Room temperature magneto-dielectric coupling in the CaMnO$_3$ modified NBT lead-free ceramics

Koyal Suman Samantaray$^1$ · Ruhul Amin$^1$ · Saniya Ayaz$^2$ · A. K. Pathak$^{3,4}$ · Christopher Hanley$^3$ · A. Mekki$^{5,6}$ · K. Harrabi$^{5,6}$ · Somaditya Sen$^1$

Received: 27 December 2022 / Accepted: 16 February 2023 / Published online: 3 March 2023
© The Author(s), under exclusive licence to Springer-Verlag GmbH, DE part of Springer Nature 2023

Abstract

The sol–gel prepared $(1-x)$Na$_{0.5}$Bi$_{0.5}$TiO$_3$-$(x)$CaMnO$_3$ ($x=0$, 0.03, 0.06, 0.12) compositions show a Rhombohedral ($R3c$) phase up to $x=0.06$ while a mixed rhombohedral ($R3c$) and orthorhombic ($Pnma$) phases for the $x=0.12$. The lattice volume consistently decreased with an increase in the CaMnO$_3$ content. The phase transition temperature ($T_c$) decreased with an increase in the CaMnO$_3$ compositions. The room temperature dielectric constant increased, and loss decreased for the $x=0.03$ composition due to a decrease in the oxygen vacancy and Bi loss confirmed by the valence state study (XPS). All the compositions show a variation of the room temperature dielectric property with an application of magnetic field confirming a magnetodielectric coupling. The $x=0.06$ composition shows the highest negative magnetodielectric coupling constant (MD$\%$) of 3.69 at 100 kHz at an applied field of 5 kG.

Keywords Lead-free materials · Room temperature magnetodielectric · Magnetism · Dielectric · Sol–gel

1 Introduction

The tuning of dielectric properties with magnetic fields is one of the most trending research problems in the current scenario. The presence of magnetoelectric (ME) coupling improves the functionality of the materials, making it one of the promising candidates for various device applications such as sensors, four-state logic in one device, spintronics, FeRAMs, MRAMs, etc. [1, 2]. Such magnetoelectric coupling is best observed in the multiferroics that simultaneously show different ferroic orders such as ferroelectricity, ferromagnetism, antiferromagnetism, etc. [3, 4]. The ferroelectric materials can be modified by introducing magnetism to them, which leads to a magnetoelectric coupling in the engineered materials [5, 6]. However, the single-phase multiferroic materials are rare, as it requires the coexistence of two mutually exclusive phenomena, i.e., cation off-centering in ferroelectrics (which originates due to the d$^0$ orbitals) and the formation of magnetic moments (which develops due to the partially filled d or f orbitals) [7, 8]. The magnetism can be introduced in a ferroelectric material due to the incorporation of (i) magnetic ions, (ii) self-defects such as cationic and oxygen vacancy, (iii) surface defects, (iv) magnetic clusters, and (v) lattice strain [9–11]. Such effects develop the coupling of the magnetic and ferroelectric orders by efficiently controlling the magnetic domains by applying an electric field [12].

Among various lead-free materials, Na$_{0.5}$Bi$_{0.5}$TiO$_3$ (NBT) is one of the best choices for producing magnetoelectric coupling [13, 14]. It shows a high dielectric constant ($\varepsilon_r \sim 800$), strong ferroelectric polarization ($P_r \sim 38 \mu$C cm$^{-2}$), high Curie temperature ($T_c \sim 320 \ ^\circ$C), and high piezoelectric coefficient ($d_{33} \sim 58–95$ pC/N) [15, 16]. The report by Ruth et al. discussed the presence of ferromagnetism in the NBT at a magnetic field lower than 800 Oe [17]. This...
phenomenon was related to the presence of Na-vacancy in the samples. The observance of a high ME coupling coefficient of 4.18 mV/cm Oe observed at zero DC magnetic bias field was reported. Another report by Ju et al. shows a giant room temperature magneto-dielectric constant ($MD\%$) of 9.48% at 1 kHz under $H = 8$ kOe [18]. This was attributed to the ferromagnetism originating from the Na-vacancy at the NBT (100) surface. Apart from these self-defects, magnetism was also achieved by the incorporation of various elements like Fe, Mn, Ni, Co, and Cu and by forming solid solutions of NBT with Bi ($Ti_{1/2}Co_{1/2}$) O$_3$, SrCoO$_{3-δ}$, CoTiO$_3$, and MgCoO$_{3-δ}$, etc. [10, 14, 19–21].

