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Effect of cerium oxide addition on optical, electrical and dielectric characteristics of \((\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\) ceramics

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Abstract
The composite ceramics, \(\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\)\(\times\text{CeO}_2\) \((x = 0, 0.05, 0.10, 0.15)\) with a general chemical composition \((\text{Bi}_{0.5}\text{Na}_{0.5})\text{Ti}_x\text{Ce}^{2-x}\text{O}_3\) were fabricated by using a solid state reaction ceramic technology. The detailed structural analysis using x-ray diffraction data exhibits the formation of composites of \(\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\) (BNT) and \(\text{CeO}_2\) in rhombohedral and cubic phase respectively. The Fourier transform infrared spectroscopy spectrums confirm the formation of compounds through the occurrence of characteristic peak corresponding to Ce–O, Ti–O and Bi–O bonds. With the increase in \(\text{CeO}_2\) content in the composite, the optical band gap decreases from 2.97 eV (for \(x = 0\)) to 2.45 eV for the sample (for \(x = 0.15\)). The impedance analysis confirms the contribution of grains only to the polarization and conduction processes. Two phase change corresponding to ferroelectric to antiferroelectric, and then to the paraelectric is observed at around 350 °C and 470 °C respectively. The addition of \(\text{CeO}_2\) in BNT significantly enhances the dielectric and ferroelectric properties with the decrease in loss tangent.

1. Introduction
The discovery of ferroelectricity in a barium titanate with multiple interesting properties has attracted lots of attention of researchers and industrialists to develop the materials of perovskite oxides with enhanced properties for devices. Lead titanate (\(\text{PbTiO}_3\)) is one such tetragonal perovskite at room temperature having good ferroelectric and piezoelectric properties [1]. It is widely used for piezoelectric, pyroelectric and ferroelectric devices, namely capacitors, transducers, thermistors, optoelectronics, nonvolatile memory FET, infrared imaging, light modulator and switches [2]. But, \(\text{PbTiO}_3\) is highly toxic and harmful for the environment, thus its application in consumer products is declining. In the process of phasing out lead based ferroelectrics, the natural choice for replacement of \(\text{Pb}^{2+}\) ion in \(\text{PbTiO}_3\) (PT) is \(\text{Bi}^{3+}\) owing to the similar electronic configuration of \(4f^{16}5d^{10}6s^2\) with a lone pair of 6S electrons [3]. However, for charge neutralization, the A-site cations need to be shared between the \(\text{Bi}^{3+}\) ions and another monovalent ion on 50–50 basis. Naturally, a \(\text{Na}^+\) ion with an ionic radius of 118 pm is the most suitable for shared occupancy with \(\text{Bi}^{3+}\) ion having almost equal ionic radius of 117 pm [4]. As such, the effort has been channelized to fabricate and study compound like \(\text{Ba}_{0.5}\text{Na}_{0.5}\text{TiO}_3\) (BNT). The \(\text{PbTiO}_3\) with a tolerance factor of 1.019 forms a tetragonal perovskite structure, whereas BNT with a tolerance factor of 0.91 crystallizes in the rhombohedral perovskite structure at room temperature. BNT is found to have strong ferroelectric properties with remanent polarization \((P_r = 38 \mu\text{C cm}^{-2})\) at room temperature and a large dielectric constant in a broad temperature range [5], and is considered as a good replacement for PT. The BNT ceramic has many industrial applications, such as random access memories (RAM), accelerators, filters, transducers, resonators and micro electromechanical systems etc [6]. However, the high conductivity of BNT leading to high leakage current and its high coercive field \((E_c = 73 \text{ KV cm}^{-1})\) puts the limitations on large scale industrial applications. The limitations of the compound can be removed by methods, such as substitution/doping/implanting at the A and/or B sites or fabricating solid solutions and/or composites.
with other materials. Rare-earth oxides are generally harmless and environmentally friendly. Cerium being a rare-earth element in the lanthanide series exists in the free metal or oxide form, and can exchange oxidation states between the cerious-cerium (III) and ceric-cerium (IV). CeO$_2$ is a semiconductor with moderate band gap (3–3.6 eV), high dielectric constant (23–26) and refractive index (2.2–2.8) [7]. As reported, it has multiple applications, such as electrolyte material for solid oxide fuel cells, high-storage capacitor devices, gas sensing, polishing materials, ultraviolet absorbents and optical devices [8–10]. It is expected that the addition of rare-earth oxide in ferroelectric compounds will result in the enhancement of dielectric and ferroelectric properties. Aiming to improve the material properties of BNT, we got motivated to add the rare-earth oxide cerium oxide (CeO$_2$) with BNT. Here, we present the study of structural, optical, electrical and polarization characteristics of the BNT-–xCeO$_2$ (x = 0, 0.05, 0.10, 0.15) composites (BNTC) with a chemical composition of (Bi$_{0.5}$Na$_{0.5}$)$x$(Ti$_{1–x}$Ce$_x$)O$_3$ as synthesized by a solid state reaction method.

