Fig. 4: Frequency dependence of $\varepsilon'$ (a) and $\tan\delta$ (c) at various temperatures for PMT. Temperature dependence of $\varepsilon'$ (b) at various frequencies for PMT. Inset (b) shows the closed view of $\varepsilon'$ with temperature. Relaxation times $\tau$ of the carriers at grains are plotted using (d) small polaron hopping model and the inset shows $\tau$ is plotted using (d) Mott’s variable range hopping model.

Fig. 5: Complex impedance plane plots at different temperatures for PMT (a, b). Solid lines are fitted data to the observed data (points). Inset (a) shows the equivalent circuit used to fit the observed data. Inset (b) shows the variation of $n$ with the temperature. Grain resistance ($R$) is plotted using (c) small polaron hopping model and (d) Mott’s variable range hopping model.
### Tables:

#### Table 1 Structural parameters extracted from the Rietveld refinement of the XRD data for PMT.

| Space group: Pnma (Orthorhombic) |
|----------------------------------|
| Cell parameters: \(a = 5.5710 \text{ Å}, \ b = 7.7893 \text{ Å}, \text{ and } c = 5.4889 \text{ Å}\). |
| Reliability factors: \(R_{exp} = 6.77, \ R_p = 5.39, \ R_w = 7.06 \text{ and } \chi^2 = 1.09\). |

#### Atoms

| Wyckoff site | \(x\) | \(y\) | \(z\) | Bond length (Å) | Bond angle (°) |
|--------------|-------|-------|-------|-----------------|----------------|
| Pr 4c        | 0.54063 | 0.25000 | 0.51200 | Mg–O1 = 2.001(10) | Mg–O1–Ti = 153.3(4) |
| Mg 4b        | 0.50000 | 0.00000 | 0.00000 | Mg–O2 = 1.91(5) |
| Ti 4b        | 0.50000 | 0.00000 | 0.00000 | Ti–O1 = 2.001(10) |
| O1 4c        | -0.02601 | 0.25000 | 0.41993 | Ti–O2 = 1.91(5) |
| O2 8d        | 0.29841 | 0.03811 | 0.72531 | Mg–O1–O1 = 153.3(4) |

#### Table 2 Observed Raman active phonon modes of PMT.

| Band no. | Frequency (cm\(^{-1}\)) | Symmetry |
|----------|--------------------------|----------|
| 1        | 107                      | \(B_{3g}\) |
| 2        | 162                      | \(B_{3g}\) |
| 3        | 262                      | \(A_g\) |
| 4        | 319                      | \(B_{2g}\) |
| 5        | 377                      | \(B_{3g}\) |
| 6        | 466                      | \(B_{3g}\) |
| 7        | 594                      | \(A_g\) |
| 8        | 675                      | Over tone |
| 9        | 709                      | Over tone |

#### Table 3 Factor group analysis for PMT.

| Atom | Wyckoff sites | Symmetry | Distribution |
|------|---------------|----------|--------------|
| Pr   | 4c            | \(m\)    | \(2A_g \oplus 2B_{1g} \oplus B_{1u} \oplus B_{2g} \oplus 2B_{2u} \oplus B_{3g} \oplus 2B_{3u}\) |
| Mg / Ti | 4b           | \(-l\)   | \(3B_{1u} \oplus 3B_{2u} \oplus 3B_{3u}\) |
| O1   | 4c            | \(m\)    | \(2A_g \oplus 2B_{1g} \oplus B_{1u} \oplus B_{2g} \oplus 2B_{2u} \oplus B_{3g} \oplus 2B_{3u}\) |
| O2   | 8d            | \(l\)    | \(3A_g \oplus 3B_{1g} \oplus 3B_{1u} \oplus 3B_{2g} \oplus 3B_{2u} \oplus 3B_{3g} \oplus 3B_{3u}\) |

| \(\Gamma\) | \(\Gamma_{\text{acoustic}}\) | \(\Gamma_{\text{inactive}}\) | \(\Gamma_{\text{Raman}}\) | \(\Gamma_{\text{IR}}\) |
|-------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| \(\Gamma\) | \(7A_g \oplus 8A_u \oplus 7B_{1g} \oplus 8B_{1u} \oplus 5B_{2g} \oplus 10B_{2u} \oplus 5B_{3g} \oplus 10B_{3u}\) | \(B_{1u} \oplus B_{2u} \oplus B_{3u}\) | \(8A_u\) | \(7A_g \oplus 7B_{1g} \oplus 5B_{2g} \oplus 5B_{3g}\) | \(7B_{1u} \oplus 9B_{2u} \oplus 9B_{3u}\) |

#### Table 4 Fitted parameters of ac conductivity spectra for PMT.

| \(T\) (K) | \(\sigma_{dc} \times 10^7\) (S/m) | \(A \times 10^9\) | \(k_l\) | \(\sigma_0 \times 10^4\) (S/m) | \(B \times 10^{14}\) | \(k_2\) |
|-----------|-------------------------------|----------------|--------|-------------------------------|----------------|--------|
| 300       | 2.09676                       | 0.78           | 1.2    | 0.55                          | 11000          | 1.12   |
| 400       | 30.3991                       | 3.9            | 0.99   | 0.58                          | 0.18            | 1.79   |
| 500       | 156.261                       | 4.2            | 0.99   | 0.9                           | 0.13            | 1.78   |
| 600       | 633.51                        | 5              | 0.99   | 1.9                           | 0.14            | 1.75   |
| 700       | 1489.87                       | 5              | 0.99   | 4.2                           | 0.15            | 1.73   |