Bulk CaMnO$_3$ (CMO) is an exciting material due to its room temperature antiferromagnetic and paraelectric properties [22]. But several reports have proved the possibility of room temperature multiferroicity in CMO by doing strain and chemical engineering [23]. One report by Dung et al.; reported the presence of ferromagnetism in the solid solution of (1-x) NBT-x CMO [24]. Their article has discussed the optical and magnetic properties of the series up to 9% substitution only. However, a complete discussion on the structure correlation, Morphotropic Phase Boundary (MPB), dielectric, and magneto-dielectric coupling of these series of materials were not provided.

In the present work, a series of (1-x) NBT-x CMO $(x=0, 0.03, 0.06, 0.12)$ compositions are critically analyzed from the structural/vibrational studies point of view using XRD and Raman studies, with support from a valence state study using XPS technique. The presence of an MPB region is also investigated in detail in this series of compositions. The effect of these factors on the dielectric properties are discussed. The shifting of phase transition temperature ($T_c$) obtained from the temperature-dependent dielectric study with the incorporation of CMO is also elaborately discussed. Further magnetism is explored, and the effect of the magnetic field on the dielectric properties is also investigated. The coupling of dielectric polarization with magnetic field and the possibility of magnetoelectricity at room temperature is detailed.

2 Methodology

(1-x) Na$_{0.5}$Bi$_{0.5}$TiO$_{3-x}$CaMnO$_3$ $(x=0, 0.03, 0.06, 0.12)$ polycrystalline powders, were synthesized using modified sol–gel technique. Our previous work also mentioned a similar synthesis route [25]. For this process sodium nitrate (purity 99.9%) for Na, bismuth nitrate pentahydrate (purity 98%) for Bi, Calcium nitrate (purity 99.9%) for Ca, dihydroxy bis (ammonium lactate) titanium (IV), 50% w/w aqua solution (purity 99.9%) for Ti, Manganese nitrate (purity 99.9%) for Mn were used as precursors. All the above-mentioned precursor materials were purchased from Alfa Aesar. The above listed precursors were soluble in de-ionized (DI) water. Hence the solutions of the individual precursors were mixed in the DI water to get a clear solution which was further stirred continuously for an hour. The citric acid and ethylene glycol were then mixed in the molar ratio of 1:1 and added to the precursor solution. The final mixture was stirred and maintained at ~80 °C until a clear gel started to form. The burnt gel powders were ground carefully and heated at 450 °C for 12 h for decarburization and denitrification and further annealed at 750 °C for phase formation.

The phase was verified from X-ray diffraction (XRD) using an X-ray diffractometer (Bruker D2-Phaser). All the physical properties reported in this work will be on these sintered samples prepared at 1100–1130°C for 3 h. The XRD pattern of all the samples was refined using Rietveld refinement. The refinement was done using the FullProf suite software considering pseudo-Voigt peak shape for all the samples.

The chemical composition and the valence states of the elements present in the prepared samples were studied using the X-ray Photoelectron Spectroscopy (XPS) experiment performed using the Thermo-Scientific Escalab 250 Xi XPS Spectrometer (Al-K$_α$ X-rays) having an energy resolution of ~0.5 eV. The spectra were deconvoluted using XPSPEAK41 software. The XPS spectra were initially calibrated using the adventitious C1s peak at a binding energy of 284.8 eV. The background was extracted correctly using the Tougaard function. A combined Gaussian–Lorentzian peak shape was used for all the peaks to get quality fitting.

Room temperature phonon modes were studied from Raman spectroscopy using Horiba-made LabRAM HR Evolution Raman spectrometer (spectral resolution 0.9 cm$^{-1}$) having He–Ne LASER of wavelength 632.8 nm. The electrical characterization for all the samples was done on the sintered pellets of the final phase polycrystals. The silver electrodes were prepared on both sides of the pellets for dielectric measurement using silver paste. After that the pellets were annealed for proper adhesion of the Ag to the pellets at 540 °C for 15 min.