2. Experimental

The BNTC composites with a general chemical composition of (Bi$_{0.5}$Na$_{0.5}$)$x$(Ti$_{1–x}$Ce$_x$)O$_3$ for different concentration x (0, 0.05, 0.10, 0.15) were fabricated by taking the high-purity oxides of Bi$_2$O$_3$ (99.0%, Lobachemie), Na$_2$CO$_3$ (99.5%, Central Drug House), CeO$_2$ (99.9%, Lobachemie) and TiO$_2$ (99.5%, Lobachemie) using a solid state reaction technique in an ambient atmosphere. Accordingly, all precursor materials were taken in stoichiometric quantity with a 2% extra Bi$_2$O$_3$ to compensate the bismuth loss at high temperature processing and mixed them thoroughly in an agate mortar by dry grinding mode followed by a wet grinding using methanol for 4 h. Then, the mixtures were calcined at 800 °C for 4 h in a high-purity alumina crucible using high temperature heat furnace. The calcined powder was pressed into a disc in a KBR hydraulic press to get pellet having dimensions of 10 mm diameter and 1–2 mm thickness. Furthermore, these samples were sintered at 800 °C in air for 4 h for the formation of high density materials. For electrical characteristic measurement, the silver paste was applied on both sides of sintered pellet, and heated at 150 °C for 45 min to dry the sample (expel any moisture present). The phase and crystal structure of the calcined powders were examined by x-ray diffractometer (Rigaku Ultima IV) using Cu–Kα radiation. The vibration bands of the compounds were identified by Fourier transform infrared spectroscopy (FTIR) spectroscopy. The optical band gap was calculated by UV–visible spectroscopy (Perkin Elmer Lambda 1050). For measurement of dielectric, impedance and related physical properties, Phase Sensitive Meter (N4L, PSM-1735) was used in a frequency range of 1 kHz–1 MHz at various temperatures. The ferroelectric property was studied by Marine India PE loop tracer.

3. Result and discussion

3.1. Structural analysis

The x-ray diffraction (XRD) patterns of the calcined powders of the BNTC composite ceramics are shown in figure 1. Pure BNT with x = 0, crystallizes in a rhombohedral structure (based on analysis of data using a standard computer software ’Powd Mult’). For x = 0.05, 0.10 and 0.15, the BNTC composites crystallize in a mixed phase with the rhombohedral structure of BNT and the cubic structure of CeO$_2$. The selection of probable cell parameters of composite ceramics (separately for BNT and CeO$_2$) was made on the basis of the best fit (negligibly small difference of experimentally observed and theoretically calculated inter-planar spacing of each reflection) and minimum standard deviation. The lattice parameters of composite ceramics (i.e. BNT and CeO$_2$) were listed in table 1. The characteristic peaks of BNT and cerinitine (CeO$_2$) have also been confirmed from JCPDS file number ICDD-00-036-0340 and ICDD-01-081-0792 respectively. As expected, a small amount of the intermediate phase of Bi$_{14}$Na$_{0.5}$Ti$_{15}$O$_{31}$ (BNT-15) (ICPDS-ICDD-01-074-1318) is found in pure and CeO$_2$ added BNT [11]. The BNT-15 compound is formed as per the chemical equation, 9Bi$_2$O$_3$ + Na$_2$CO$_3$ + 16TiO$_2$ = 4Bi$_{14}$Na$_{0.5}$Ti$_{15}$O$_{31}$ + CO$_2$. The most intense BNT-15 (109) peak at 30.5° bears an intensity ratio of 0:3:1 with that of the intense BNT peak (110) at 32.6°. We have stacked the diffraction pattern of BNT and CeO$_2$ in the XRD spectrum for ready comparison. The crystallite size (p) of the compound is calculated by using Scherrer equation [12]

\[ p = \frac{k \lambda}{\beta \cos \theta} \]

In the above equation, λ is the wavelength of the incident x-ray corresponding to Cu–Kα line, β is the full width at half maxima (FWHM) of the diffraction peak whose Bragg angle is θ; k being an anisotropic constant. The average particle size of the composite ceramics calculated based on few intense peaks is presented in the table 2. The particle size has a general tendency to increase with increase in CeO$_2$ content in the composite.
3.2. Fourier transform infrared spectroscopy (FTIR)

The Fourier transform infrared spectra of the BNTC composites with \(x = 0, 0.05, 0.10, 0.15\) in the wave number range 400–1800 cm\(^{-1}\) are shown in figure 2. Though Ce–O vibration band correspond to 450 cm\(^{-1}\) [13, 14], but in our BNTC composites, multiple peaks are observed in between 440 and 466 cm\(^{-1}\). The composites with cerium oxide content \(x = 0.05\) and 0.10 exhibit a single Ce–O vibration peak at 466 and 441 cm\(^{-1}\) while the composition with \(x = 0.15\) exhibits two bands around 440 and 459 cm\(^{-1}\). This aspect is also reflected in the XRD spectra.

