Small polaron hopping-assisted electrical conduction and relaxation in BCT and Mn-doped BCT samples

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ABSTRACT
Polycrystalline samples of $\text{Ba}_0.96\text{Ca}_{0.04}\text{TiO}_3$ (BCT) and $\text{Ba}_0.96\text{Ca}_{0.04}\text{Ti}_{0.96}\text{Mn}_{0.04}\text{O}_3$ (BCMT) were synthesized using the solid-state reaction route. XRD analysis confirmed the presence of the tetragonal phase in both as well as an additional hexagonal phase in the BCMT samples. The wt % of the segregated phase was found to be $\approx 8.96\%$ using Rietveld refinement. SEM micrographs showed an increase in the density and a decrease in the grain size of the BCMT sample. P-E measurements confirmed higher remnant polarization in the BCT samples. A single depressed semicircle was observed in the Nyquist plots indicating non-Debye-type behavior and overlapping contributions of the grains and grain boundaries. The increase in the value of the conductivity exponent “n” (and $n < 1$) with temperature suggested that the electrical conduction mechanism was non-overlapping small polaron tunneling. The electron acceptor nature of the Mn ions and lower grain size of the BCMT samples resulted in higher activation energy as compared to the BCT samples.

1. Introduction
Ferroelectric materials are of considerable importance due to their wide range of applications in a number of devices such as sensors, transducers, thermally stable ceramic capacitors and, most importantly the microwave domain. The utility of these materials is primarily based on such properties as their high dielectric constant and high piezoelectric, pyroelectric coefficients. A number of important ferroelectric materials crystallize in perovskite structures [1,2]. Barium titanate (BT) is one such typical perovskite which possesses outstanding ferroelectric and dielectric properties. Being nontoxic, it is also environmentally friendly. BT is most widely used to substitute for lead in a number of applications including dynamic random access memories (DRAM), ferroelectric nonvolatile memories (FeRAM) and the microwave domain. Its dielectric properties can be easily tailored using dopants such as Sr, Ca, Mn, Fe, etc. Calcium (Ca) substitution is one such substitution which significantly impacts the performance of BT [3,4]. It has been reported that Ca doping in BT (BCT) results in high piezoelectric coefficients of resistance and increases ferroelectric $T_c$. It also helps in inhibiting formation of the unwanted non-ferroelectric hexagonal phase of BT [5,6]. BCT is generally used in multilayer ceramic capacitors (MLCCs) which are widely used for applications such as infrared detectors, gate dielectrics, wave-guide modulators and piezoelectric transducers [6,7]. In general, the physical properties (conductivity, etc.) of perovskites (BT, BCT, etc.) depend on the nature of the dopants as well as the processing parameters (sintering temperature, etc.) [8]. High-temperature sintering of BCT (perovskites in general) results in the formation of large numbers of conduction electrons and ionized oxygen vacancies. These electrons are almost completely delocalized by hopping from one titanium site to another. This results in poor electrical insulation and imparts semiconductor behavior to BCT (perovskites in general). The confinement of these electrons to smaller regions is a must to prevent deterioration of the electrical properties of ceramics. In this connection, electron acceptor ions (at low concentrations) can be used as one of the alternatives for trapping electrons [9]. Manganese has been reported as a potential acceptor as it can exist in three valance states: Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$. The Mn$^{3+}$ and Mn$^{4+}$ ions are more reducible than Ti$^{4+}$ and hence result in electron trapping, which can be helpful in preventing conductivity deterioration [10]. Thus, this study reports the effect of Mn doping on the structural, surface morphological and ferroelectric properties of BCT. The physical properties of Mn-doped BCT are compared with those of pure BCT. A detailed electrical characterization of BCT and BCMT using impedance spectroscopy is presented.