The morphological studies of the sintered pellet samples were done using a Supra55 Zeiss Field Emission Scanning Electron Microscope (FE-SEM). The elemental composition was recorded using the Oxford AZTec X-Max dispersive X-ray spectrometer.

The dielectric measurement was done using a broadband dielectric spectrometer using Newton’s 4th Ltd. phase-sensitive multimeter having signal strength 1 $V_{rms}$ in the temperature range 50–450 °C and frequency range 1 Hz–1 MHz.

The magnetic properties were performed in a Physical Property Measurement System (PPMS, Quantum Design) using a vibrating sample magnetometer (VSM).

The magnetodielectric measurement was carried out using the electromagnet connected to a current source and
digital gauss meter (SES Instruments Pvt. Ltd.). The corresponding room temperature dielectric was measured using the Newton’s 4th Ltd. phase-sensitive multimeter having signal strength 1 V$_{\text{rms}}$.

3 Results and discussions

3.1 X-ray diffraction

The phase of the (1-x) Na$_{0.5}$Bi$_{0.5}$TiO$_3$-(x)CaMnO$_3$ solid solution with x = 0.6 was observed to be in the rhombohedral (R3c) phase. For higher values of substitution, i.e., for x = 0.12 a mixed phase of Rhombohedral (R3c) and orthorhombic (Pnma) structures were observed (Fig. 1a). CaMnO$_3$ is known to be in the orthorhombic (Pnma) phase at room temperature. The mixed-phase is due to the higher concentration of CaMnO$_3$ [26]. The obtained XRD pattern was refined using Rietveld refinement by taking pseudo-Voigt peak profiles to study the structures in detail further. The goodness of fit ($\chi^2$) was within acceptable limits (Fig. 1b–e). The Rietveld analysis shows a presence of 25% Pnma and 75% R3c phase for x = 0.12. The lattice volume was observed to decrease with an increase in the CaMnO$_3$ content. The Shannon radii of Ca$^{2+}$(XII) ~ 1.34 Å ions is smaller than that of Na$^+$ (XII) ~ 1.39 Å and Bi$^{3+}$ (XII) ~ 1.36 Å ions. Also, the Mn$^{3+}$ (VI-LS) ~ 0.58 Å, and Mn$^{4+}$ ~ 0.53 Å are smaller in comparison to the Ti$^{4+}$ (VI) ~ 0.605 Å, while Mn$^{2+}$ (VI-LS) ~ 0.67 Å, is larger than Ti$^{4+}$ (VI) but is comparable to Ti$^{3+}$ (VI) ~ 0.67 Å [27]. One expects an Mn$^{4+}$ ion to substitute a Ti$^{4+}$ ion. Hence, this leads to a decrease in the lattice volume with substitution. The lattice micro strain was calculated using the Williamson–Hall equation: $\varepsilon = \beta_{hkl}/4\tan(\theta)$, where $\varepsilon$ is the lattice micro strain, $\beta_{hkl}$ is the full width at half maxima corresponding to a particular XRD peak having certain ‘hkl’ plane, and tan(θ) is the tangent of the Bragg’s angle corresponding to this particular XRD peak [28, 29]. The lattice micro strain was calculated considering the highest intense peak (110) for all the compositions. The strain was observed to decrease for x = 0.03 and thereafter continuously increase for the other two compositions. To understand such a trend in the lattice strain, the tilt angle of the octahedra (ω) was calculated from the atomic positions [30]. The octahedral tilt angle (ω) was observed to be responsible for such lattice strain variation [25]. The lattice parameters (a = b), after experiencing an increase for x = 0.03, continuously decreased for the other two compositions (Fig. 1f). On the other hand, the “c” parameter shows a sporadic up and down variation with an increase in CaMnO$_3$ composition (Fig. 2a). To study such variation in the lattice parameters, a detailed bond length and bond angle analysis is done.