Figure 1. XRD pattern of Bi\(_{0.5}\)Na\(_{0.5}\)TiO\(_3\)–\(x\)CeO\(_2\) composite ceramics \((x = 0, 0.05, 0.10, 0.15)\).

| Composition \((x)\) | Crystal structure | Cell parameters (Å) | Volume (Å\(^3\)) |
|---------------------|-------------------|---------------------|------------------|
| 0                   | Rhombohedral (BNT)| 5.4888 13.4342      | 350.50           |
| 0.05                | Rhombohedral (BNT)| 5.4954 13.4346      | 350.42           |
| 0.10                | Rhombohedral (BNT)| 5.4829 13.4320      | 350.50           |
| 0.15                | Rhombohedral (BNT)| 5.4855 13.5452      | 351.42           |

| Cell parameters (Å)     | Volume (Å\(^3\)) |
|-------------------------|------------------|
| 5.4094 158.29           |                  |
| 5.4113 158.45           |                  |

Table 2. The particle/crystallite size of Bi\(_{0.5}\)Na\(_{0.5}\)TiO\(_3\)–\(x\)CeO\(_2\) composite \((x = 0, 0.05, 0.10, 0.15)\) (# symbol represents CeO\(_2\) peak).

| Composition of \(x\) | Crystallite size (nm) |
|-----------------------|-----------------------|
| 2θ (°)                | 0.00 0.05 0.10 0.15   |
| 22.9                  | 73 64 70 71           |
| 28.6 (#)              | 77 68 66              |
| 32.6                  | 45 47 47 50           |
| 40.2                  | 35 34 38              |
| 46.7                  | 41 43 48              |
| 47.4 (#)              | 45 46 45              |
| Average particle size (nm) | 49 52 51 53          |

The Fourier transform infrared spectra of the BNTC composites with \(x = 0, 0.05, 0.10, 0.15\) in the wave number range 400–1800 cm\(^{-1}\) are shown in figure 2. Though Ce–O vibration band correspond to 450 cm\(^{-1}\) [13, 14], but in our BNTC composites, multiple peaks are observed in between 440 and 466 cm\(^{-1}\). The composites with cerium oxide content \(x = 0.05\) and 0.10 exhibit a single Ce–O vibration peak at 466 and 441 cm\(^{-1}\) while the composition with \(x = 0.15\) exhibits two bands around 440 and 459 cm\(^{-1}\). This aspect is also being reflected in the XRD spectra. The absorption band between 472 and 517 cm\(^{-1}\) in the pure BNT and that between 470 and 850 cm\(^{-1}\) in BNTC composites correspond to the vibration band of Ti–O [15–18]. The absorption band near 933 cm\(^{-1}\) in all the composition of \(x\) corresponds to the Bi–O and/or Bi–O–Bi in [BiO6] octahedral vibration mode [19]. The vibrating band from 1240 to 1800 cm\(^{-1}\) indicates the existence of residual organic compounds in the fabricated powder. The FTIR spectrum of the composite with \(x = 0.10\) seems to be a...
bit flat with asymmetric peak broadening albeit exhibiting all the peaks corresponding to the bonds as depicted for the composites with $x = 0.05$ and $0.15$. To make this point more clear we have presented the FTIR spectra for all the compositions separately in figure 2 including $x = 0.10$ with higher resolution. It is worth pointing out here that the particle size of the composite for $x = 0.10$ is comparatively less than that of the composition with $x = 0.05$ and $0.15$, that could be a reason for difference in pattern. The broadening of the peaks may be from the impact of the other scenario like induced electronic, spatial (in a plane or out of plane vibrations) or entropy-related effect.

3.3. Ultraviolet–visible absorption spectroscopy
The UV–vis absorbance spectrum of the synthesized BNTC composites is shown in figure 3. The optical band gap of the composites is calculated from the absorbance versus wavelength plot. The cutoff wavelength of the compounds was estimated by extrapolating the linear portion of the curve. All the composites exhibit a strong absorption in between 417 and 506 nm. In BNT, the cut off wavelength is found to be 417 nm corresponding to the optical band gap energy ($E_g$) of 2.97 eV. The value of $E_g$ obtained for pure BNT tallies with that reported earlier [20]. With the increase in the addition of cerium oxide, the $E_g$ of the composites changes to 2.49, 2.56 and 2.45 eV for $x = 0.05, 0.10$ and $0.15$ respectively. Broadly, our results indicate a decrease in the optical energy.
band gap with an increase of CeO₂ in the composite. Further, with increase in \( x \), the particle size increases and this aspect in the nanometric range has also a bearing on the band gap which decreases with increase in particle size \([21–23]\). The relatively larger particles cause a broadening of energy band, as a result the band gap (i.e., the energy gap) between the highest occupied molecular orbital in the valence band to the lowest unoccupied molecular orbital in the conduction band gets decreased. The slightly higher value of the band gap for \( x = 0.10 \) with respect to that of 0.05 and 0.15 is most likely due to the relatively lower particle size of the BNTC composite (i.e. \( x = 0.10 \)) as compared to that of the other two compositions.