2. Experimental
Bulk samples of $\text{Ba}_{0.96}\text{Ca}_{0.04}\text{TiO}_3$ (BCT) and $\text{Ba}_{0.96}\text{Ca}_{0.04}\text{Ti}_{0.96}\text{Mn}_{0.04}\text{O}_3$ (BCMT) were synthesized by the conventional solid-state reaction route. The stoichiometrically weighed raw materials (99.9% pure BaCO$_3$, CaCO$_3$ and Mn(OH)$_2$) were mixed in a ball mill for 24 hours. The weighed powdered samples were then sintered at $1200^\circ\text{C}$ for 2 hours in a muffle furnace. The sintered samples were then ground for 24 hours and these samples were further characterized by XRD, SEM, P-E measurements and impedance spectroscopy.
TiO$_2$, MnO$_2$ from Sigma Aldrich) were ball-milled for 48 h in acetone medium. The milled powder was then calcined for 12 h at 1000°C to allow phase formation. The calcined powder was then mixed with polyvinyl alcohol (2 wt %) as a binder. The resultant powder was then used to prepare small discs with 1 mm thicknesses and 10 mm diameters using a hydraulic press to apply pressure of 1 ton. The pressed pellets were finally sintered at 1260°C for 3 h to allow proper grain growth. Some of the sintered pellets were coated with silver paste to make electrical contacts for carrying out electrical measurements.

XRD data of the samples were recorded using a SHIMADZU (MAXima XRD-7000) equipped with a Cu $K_\alpha$ anode ($\lambda$ = 1.54 Å). The data were collected from 10 to 120° with a step size of 0.02° and a scan speed of 2°/min. Rietveld refinement of the XRD data was carried out using FULLPROF 2015 software. FESEM micrographs were recorded using a Carl Zeiss “Supra 55” at an accelerating voltage 10 KV. The sintered pellets were coated with silver electrodes for ferroelectric measurements. An automatic ferroelectric loop tracer based on a sawyer-Tower circuit (from Marine India) was used to conduct P-E loop measurements at a frequency of 50 Hz. Complex impedance and AC conductivity studies were conducted using an impedance analyzer (E4990A) from KEYSIGHT TECHNOLOGIES.

3. Results and discussion

3.1. Structural properties

XRD diffractograms of BCT and BCMT samples are shown in Figure 1(a,b). The presence of sharp high-intensity peaks shows that the samples are well crystallized. The splitting of the diffraction peak at 2$\theta$ = 45° provides initial evidence of the tetragonal structure of these samples. A comparison of the experimental data (for BCT) with the reference data shows that all the peaks can be indexed to tetragonal unit cells (space group $P4_{2}m$ (ICSD 98-000-3900)). No impurity peaks were detected in the BCT sample. However, additional low-intensity peaks were found to be present at 2$\theta$ = 26.28°, 41.47° and 49.24° the BCMT sample, indicating the presence of a secondary phase. These additional peaks could be indexed to the hexagonal BT (space group $P6_{3}m$a (ICSD98-000-2922)) phase.

In order to retrieve structural information about these samples, Rietveld analysis of the powder data was carried out using FULLPROF SUITE 2015 software. A single-phase refinement model was employed to fit the XRD data of the BCT sample. The BCMT sample was observed to be composed of two phases (tetragonal (“T”) and hexagonal (“H”)). A double-phase model was hence adopted for its structural analysis. For the “T” phase, the initial structural model was assumed to be very close to ICSD 98-000-3900. In this phase, Ba/Ca were placed at Wycko site 1a (0, 0, 0), Ti/Mn at 1b (1/2, 1/2, 1/2±$\delta$), O1 at 1b (1/2, 1/2, 0±$\delta$) and O2 at 2c (1/2, 0, 1/2±$\delta$), where $\delta$ represents the refineable parameter. The occupancy parameters were fixed according to the stoichiometric compositions. The “Z” coordinate of Ti/Mn, O1 and O2 was refined, while it was fixed for Ba/Ca. The lattice parameters and isotropic thermal parameters for all the elements of this phase were also refined. In the “H” phase, the Ba ion was placed at Wyckoff’s site 1a (0, 0, 0), Ti at 1b (1/3, 2/3, 1/2±$\delta$), O1 at 1b (0 ±$\delta$, 1/2 ±$\delta$, 0±$\delta$) and O2 at 2c (1/2 ±$\delta$, 0 ±$\delta$, 1/2 ±$\delta$), where $\delta$ represents the refineable parameter, respectively. The lattice parameters and isotropic thermal parameters of all the elements were also refined for this phase. A Thomson–Cox–Hasting Pseudo-Voigt function was used to describe the peak profiles, and a sixth-order polynomial was used to fit the background. The zero-shift parameter was also refined. The various refineable parameters were refined sequentially till the minimum values of different agreement indices were obtained. The values of various refined parameters are listed in Table 1. It can be seen from Table 1 that the GOF values for the two samples are 1.31 to 1.38, respectively. This shows very good agreement between the experimental and theoretical simulated data. Mn addition was not found.
to significantly affect the c/a ratio (≈1.006) for the tetragonal phase. The wt % of the H phase in the BCMT sample was calculated as 8.96%. This implies that the solubility of Mn in BCT is ≤4 atomic%. Phan et al. and Chen et al. also reported the presence of the hexagonal BT phase at 2% and 1.3% Mn doping in BT, indicating that Ca addition had enhanced the Mn solubility [11,12].