In the BO$_6$ octahedra, there are two sets of B–O bond lengths. One set is larger than another one [25]. The short B–O bond lengths vary similarly to the variation in the “c” lattice parameter (Fig. 2b) The long B–O bond

![Fig. 1](image-url)  
**Fig. 1** a XRD pattern of (1-x) Na$_{0.5}$Bi$_{0.5}$TiO$_3$-(x)CaMnO$_3$ (x = 0, 0.03, 0.06, and 0.12), Rietveld plot of b x = 0, d x = 0.12, f tilt angle and strain with composition; inset shows variation of volume with composition.
It can be concluded that the “c” lattice parameter is affected by the B–O bond lengths variation. The O–B–O bonds associated with the B–O bonds also show a similar trend with the composition (Fig. 2d). There are four types of A–O bonds present in the NBT-based rhombohedral structure, denoted as $A_1$–O, $A_2$–O, $A_3$–O, and $A_4$–O. The $A_1$–O and the $A_2$–O bond lengths increased for $x = 0.03$ and thereafter continuously decreased for the other two compositions while an exactly opposite trend was observed for the $A_3$–O and $A_4$–O bonds (Fig. 2c). A similar variation was observed for the associated A–O–A bond angles (Fig. 2e). The variation in the displacement of B-site atoms with composition shows a similar trend as the variation in the B–O bond lengths (Fig. 2f). The off-centering of the O-atoms increased for $x = 0.03$ and further decreased continuously for the other compositions. Such variation in the off-centering of O-atoms is responsible for the A–O bond variations, consequently affecting the lattice strain.

The bond lengths and the lattice strain are affected by various cationic and anionic defects present in the lattice. NBT is known to show cationic (Na/Bi) vacancies due to the high-temperature sintering of the ceramics leading to Na and Bi loss. This leads to a proportionate oxygen loss creating oxygen vacancies [31]. To confirm such losses from the lattice, a detailed analysis of the XPS spectra is reported in the following section.

### 3.2 XPS analysis

#### i. O1s core-level spectra

The O1s spectra consisted of three peaks corresponding to the binding energy (BE) of lattice oxygen ($O_L$) at 529–530 eV, oxygen vacancy ($O_V$) at 530–532 eV, and adsorbed oxygen ($O_A$) at 533–534 eV [32, 33]. The $O_L$ and $O_V$ are the ones that contribute to the lattice. The numerical estimation shows the $O_V$ fraction ($O_V/(O_V + O_L)$) decreased continuously for $x = 0$ to $x = 0.06$ but thereafter increased for $x = 0.12$ (Fig. 3a–d). Hence, the incorporation of CaMnO$_3$ seems to reduce the $O_V$ in general. The least value of $O_V$ was recorded for $x = 0.06$. The creation of $O_V$ may be triggered by probable cation-loss in the compositions. Hence, a valence state study of the individual cations becomes significant. However, losses in lattice oxygen associated with cation loss imply probable distortions in the lattice which is expected to affect the lattice parameters and bond strengths.

#### ii. Na1s core-level spectra

The core Na1s peak at 1072.62 eV confirmed the Na\(^{+}\) state for all the samples (Fig. 4a–d) [34]. Extra peaks observed in this region indicate the presence of Ti-LMM Auger transitions and will be discussed in the following section. The Ti-LMM Auger peaks are observed to be in the proximity of the Na 1s peak for
all the samples [35]. The binding energy of Na 1s peak continuously decreased from 1072.62 to 1071.44 eV with an increase in the CaMnO$_3$ composition. This indicates the weakening of Na–O bonds, which originated due to the volatilization of Na at high-temperature sintering [36].