### 3.4. Impedance spectroscopy

For the electrical characterization of the composites, we resort to the impedance measurement. The experimental measurements have been done in a wide range of frequencies (1 kHz–1 MHz) and temperature (25 °C–400 °C). The analysis of the impedance data, \( Z = Z' + jZ'' \), is helpful in understanding the kinetics of bound and mobile charges in the bulk and interfacial parts and also the relaxation mechanism present in the system \([24]\). In figure 4, for all the composition of \( x \), \( Z' \) exhibits the normal behavior, i.e. it decreases with increase in frequency and becomes negligibly small beyond 100 kHz. Figure 4 indicates that for the samples with composition \( x = 0.05 \) and 0.10, the composite exhibits PTCR behavior above 100 °C, and for the samples with \( x = 0 \) and 0.15, this behavior is found to start from 150 °C \([25]\). Further, with an increase in frequency the temperature at which the PTCR behavior sets in shifts to higher temperature. The PTCR behavior implies a decrease in mobility/hopping probability of the ions with increase in temperature.

In figure 5, the variation of \( Z'' \) with frequency plots exhibits almost similar monotonically decreasing variation up to a certain frequency limit (100 kHz), above that they merge together and shows the frequency independent nature for all the temperatures in our experimental range.

For the samples with composition \( x = 0 \) and 0.15, \( Z'' \) increases from room temperature to 50 °C, and then decreases with increase in temperature. For the other two compositions (i.e., \( x = 0.05 \) and 0.10), \( Z'' \) increases from room temperature to 100 °C, and then decreases with increase in temperature. The relaxation in the
ceramic compound is most likely associated with the immobile defects and orientation effects of relaxation species [26]. For ready reference we provide in table 3 the values of $Z'$ and $Z''$ at room temperature corresponding to the three frequencies.

3.4.1. Nyquist plot

Figure 6 represents $Z'$ versus $Z''$ (Nyquist plot) of BNTC composite ceramics for the compositions with $x = 0, 0.05, 0.10, 0.15$. The complex impedance plots are analyzed for determining the contribution from grain, grain boundary and electrode interface effect to the polarization. Each effect is characterized by a semicircular curve in the $Z'$ versus $Z''$ plot and is modeled by an equivalent circuit of resistance and capacitance. The complete network is taken as the series combination of the RC networks corresponding to the three different contributions. The relaxation mechanism can be identified by the nature of the curve. The semicircle curve with a center on the real $Z'$-axis indicates the ideal Debye type relaxation, which is the characteristic of an ideal material with grain homogeneity. But in ceramic materials with an inhomogeneity in the grain size and due to electromagnetic diffusion [27, 28], semicircles get depressed and tilted to the real axis indicating the distribution of relaxation time [29]. Figure 6(a) represents the $Z'$ versus $Z''$ plot for different compositions of $x$ at 350 °C. The fitting of the plots have been done by using Zsimpwin Software. The corresponding semicircular curves are drawn by considering three pairs of $Z'$ and $Z''$ from experiment data and fitted with a circle equation [30]. The fitting process was repeated many times till the experiment data fit well with the depressed semicircle. It was observed that impedance plots for all compositions were made of single depressed semicircle curve suggesting the contribution of only grains to the polarization process and the grain effect can be modeled through a single parallel R and C network with a constant phase element Q, i.e. RQC circuit. The Q (constant phase element/ CPE) indicates a divergence from the ideal Debye type behavior. The values of the grain resistance ($R_g$) and grain capacitance ($C_g$) obtained from the Zsimpwin software for all the compositions match well with those obtained from semicircular curve fitting. The values of $R_g$, $C_g$ and depression angle ($\theta_g$) for all the compositions at 350 °C are listed in table 4.

![Figure 5. Variation of $Z'$ with frequency of Bi$_{0.5}$Na$_{0.5}$TiO$_3$–xCeO$_2$ composite ceramics ($x = 0, 0.05, 0.10, 0.15$) at some selected temperatures.](image)

**Table 3.** Comparison of the value of $Z'$ and $Z''$ of Bi$_{0.5}$Na$_{0.5}$TiO$_3$–xCeO$_2$ composite.

| Composition ($x$) | $Z'$ 1 kHz | $Z'$ 10 kHz | $Z'$ 100 kHz | $Z''$ 1 kHz | $Z''$ 10 kHz | $Z''$ 100 kHz |
|------------------|----------|-----------|------------|----------|-----------|------------|
| 0                | 142 229  | 13 067    | 944        | 572 466  | 73 635    | 9371       |
| 0.05             | 169 130  | 13 026    | 754        | 720 022  | 93 040    | 10 884     |
| 0.10             | 230 674  | 8889      | 461        | 874 725  | 105 767   | 11 369     |
| 0.15             | 76 499   | 6976      | 497        | 830 624  | 91 738    | 10 201     |

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Table 3. Comparison of the value of $Z'$ and $Z''$ of Bi$_{0.5}$Na$_{0.5}$TiO$_3$–xCeO$_2$ composite.
Figure 6. Nyquist plot of Bi$_{0.5}$Na$_{0.5}$TiO$_3$–xCeO$_2$ composite ceramics ($x = 0, 0.05, 0.10, 0.15$) compound and part (a) graph represents $Z'$ versus $Z''$ with red fitting line at 350 °C temperature.