3.2. Micro-structural properties

Figure 2(a,c) shows FESEM images of BCT and BCMT samples. These micrographs were recorded at a magnification of 20,000 X. Both micrographs show well-interconnected and non-uniform (in shape and size) grains. Agglomeration of particles is clearly visible in both the samples, though it is more pronounced in BCT. The BCT sample also appears to be more inhomogenous with respect to size distribution as compared to the BCMT sample. The non-uniformity of the grains is due to the matter transport mechanism between the grains during the sintering process. The average grain size (calculated using Image J software) was observed to be ≈2.67 µm and ≈0.78 µm for the BCT and BCMT samples, respectively. The corresponding histograms are also shown in Figure 2(b,d). The reduction in grain size (in the Mn-doped samples) could be due to generation of the local strain inhibiting grain growth. It can also be observed from the micrographs that Mn addition to BCT leads to a decrease in porosity and, hence, enhancement of the density of these samples.

3.3. Ferroelectric properties

Room-temperature polarization vs. electric field (P-E loop) data for the BCT and BCMT samples are shown in Figure 3. It is clear from the figure that the BCT sample exhibits

![Figure 2](image-url)
a better ferroelectric loop as compared to the BCMT sample. The measured remnant polarizations ($P_r$) of the two samples were found to be 2.01 µC/cm² and 0.93 µC/cm², and the electric coercivity was found to be 2.71 KV/cm and 6.58 KV/cm for the BCT and BCMT samples, respectively. Thus, the $P_r$ value decreased with the addition of Mn to BCT. A number of factors can play deciding roles in decreasing polarization (and hence the $P_r$) of ferroelectric materials. It may decrease because of (a) a decrease in the $c/a$ ratio, (b) a decrease in the grain size or $c$) interplay between the majority and segregated phases. Our XRD data show that the $c/a$ ratio does not vary significantly with the addition of Mn to BCT. Therefore, the $c/a$ ratio does not play significant role in controlling the ferroelectric behavior of the sample. In this case, two other factors may thus be responsible for the decrement in the $P_r$ value. It has previously been reported that reversal of the polarization process is difficult in smaller grains as compared to larger grains [13,14]. When the grain size decreases, higher polarization discontinuity occurs as the number of grain boundaries increases. The hexagonal BT phase is moreover, a nonferroelectric in nature [5]. Thus, the ferroelectric properties in our samples are controlled by increasing leakage current values with transition metal ion doping as well as due to segregation of a non-ferroelectric phase.

3.4. Complex impedance analysis

Complex impedance spectroscopy is a nondestructive technique for characterizing the electrical behavior of polycrystalline samples over a wide frequency and temperature range. The technique involves measurement of complex impedance of a sample (sandwiched between two metal electrodes) as a function of frequency at different temperatures. Grains and grain boundaries as well as electrodes contribute the overall measured impedance of the samples. This technique thus allows direct determination of the grain, grain boundary and electrode contributions to the overall impedance of the sample. The impedance of a sample has two parts: (a) resistive, arising from resistance of grains, grain boundaries and electrode and (b) reactive arising from grains, grain boundaries and electrode capacitance [8,15–17]. In the present study complex impedance (CI) and complex modulus (CM) studies have been carried out. These are defined as follows:

$$\text{Complex impedance } Z'(\omega)=Z'(\omega)+jZ''(\omega) \quad (1)$$

Complex Modulus $M'(\omega)=M'(\omega)+jM''(\omega)=\frac{\omega C_0 Z}{A/t}$

where $\omega = 2\pi f$ represents the angular frequency, $C_0 = e_0$ A/t represents geometrical capacitance ($A$ and $t$ are the area and thickness of the sample), $Z'$, $M'$, and $Z''$, $M''$ represent the real and imaginary parts of the CI and CM, respectively.