iii. Bi 4f core-level spectra

Bi was observed to be in the Bi$^{3+}$ state. Along with the Bi$^{3+}$ states, Bi loss was observed for all the samples. However, the ratio of Bi$^{3+}$ to Bi-loss varied with the composition (Fig. 5a–d). The Bi$^{3+}$ 4f$_{7/2}$ and Bi$^{3+}$ 4f$_{5/2}$ peak binding energy continuously decreased
from (159.15 eV, 165.35 eV) for \(x=0\) to (157.17 eV, 162.48 eV) for \(x=0.12\) [37]. The spin–orbit splitting energy for Bi\(^{3+}\)\(4f_{7/2}\) and Bi\(^{3+}\)\(4f_{5/2}\) was observed to continuously decrease from 6.20 eV for \(x=0\) to 5.31 eV for \(x=0.12\). This decrease in BE is due to the weakening of the Bi-O bonding due to Ca and Mn incorporation. The Bi-loss peaks were observed at (161.57 eV, 167.24 eV) for \(x=0\), (162.11 eV, 166.98 eV) for \(x=0.03\), (159.38 eV, 164.70 eV) for \(x=0.06\) and finally at (158.87 eV, 164.17 eV) for \(x=0.12\) [38, 39]. The spin–orbit splitting energy for Bi-loss peaks was observed to be decreased from 5.67 eV for \(x=0\) to 4.98 eV for \(x=0.03\) and then continuously increased to 5.30 eV for \(x=0.12\) composition. The fraction of Bi-loss to Bi\(^{3+}\) was estimated to decrease from 0.50 for \(x=0\) to 0.37 for \(x=0.03\) and further continuously increased to 0.89 for \(x=0.12\). The variation of the spin–orbit splitting energy, binding energy, and the Bi-loss to Bi\(^{3+}\) composition and further continuously increased. The Bi satellite peak detected in the Ti main peak region at 465.86 eV was observed to continuously shifted to a lower BE of 465.44 eV for \(x=0.12\) [17].

iv. Ti-2p core-level spectra

The Ti ion is supposed to be in the Ti\(^{4+}\) state. However, for all the compositions a presence of a mixed oxidation state of Ti\(^{3+}\) and Ti\(^{4+}\) was observed (Fig. 6a–d). The Ti\(^{3+}\) 2p\(^{3/2}\) and 2p\(^{1/2}\) peaks were observed to increase continuously from (456.68 eV, 462.18 eV) for \(x=0\) to (458.68 eV, 462.77 eV) for \(x=0.06\) but decreased to (457.50 eV, 462.99 eV) for \(x=0.12\) compositions [40]. The same variation was also observed for the average B–O bond strength i.e., the B–O bond strength increased up to \(x=0.06\) and further decreased for the \(x=0.12\). The Ti\(^{4+}\) 2p\(^{3/2}\) and Ti\(^{4+}\) 2p\(^{1/2}\) peaks were observed to continuously increased from (458.26 eV, 463.92 eV) for \(x=0\) to (459.64 eV, 464.37 eV) for \(x=0.06\) but decreased to (458.97 eV, 463.87 eV) for \(x=0.12\) [41]. The spin–orbit splitting for Ti\(^{3+}\) states and Ti\(^{4+}\) states (5.5 eV, 5.66 eV for \(x=0\)) was observed to decreased continuously to (4.09 eV, 4.83 eV for \(x=0.06\) and thereafter increased to (5.49 eV, 4.90 eV) for the \(x=0.12\) sample. A plasmon peak of Ti is observed in all the samples at ~468.98 eV. Such variations in binding energy affected the <O–B–O> bond angles. The fraction of Ti\(^{3+}\) to Ti\(^{4+}\) fraction was found to increase continuously from 0.49 for \(x=0\) to 0.53 for \(x=0.03\), 0.58 for \(x=0.06\) to 0.70 for \(x=0.12\) composition respectively. Such preference for Ti\(^{3+}\) is due to the substitution of Mn at the Ti site.

The Ti-LMM Auger peaks observed with the Na-1s prominent peak were observed to decrease from 1074.72 eV for \(x=0\) to 1072.07 eV for \(x=0.12\) compositions. This may be due to the increased contribution of Mn. The broad region in the spectra is due to the overlapping of Bi\(^{3+}\) 4d\(^{3/2}\) peak (~465 eV) with Ti\(^{4+}\) 2p\(^{3/2}\) (~463.92 eV) peak, which is observed to be present in all the samples.
v. Ca-2p core-level spectra

The Ca-2p core-level spectra confirmed the presence of Ca$^{2+}$ in all the samples (Fig. 7a–c). The Ca$^{2+}$ $2p_{3/2}$ and Ca$^{2+}$ $2p_{1/2}$ was observed to be present at (347.66 eV, 351.58 eV) for $x = 0.03$, (347.67 eV, 351.26 eV) for $x = 0.06$, and (346.36 eV, 349.92 eV) for $x = 0.12$. 