Table 4. Value of $R_g$, $C_g$ and $\theta_g$ of Bi$_{0.5}$Na$_{0.5}$TiO$_3$–xCeO$_2$ composites at 350 °C.

| Composition (x) | $R_g$ (kΩ) | $C_g$ (pF) | $\theta_g$        |
|----------------|------------|------------|-------------------|
| 0              | 730        | 44.2       | 14.74°            |
| 0.05           | 435        | 151        | 12.76°            |
| 0.10           | 432        | 112.5      | 12.43°            |
| 0.15           | 370        | 169.7      | 14.85°            |
3.4.2. Cole–Cole plot

The Cole–Cole plot refers to the complex dielectric plot of the samples obtained from the impedance/admittance data. In the samples, whose Nyquist plots consist of a single semicircular curve representing the grain effect only and being modeled through a single parallel RQG circuit, the admittance appears as;

\[ Y(\omega) = Y'(\omega) + jY''(\omega) = (\omega C'' + G_{dc}) + j\omega C', \]

where, \( G_{dc} \) is the conductance of the sample and can be obtained from the experimental data as the intercept of \( Y^* \sim \omega \) graph. After determination of \( G_{dc} \), the relative permittivity \( \varepsilon'_r \) and \( \varepsilon''_r \) can be obtained as

\[ \varepsilon'_r = \varepsilon''_r = \frac{Y'}{\omega C_0} \quad \text{and} \quad \varepsilon''_r = \frac{Y'' - G_{dc}}{\omega C_0}, \]

where \( C_0 = \frac{\rho}{d} \) (A and \( d \) are the area and thickness of the composites)

At 25 °C, for the compositions \( x = 0, 0.05, 0.10, 0.15 \), the \( G_{dc} \) values obtained from the intercept of \( Y' \sim \omega \) graph amounts to 1.7632 \( \times 10^{-7} \), 1.3872 \( \times 10^{-7} \), 1.9953 \( \times 10^{-7} \) and 3.42303 \( \times 10^{-8} \) \( \Omega^{-1} \) respectively. The \( \varepsilon'_r \) and \( \varepsilon''_r \) obtained on the basis of equation (2) from the experimental data are graphically presented as Cole–Cole plots (in figure 7(i)) for all the samples at the room temperature of 25 °C. The Cole–Cole plots for all the samples exhibit a single semicircle and tilted below the real axis by an angle \( \theta \). The tilt angle \( \theta \) is related to the relaxation distribution function \( \beta \) through the relation \( \beta = 1 - \frac{2\theta}{\pi} \). The complex dielectric constant and its real and imaginary components for such a plot appear as [31, 32]:

\[ \varepsilon'_r(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_{ss} - \varepsilon_{\infty}}{1 + (i\omega \tau)^{\beta}} \]

\[ \varepsilon''_r(\omega) = \varepsilon_{\infty} + \frac{(\varepsilon_{ss} - \varepsilon_{\infty}) \left[ 1 + (i\omega \tau)^{\beta} \cos \left( \frac{\beta \pi}{2} \right) \right]}{1 + 2(i\omega \tau)^{\beta} \cos \left( \frac{\beta \pi}{2} \right) + (i\omega \tau)^{2\beta}}, \]

\[ \varepsilon''_r(\omega) = \frac{(\varepsilon_{ss} - \varepsilon_{\infty}) \left( \omega \tau \right)^{\beta} \sin \left( \frac{\beta \pi}{2} \right)}{1 + 2(i\omega \tau)^{\beta} \cos \left( \frac{\beta \pi}{2} \right) + (i\omega \tau)^{2\beta}}, \]

where \( \varepsilon_{ss} \) and \( \varepsilon_{\infty} \) are the static dielectric constant and the dielectric constant at an infinitely high frequency respectively \( \omega \) is the angular frequency and \( \tau \) is the characteristic time constant. The relaxation distribution function \( \beta = 1 \), corresponds to a perfect semicircular Cole–Cole plot with the center of the circle on the real axis and identify with perfect Debye type relaxation. The relaxation time, \( \tau \) is equal to the inverse of angular frequency corresponding to the peak of the semicircular arc, \( \omega_p \). For \( x = 0 \) the relaxation time as obtained from the Cole–Cole plot amounts to 4.9306 \( \times 10^{-3} \) s. The value broadly agrees with the value of the product \( R_{dc}C_{gg} \) obtained in the corresponding Nyquist plot. The value of \( \varepsilon_{\infty}, \varepsilon_{ss} \) and \( \beta \) obtained from figure 7 are listed in table 5 for all the compositions.

The experimental data and the data computed for \( \varepsilon'_r(\omega) \) and \( \varepsilon''_r(\omega) \) on the basis of the model equations (4) and (5) for the composition \( x = 0 \) at room temperature is presented in figure 7(ii)-(a). The experimental data of \( \varepsilon'_r(\omega) \) and \( \varepsilon''_r(\omega) \) match very well with the computed data obtained through the equations (4) and (5) respectively. Further, the loss tangent consists of two components and appears as [33]

\[ \tan \delta = \frac{\varepsilon''_r}{\varepsilon'_r} + \frac{\varepsilon_{dc}}{\omega C_0 \varepsilon'_r}. \]

The first term represents from Debye type dipolar relaxation while the second term is the contribution from DC conductivity based loss. While the Debye relaxation mechanism is identified by a Gaussian peak in the loss tangent, the conductivity based loss is dominant at lower frequency and high temperature.