Figure 4(a,b) shows variations in the real part of impedance $Z'$ as a function of frequency at different temperatures for the BCT and BCMT samples, respectively. The impedance of both the samples (at a given temperature) can be divided into three ranges: (a) a plateau range characterized by high impedance (at low frequencies) (b) a dispersion range in which $Z'$ decreases rapidly with frequency (at intermediate frequencies) and (c) a plateau range again characterized by low impedance values (at high frequencies). The magnitude of $Z'$ also decreases with increase in temperature in the plateau as well as the intermediate frequency range. This phenomenon is typical of materials exhibiting a negative temperature coefficient of resistance (NTCR-type) [18]. All the curves merge into a single curve above at 100 kHz for all the temperatures for both the samples. The observed behavior may be due to the release of space charge carriers as a result of reductions in the barrier properties of the material with increase in temperature and may be responsible factor for the increase in AC conductivity at high temperatures and frequencies [19–21].

Figure 4(c,d) shows the variations in $Z''$ as a function of frequency at different temperatures for BCT and BCMT samples, respectively. The graph clearly reveals that $Z''$ for both the samples (a) attains the maximum value at a particular frequency, which increases with temperature and (b) decreases significantly in magnitude of $Z''$ with increase in temperature. The variations become more prominent at higher temperatures. A broadening of the peaks with increase in temperature suggests that there is fairly a large spread of relaxation times in both materials. The merging of all the curves at higher frequencies is due to an absence of the space charge polarization at high frequencies [17]. It should be noted that the position of $Z''$ maxima coincides with the inflection point of the $Z'$ data. This frequency is referred to as a characteristic relaxation frequency of
the dipoles formed in the material [22,23]. The characteristic relaxation time ($\tau^*$) can be calculated by determining the position of the peak maxima in $Z''$ using the relation $\omega \tau^* = 1$ (for different temperatures). The activation energy corresponding to the relaxation process taking place in the sample can be obtained by fitting of $\ln \tau^*$ vs $1000/T$ data with the Arrhenius relation given as $Z''$:

$$\tau^* = \tau_0^* e^{\left(\frac{E_z}{k_B T}\right)}$$

(3)

where $\tau_0^*$ is the characteristic time constant and $E_z$ is the activation energy, $k_B$ is the Boltzmann constant and $T$ is the absolute temperature [22]. The plot and the fitted straight line are shown in the insets in Figure 4(e,f). The activation energy $E_z$ has been found to be 0.93 eV and 1.11 eV for the BCT and BCMT samples, respectively. Thus, Mn doping leads to a very small increase in activation energy. To determine whether the nature of the relaxation mechanism is temperature dependent/independent, moreover, normalized values of $Z''/Z_{\text{max}}$ were plotted against $\ln \omega/\omega_{\text{max}}$ (where $\omega_{\text{max}}$ is the angular frequency corresponding to the maximum value of $Z''$). In this plot, the peaks corresponding to different temperatures collapse into one master curve, as shown in Figure 4(e,f). This indicates that the nature of the relaxation mechanism is temperature-independent in both the samples [24].

In order to separate out the grain, grain boundary and electrode contributions, $Z'$ data were plotted against $Z''$ (also known as Nyquists plots). It should be noted that in Nyquist plots, contributions from the
grains, grain boundaries and electrodes are manifested as successive semicircles (which may be distinct or overlapped) toward increasing $Z'$. These plots are shown in Figure 5(a,b). It can be clearly seen that (a) the plots (at a particular temperature) do not contain distinct semicircles, (b) the radii of the semicircles decrease with increases in temperature (typical of NTCR behavior) and (c) the semicircle arcs are not centered on real $Z$-axis. This might be due to overlapping contributions from the grains and grain boundaries, possibly as a result of a decreased difference between the most relaxed frequencies [25]. In homogeneous materials, these arcs are perfect semicircles with centers lying on the real $Z$-axis, indicating a static distribution of capacitance and CPE element which is useful for modeling non-Debye type behavior in impedance spectroscopy [28]. The impedance of a CPE element is given by $Z_{CPE} = 1/(j\omega)^{\beta}C$, where $\beta$ varies from 0 to 1 ($\beta = 0$ represents an ideal resistor and $\beta = 1$ an ideal capacitor). The model equations employed to fit data for the ideal RC circuit are as follows:

$$Z' (\omega) = \frac{R_g}{1 + (\omega R_g C_g)^2} + \frac{R_{gb}}{1 + (\omega R_{gb} C_{gb})^2}$$  \hspace{1cm} (4)
$$Z'' (\omega) = \frac{\omega R_g^2 C_g}{1 + (\omega R_g C_g)^2} + \frac{\omega R_{gb}^2 C_{gb}}{1 + (\omega R_{gb} C_{gb})^2}$$  \hspace{1cm} (5)

where $(\omega_g, R_g, C_g)$ and $(\omega_{gb}, R_{gb}, C_{gb})$ represent the frequency at the peak of the semicircle, resistance and capacitance coming from the grains and grain boundaries, respectively. The value of the resistance can be calculated from the intercepts of the circular arcs on the $Z'$ axis, and that of capacitance can be calculated using following relations [17]:

$$C_g = \frac{1}{\omega_g R_g}$$  \hspace{1cm} (6)
$$C_{gb} = \frac{1}{\omega_{gb} R_{gb}}$$  \hspace{1cm} (7)

In case of a distributed relaxation time, $C_g$ and $C_{gb}$ are replaced by CPE$_g$ and CPE$_{gb}$, respectively. The model equations are then given as follows:

$$Z' (\omega) = R_g \left(1 + R_g Q_g \omega^{\beta} \cos(\frac{\beta \pi}{2})\right) \frac{1}{1 + 2 R_g Q_g \omega^{\beta} \cos(\frac{\beta \pi}{2}) + (\omega^{\beta} R_g Q_g)^2} + \frac{R_{gb}}{1 + R_{gb} Q_{gb} \omega^{\beta} \cos(\frac{\beta \pi}{2}) + (\omega^{\beta} R_{gb} Q_{gb})^2}$$  \hspace{1cm} (8)

$$Z'' (\omega) = -\frac{R_g^2 Q_g \omega^{\beta} \sin(\frac{\beta \pi}{2})}{1 + 2 R_g Q_g \omega^{\beta} \cos(\frac{\beta \pi}{2}) + (\omega^{\beta} R_g Q_g)^2} - \frac{R_{gb}^2 Q_{gb} \omega^{\beta} \sin(\frac{\beta \pi}{2})}{1 + 2 R_{gb} Q_{gb} \omega^{\beta} \cos(\frac{\beta \pi}{2}) + (\omega^{\beta} R_{gb} Q_{gb})^2}$$  \hspace{1cm} (9)

All the parameters derived obtained from fitting are listed in Table 2. It is clear that grain boundary resistance $R_{gb}$ is higher than grain resistance $R_g$ at every temperature. This may be due to a lower number of trapped electrons and oxygen vacancies in the grain boundaries [29]. High-temperature sintering results in oxygen loss, leading to formation of oxygen vacancies. As the temperature is slowly cooled to room temperature, a re-oxidation process occurs. This re-oxidation process leads to formation of highly conductive oxygen-deficient grains and insulating grain boundaries. As the temperature increases, the

![Figure 5. Nyquist plot complex impedance ($Z'$ vs $Z''$) of the (a) BCT and (b) BCMT samples at different temperatures.](image-url)
$R_g$ and $R_{gb}$ values decreases, moreover, indicating a negative temperature coefficient of resistance (NTCR) effect in the material. The activation energies obtained from linear fitting of $\ln R_g/\ln R_{gb}$ vs $1000/T$ data using the Arrhenius equation are observed to be $E_g = 0.56$ eV, $E_{gb} = 0.99$ eV and $E_g = 0.77$ eV, $E_{gb} = 1.11$ eV for the BCT and BCMT samples, respectively. The higher activation energy of the grain boundaries as compared to the grains for both the samples again indicates their higher resistive nature. Also, the higher activation energy (both $E_g$ and $E_{gb}$) of BCMT with respect to BCT indicates that both the grains and grain boundaries of the BCMT samples are more resistive than those of BCT.

### 3.5. Electric modulus analysis

Complex modulus formulism is a very handy tool for analyzing the dynamic nature of carrier transport in ceramics. It can also be used for studying the inhomogeneity and dielectric relaxation processes in polycrystalline ceramics. Moreover, the smallest capacitive elements receive emphasis in this formulism. Figure 6(a,b) shows the frequency dependence of the real part of the electrical modulus at different temperatures for the BCT and BCMT samples, respectively. The $M'$ values clearly approach zero at low frequencies and rise asymptotically with increases frequency (at all temperatures). The $M''$ values also tend to become saturated at higher frequencies and the saturation values keep increasing with increase in temperature in both the samples. This behavior can be related to a lack of a restoring force governing the flow of charge under the action of an induced electric field [19,30,31]. This trend in the behavior of $M'$ also confirms the negligible contribution of the electrode effect.