To understand the contribution of both the mechanisms to the loss tangent, in figure 7(ii)-(b) we have plotted the Debye contribution, conductivity based contribution and \( \tan \delta \) computed on the basis of equation (6) using the parameters obtained from the Cole–Cole plot and compared with the experimental data for the composition \( x = 0 \) and temperature of 25 °C. It is seen that the computed values of \( \tan \delta \) matches quite well with the experimental data. For the sample, though the Debye mechanism has its peak around 20 kHz, the conductivity driven losses screen the peak and the \( \tan \delta \) curve appears as if it decreases continuously with frequency. The matching of the computed data with that of the experimental data in figure 7(ii)-(a) and (b) confirms the Cole–Cole plot drawn in figure 7(i) and validity of the parameters \( \varepsilon_{\infty}, \varepsilon_{ss}, \beta \) and \( \tau \) obtained from the plot.
Figure 7. (i) Cole–Cole plot of Bi$_{0.5}$Na$_{0.5}$TiO$_3$–xCeO$_2$ composite ceramics ($x = 0, 0.05, 0.10, 0.15$) at 25 °C. (ii) (a) Variation of $\varepsilon'_r$ and $\varepsilon''_r$ with frequency and red line represents theoretical fitting, (b) variation of $\tan\delta$ with frequency and theoretical fitting with experimental data, at 25 °C for $x = 0$.

Table 5. Comparison of $\varepsilon_{\infty}$, $\varepsilon_r$, and $\beta$ of all the samples Bi$_{0.5}$Na$_{0.5}$TiO$_3$–xCeO$_2$ at 25 °C.

| Composition ($x$) | $\varepsilon_{\infty}$ | $\varepsilon_r$ | $\beta$ |
|-------------------|-------------------------|-----------------|--------|
| 0                 | 309.48                  | 620.22          | 0.52   |
| 0.05              | 285.60                  | 724.54          | 0.44   |
| 0.10              | 313.00                  | 586.66          | 0.34   |
| 0.15              | 202.52                  | 363.28          | 0.55   |
3.5. Dielectric analysis
3.5.1. Temperature dependent dielectric characteristics

The variation of dielectric constant ($\varepsilon_r$) and dielectric loss with temperature for various compositions of the BNTC composites at some selected frequencies are shown in figures 8 and 9. In pure BNT ceramic (i.e., $x = 0$), $\varepsilon_r$ exhibits two peaks. While, the temperature corresponding to the first peak decreases with increase in frequency (398 °C at 1 kHz to 303 °C at 1 MHz) and that of second peak shifts to the right with increase in frequency (438 °C at 1 kHz to 528 °C at 1 MHz). With an increase in $x$, the first peak in the ceramic composites occurs between 358 °C and 449 °C while the second peak is observed between 507 °C and 576 °C. The dielectric peak at the lower temperature corresponds to the ferroelectric–antiferroelectric transition and that at the relatively higher temperature to the antiferro–paraelectric transition. It is worth mentioning here that the phase transition in pure BNT occurs at around 200 °C and 330 °C respectively. Further, it has been reported that in the composite ceramics of BNT and BNT-15, the transition temperature increases with increase in % of BNT-15 in the compound. For example, in the presence of more than 50% of BNT-15 in the compound the second dielectric peak i.e. peak corresponding to antiferroelectric to paraelectric transition was reported in the range of 650 °C–660 °C [35]. Hence, the volume fraction of BNT-15 in composite ceramics estimates the characteristics of dielectric curves. As in our samples a smaller percentage of BNT-15 is present along with BNT, the observed transition temperature is somewhat higher to that reported for the BNT ceramics. Although the dielectric constant decreases for $x = 0.05$, it increases with an increase in the cerium oxide content from $x = 0.05$ to 0.15 at all the temperatures.

The loss tangent $\tan \delta$ is very low up to 200 °C in all the studied composites for the entire frequency range. Above this temperature, $\tan \delta$ increases with increasing temperature, it is due to rise in conductivity and the increases are more pronounced at low frequencies. The loss tangent decreases with an increase in the cerium oxide content.
3.5.2. Frequency dependent dielectric properties

The frequency (1 kHz–1 MHz) dependence of $\varepsilon'_r$ and $\tan \delta$ for the BNTC composites at some selected temperatures (25 °C–400 °C) is shown in figures 10 and 11. In the experimental frequency range of 1 kHz–1 MHz, the variation in the dielectric constant is mainly due to space charge polarization. The other components of polarizations like electronic, ionic and dipolar polarization are not being affected by frequency variation in the experimental frequency range. At higher temperature, the activation and blocking of the defect ions and oxygen vacancies in the grain and grain boundary results the high value of dielectric constant.

However, in our samples, the Nyquist plots in figure 6 exhibit a single semicircle indicating the absence of grain boundary effect. The short circuiting of the grain boundary impedance is most probably has its origin in good inter granular contact over substantial regions of grain boundaries in the sample resulting in the blockage of the hopping/mobile ions in the grain causing granular polarization only. With an increase in frequency, these
mobile ions due to inertia unable to follow the field variations and thus the dielectric constant decrease with increase in frequency for all the samples and in the entire temperature range [36]. With increase in temperature, the dielectric constant increases due to thermal activation of defects//oxygen vacancy resulting in increase in the mobile ions and their blockage in the grain. A small anomaly or a change in slope can be observed in figure 10 at around the frequency of 10 kHz at low temperature which shifts right with increase in temperature. This change in slope indicates an additional polarization mechanism, may be the onset of a small grain boundary contribution.

As can be seen in figure 11, the loss tangent exhibits a relaxation peak at frequency $\omega = \omega_p$, representing some sort of Debye type relaxation. The peak frequency $\omega_p$ increases with increase in temperature indicating a somewhat relaxor behavior. At low frequency and high temperature, the increase in $\tan \delta$ is mainly due to conductivity based loss and represented through the second term $[\sigma_d/\omega e_0 e_t']$ in equation (6). Up to 200 °C, the cerium oxide added compounds have lower loss tangent compared to that of the BNT sample.

3.6. Ferroelectric property

Figure 12 shows the $P–E$ hysteresis loops of BNT ceramic along with different $x$-component of cerium oxide at room temperature. As the applied field in our experimental setup is only 18 kV cm $^{-1}$, we could not obtain a saturated $P–E$ loop. However, the loops exhibit the ferroelectric nature of the composites. Cerium oxide added samples exhibit better ferroelectric properties with higher remanent polarization and higher coercive field. The remanent polarization of the samples with $x = 0.05–0.15$ increases up to 0.07 $\mu$C cm $^{-2}$ improved from the corresponding value of 0.02 $\mu$C cm $^{-2}$ of the pure BNT sample. The coercive field and area under the loop (hysteresis loss) also increase with increase in cerium oxide content in the composite.

For complete reference we provide in table 6 the values of $e_t'$, $\tan \delta$ and $P_t$ of Bi0.5Na0.5TiO3–$x$CeO2 composites at 25 °C corresponding to the three frequencies.
Figure 11. Variation of loss tangent ($\tan \delta$) with frequency at different temperatures of Bi$_{0.5}$Na$_{0.5}$TiO$_3$--$x$CeO$_2$ composite ceramics ($x = 0, 0.05, 0.10, 0.15$).

Figure 12. Variation of polarization with electric field of Bi$_{0.5}$Na$_{0.5}$TiO$_3$--$x$CeO$_2$ composite ceramics ($x = 0, 0.05, 0.10, 0.15$).
3.7. Ac conductivity study

The ac conductivity ($\sigma_{ac}$) of the composites were determined by the relation, $\sigma_{ac} = \omega \varepsilon_0 \varepsilon''_r \tan \delta = \sigma_d + \omega \varepsilon_0 \varepsilon''_r$, where all the physical parameters have the usual meaning. The graphical image of $\sigma_{ac}$ versus $1000/T$ in a wide range of frequency ($1 \text{ kHz} – 1 \text{ MHz}$) is shown in figure 13. The dc conductivity term dominates at low frequency and is larger at higher temperature. As such, for low frequency, $\sigma_{ac}$ exhibits as a steep slope. With the increase in frequency $\omega \varepsilon_0 \varepsilon''_r$ term dominates the ac conductivity and the graphs look bit shallow with lower activation energy. The variation of $\sigma_{ac}$ with absolute temperature can be explained by the Arrhenius equation [37]

$$\sigma_{ac} = \sigma_0 \exp \left( -\frac{E_a}{K_B T} \right)$$

In the above equation of ac conductivity, $\sigma_0$, $K_B$ and $E_a$ represent the pre-exponential factor, Boltzmann constant and activation energy respectively. The value of $E_a$ is figured out from the linear fitting of $\ln \sigma_{ac}$ versus

| Composition (x) | $\varepsilon'_r$ | $\tan \delta$ | $\delta$ | $\varepsilon''_r$ | $P_r$ |
|-----------------|-----------------|---------------|----------|-----------------|-------|
| 0               | 553             | 0.25          | 0.02     | 355             | 0.14  |
| 0.05            | 452             | 0.23          | 0.07     | 362             | 0.14  |
| 0.10            | 410             | 0.26          | 0.04     | 360             | 0.08  |
| 0.15            | 340             | 0.09          | 0.04     | 309             | 0.07  |

Figure 13. Variation of $\sigma_{ac}$ with 1000/T at different frequencies of Bi$_{0.5}$Na$_{0.5}$TiO$_3$−xCeO$_2$ composite ceramics (x = 0, 0.05, 0.10, 0.15).