Figure 6(c,d) shows the frequency dependence of the imaginary part of the electrical modulus at different temperatures for the BCT and BCMT samples, respectively. It can be seen that the value of $M''$ also approaches zero at lower frequencies, again confirming the insignificant contribution of electrode polarization in our samples. In addition, $M''$ exhibits the maximum value at a frequency denoted as $\omega_{max}$. The frequency region below $\omega_{max}$ determines the range of frequencies up to which charge carriers are mobile over long distances. The region above $\omega_{max}$ shows the range of frequencies for which the charge carriers are mobile for short distances [32]. The modulus $M''$ was fitted using the Kohlrausch – Williams – Watt (KWW) stretched exponential function given as follows:

$$M'' = \frac{M''_{\max}}{(1 - \beta) + \frac{\beta}{\tau_{TB}}} \left[ \left( \frac{\omega}{\omega_{\max}} \right)^\beta + \left( \frac{\omega}{\omega_{\max}} \right)^{3\beta} \right]$$

where $M''_{\max}$ gives the maximum value of $M''$, $\omega_{\max}$ is the value of angular frequency at which $M''$ is maximum and $\beta$ ($0<\beta<1$) is the stretched exponent parameter that gives us the deviation from the Debye-type relaxation [33–35]. The fitted data are shown in the inset in Figure 6(e,f). Close agreement between the experimental and theoretical fitting is quite evident. It can be seen that the values of $\beta$ for BCMT sample are smaller as compared to BCT sample. Thus, addition of Mn to BCT imparts more Debye-type behavior to the samples. The values of $\beta$ were also found to be independent of temperature, implying that the distribution of relaxation times is also independent of temperature. This was further confirmed by plotting the normalized plots of $M''/M''_{\max}$ vs. $\ln (\omega/\omega_{\max})$ (shown in Figure 6(e,f)). All the peaks (corresponding to different temperatures) collapse into one master curve indicating that the nature of relaxation and distribution of relaxation times is temperature-independent in both samples [24]. The relaxation time $\tau^M$ can be calculated from $M''$ using the relation $\tau^M = \frac{1}{\omega_{\max}}$. The variation of $\ln \tau^M$ as a function of $1000/T$ shows a linear trend and is well fitted by the Arrhenius relation given as follows:

$$\tau^M = \frac{\omega_{\max}^\beta}{\alpha_0 e(E_{\text{act}}/kT)}$$

where the symbols have their usual meanings. The activation energy $E_{\text{act}}$ calculated by least square fitting is found to be $0.86$ eV and $1.06$ eV for the BCT and BCMT samples, respectively. These activation energy values are almost the same as those calculated from the $Z''$ vs. frequency plots which suggests that the conduction and relaxation processes can both be attributed to the same type of charge carriers. In order to distinguish whether the long-range or short-range movement of charge carriers results in the given relaxation process, the normalized plots of $M''/M''_{\max}$ and $Z''/Z_{\max}$ were plotted against $\ln (\omega/\omega_{\max})$ (shown in
It should be noted that the separation of peaks in these plots indicates that the relaxation process is dominated by short-range movement of charge carriers while the coincidence of peaks indicates long-range moment of charge carriers. In our case, the two plots overlap, hence confirming that long-range conduction is present in both the samples. The activation energy of bulk BaTiO$_3$ is reported to be 0.84 eV [24]. Thus, the addition of Ca and Mn results in an increase in activation energy.

### 3.6. Electrical conductivity formalism

The AC conductivity of these samples was studied to determine their conduction mechanism, the electric conductivity of ceramics is generally explained using (a) quantum mechanical tunneling (QMT), (b) carrier barrier hopping (CBH), c) overlapping large – polaron tunneling (OLPT) and d) non-overlapping small polaron tunneling (NSPT) models [36]. Figure 8(a,b) shows the frequency-dependent AC conductivity at different temperatures for the BCT and BCMT samples, respectively. It is clear that a plateau in the conductivity spectra is reached at lower frequencies, indicating the dominance of the DC conductivity, whereas dispersion is observed in the high-frequency range. It is also observed that both $\sigma_{dc}$ and $\sigma_{ac}$ rise with increase in temperature which again indicates NTCR behavior. The ac conductivity data have been analyzed using Jonscher’s Power law:

$$\sigma_{ac} = \sigma_{dc} + A\omega^n$$

where $\sigma_{dc}$ is DC conductivity and is a frequency-independent term at low frequencies, $\omega$ is angular
frequency, “A” is a temperature-dependent pre-exponential factor (constant) which measures the strength of polarization and “n” is an exponent representing the degree of interaction between the mobile ions in the lattice surrounding [37–39]. The variations in fitting parameter n are shown in Figure 9 for both samples. The figure elucidates that, for both the BCT and BCMT samples, the value of n increases with increase in temperature and is less than 1, implying that the conduction mechanism operating in our samples is non-overlapping small polaron tunneling [40,41].

The activation energy of conduction can be obtained by fitting the ln $\sigma_{dc}$ vs 1000/T Arrhenius equation:

$$\ln \sigma_{dc} = \ln \sigma_o + \frac{E_a}{k_B T}$$

(13)

where the symbols have their usual meaning. The inset in Figure 8(a,b) shows the variations of ln $\sigma_{dc}$ vs (1000/T) as well as of the fitted data. The activation energy was found to be 1.02 eV and 1.14 eV for BCT and BCMT samples, respectively. The higher activation energy in the case of the BCMT sample can be explained as follows: In BCT, high-temperature sintering results in the formation of a large number of conduction electrons along with ionized oxygen vacancies, as follows:

$$O_o \rightarrow 1/2O_2 + V_o + 2e$$

(14)

The equilibrium state of the electron concentration (in BCT) is maintained via almost complete delocalization of these electrons by hopping among titanium sites, resulting in poor electric insulation and dielectric behavior. Mn is an acceptor ion which can exist in three valance states,

Figure 7. Normalized plots of $M''/M_{max}$ and $Z''/Z_{max}$ at different frequencies for (a) BCT and (b) BCMT samples.

Figure 8. Variations in AC conductivity with frequency at different temperatures for (a) BCT and (b) BCMT samples. The inset shows the Arrhenius fit to the $\sigma_{dc}$.

Figure 9. Variations in n obtained from $\sigma_{dc}$ fitting using the Jonscher power law at different temperatures for (a) BCT and (b) BCMT samples.
Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$. The doping of Mn (3+ or 4+) at Ti sites leads to electrons trapping, as they are more reducible than Ti$^{4+}$. Further, the lower concentration of Mn ions restricts the hopping activity of electrons from one Mn/Ti site to another, thereby localizing electrons at these sites [10,42,43]. Also, SEM data have shown that the grain size of BCMT samples is smaller than that of BCT samples. This means that resistive as well as scattering effects of grain boundaries will be more pronounced in BCMT samples. The combination of these two factors leads to a reduction in conductivity (higher activation energy) in Mn-doped BCT ceramics. It has been pointed out in the literature that the activation energy required for singly and doubly ionized oxygen vacancies is in the ranges of 0.3–0.6 eV and 0.7–1.2 eV, respectively [22]. In our samples, the activation energies lie in the latter range, implying the existence of doubly ionized oxygen vacancies in both samples.

4. Conclusions

Ba$_{0.96}$Ca$_{0.04}$TiO$_3$ (BCT) and Ba$_{0.96}$Ca$_{0.04}$Ti$_{0.96}$Mn$_{0.04}$O$_3$ (BCMT) samples were successfully synthesized by the solid-state reaction route. XRD analysis confirmed the presence of a tetragonal phase in both the samples with an additional hexagonal BT phase in the BCMT samples. The decrease in the remnant polarization of the BCMT samples was attributed to lower grain size and the presence of an additional non-ferroelectric hexagonal phase. Complex impedance spectroscopy data showed that the grain boundaries were more resistive than the grains in both the samples. This was explained by the preferential re-oxidation of grain boundaries as compared to grains during sample cooling. The activation energies calculated from $Z''$, $M''$ and AC conductivity data were found to be almost equal implying that the conduction and relaxation processes can both be attributed to the same type of charge carriers. The increase in the value of “n” with increase in temperature suggests that conduction takes place via a small polaron hopping mechanism in both the samples. The higher activation energy of the BCMT samples can be attributed to decreased conductivity in the BCMT samples due to trapped electrons at the Mn sites and small grain size.

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Disclosure statement

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