Table 6. Comparison values of $\varepsilon'_r$, $\tan \delta$ and $P_r$ of Bi$_{0.5}$Na$_{0.5}$TiO$_3$−xCeO$_2$ composites at 25 °C.
In Figure 13, for $x = 0$, the calculated activation energy was found to reduce from 0.936 eV at 1 kHz to 0.429 eV at 1 MHz in the high temperature region. For cerium oxide added ceramics, the calculated value of $E_a$ also reduces as frequency increases for both high as well as low temperature regions. For example, the activation energy for $x = 0.05$ is 1.203 eV at 1 kHz, which reduces to 0.47 eV at 1 MHz. The activation energy of cerium oxide added BNT ceramics are more than 1 eV at low frequency and high temperature. In the conduction process, the activation energy accounts for the activation of the charge carriers and the free energy for hopping of the charge carrier over long distances. The activation energy for the oxygen vacancy was reported to be 0.83 eV for bismuth iron niobate \[38\]. Thus, it can be predicted that the charge carriers involved in the activation energy in our sample are produced through the activation of oxygen vacancies \[39\].

In Figure 13, the conductivity first decreases with increase in temperature, this indicates the PTCR behavior. Further the value of $\log \sigma_a$ increases with respect to increasing temperature and exhibits NTCR behavior. In the low temperature region the collision effect dominates over the activation of charge carriers, while in the high temperature region the creation of oxygen vacancy for that matter and the number of ions participating in the hopping process dominates over the collision effect.

### 3.8. Electric modulus analysis

The electric characteristics like grain boundary, conduction effect, bulk properties, electrical conductivity and relaxation time can easily be explained by the analysis of electric modulus \[40, 41\]. The complex electric modulus ($M$) can be obtained from the complex impedance data using the relation $M = M' + jM''$, where $M' = (-1) \omega C_0 Z''$ and $M'' = \omega C_0 Z'$ ($C_0$ is the geometrical capacitance, $\varepsilon_0 A / d$).

For all the compositions, the value of $M'$ in the lower frequency region tends to zero value and it increases with increase in frequency and gets saturated at higher frequency. This analysis of Figure 14 indicates that with a rise in frequency, each ion gets a very short movement in the electric field until the change of electric field

![Figure 14: Variation of $M'$ with frequency at different temperatures of Bi$_{0.5}$Na$_{0.5}$TiO$_3$–xCeO$_2$ composite ceramics ($x = 0, 0.05, 0.10, 0.15$).](image-url)
become so fast that the ions only vibrate within the confinement of their potential energy wells \[42\]. The flat region or its tendency found at high frequency implies the insensitivity of the compounds to electric field at high frequencies. The value of \(\varepsilon''\) in the cerium oxide added BNT is found to be slightly higher than that of the BNT.

The variation of \(\varepsilon''\) (imaginary component of electric modulus) of the BNTC composites with frequency at some selected temperatures is presented in Figure 15. In all the samples including that of pure BNT, a peak is observed in the \(\varepsilon''\) curve, which shifts to a higher frequency with rise in temperature indicating some sort of relaxor behavior and thermally activated relaxation mechanism. Further, this relaxation peak owes its origin to the confinement of the ions in their potential well. We have also observed a low frequency peak in the cerium oxide added samples at high temperatures of 350 °C–400 °C. The low frequency peak suggests long distance ion movement. From, the peak position, it can be said that the transition from long to short range mobility occur with a rise in frequency \[43\]. The asymmetry in peaks, especially in cerium added samples imply a distribution in the relaxation time leading to non-Debye relaxation mechanism in the composites. A similar phenomenon has also found in the modulus spectra of real ionic conductors \[44, 45\].

4. Conclusion

The Bi\(_{0.5}\)Na\(_{0.5}\)TiO\(_3\)−\(x\)CeO\(_2\) composites \((x = 0, 0.05, 0.10, 0.15)\) were fabricated by a solid state reaction technique at the sintering temperature of 800 °C. From the XRD analysis, it was found that the samples have a rhombohedral structure of BNT and cubic structure of cerium oxide with trace of BNT15. FTIR spectroscopy had confirmed the presence of Bi–O, Ti–O and Ce–O band. From the UV–visible spectroscopy, we found that the band gap decreases with the addition of cerium oxide contents in BNTC composites. The Nyquist plots exhibit a single tilted semicircle, indicating the contribution from grain effect only to the polarization mechanism and the presence of a modified Debye relaxation mechanism. The impedance and modulus analysis

![Figure 15. Variation of \(\varepsilon''\) with frequency at different temperatures of Bi\(_{0.5}\)Na\(_{0.5}\)TiO\(_3\)−\(x\)CeO\(_2\) composite ceramics \((x = 0, 0.05, 0.10, 0.15)\).](image-url)
also favor the existence of the non-Debye type of relaxation mechanism in the composite ceramics. The Cole–Cole plots provide the values of static and infinitely high frequency dielectric constant and the characteristic relaxation time. A low temperature transition from the ferroelectric to antiferroelectric and high temperature phase transition from the antiferroelectric to paraelectric is observed in the dielectric versus temperature graphs. The addition of cerium oxide enhances the dielectric properties, strengthens ferroelectric properties in BNT and decreases the loss tangent value in comparison to pure BNT. The loss tangent variation with frequency shows relaxor properties. Though the loss tangent exhibits the Debye type and conduction based losses, at low frequency the conductivity component screens the loss due to Debye relaxation.

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