![Fig. 6 Deconvoluted Ti-2p XPS pattern of a $x = 0$, b $x = 0.03$, c $x = 0.06$, and d $x = 0.12$ compositions](image)

![Fig. 7 Deconvoluted Ca-2p XPS pattern of a $x = 0.03$, b $x = 0.06$, and c $x = 0.12$ compositions, Deconvoluted Mn-2p XPS pattern of d $x = 0.03$, e $x = 0.06$, and f $x = 0.12$ compositions](image)
eV) for \( x = 0.12 \) \cite{42, 43}. The BE decreased with an increase in Ca content in the sample. The spin-orbit energy was also observed to be continuously decreased from 3.92 eV for \( x = 0.03 \) to 3.56 eV for \( x = 0.12 \). Such variation is also reflected in the change in A–O bond strength with composition.

vi. Mn 2p core-level spectra

The Mn-2p XPS spectra was deconvoluted to eight peaks associated with \( 2p_{3/2}, 2p_{1/2} \) peaks of Mn\(^{2+} \) (639.36 eV, 651.24 eV), Mn\(^{3+} \) (640.79 eV, 652.54 eV), and Mn\(^{4+} \) (642.63 eV, 656.22 eV) and satellite peaks at (644.79 eV, 657.63 eV) corresponding to Mn\(^{2+} \), (646.49 eV, 657.34 eV) to Mn\(^{3+} \), and (648.85 eV, 659.96 eV) to Mn\(^{4+} \) (Fig. 6a) \cite{36, 40, 44, 45}. It was observed that there is a presence of a mixed oxidation state of Mn\(^{2+} \), Mn\(^{3+} \), and Mn\(^{4+} \) in the \( x = 0.03 \) and 0.12 compositions, while only Mn\(^{3+} \) and Mn\(^{4+} \) states are present in the \( x = 0.06 \) composition (Fig. 7d–f). The Mn\(^{3+} \) content was estimated by using the area ratio of Mn\(^{3+} \) to the sum of the area of Mn\(^{2+} \), Mn\(^{3+} \), and Mn\(^{4+} \). It was found that the Mn\(^{3+} \) content is nearly the same for both the \( x = 0.03 \) (0.30) and \( x = 0.06 \) (0.35) composition while it increased to 0.51 for the \( x = 0.12 \) composition. The spin–orbit splitting energy for Mn\(^{3+} \) and Mn\(^{4+} \) was found to be decreased continuously from (11.53 eV, 11.34 eV) for \( x = 0.03 \) to (11.20 eV, 11.38 eV) for \( x = 0.06 \), and (11.05 eV, 11.11 eV) for \( x = 0.12 \) compositions respectively. The total content of the Mn at Ti place was estimated by multiplying the charge. The corresponding stoichiometry was found to be increased from 0.0868 for \( x = 0.03 \) to 0.2281 for \( x = 0.06 \) and 0.3587 for \( x = 0.12 \) compositions. The total charge of the Mn was calculated from the area ratio. It was observed to increase from 2.61 for \( x = 0.03 \) to 3.65 for \( x = 0.06 \) and decrease to 2.87 for \( x = 0.12 \). Such variation in the charge content was reflected in the B–O bond strength variation.

3.3 Raman spectroscopy

The room temperature Raman spectra were recorded in 100–900 cm\(^{-1} \) range for all the compositions (Fig. 8a). The Raman spectra were deconvoluted using Fityk software for all the compositions (Fig. S1). Twelve Raman active modes are present in the NBT (\( R\bar{3}c \)) structure \cite{25}. The first mode \( A(1) \) at ~135 cm\(^{-1} \) continuously redshifted with

![Fig. 8](https://example.com/fig8.png)

**Fig. 8** a Raman Spectra for \( x = 0, 0.03, 0.06, \) and 0.12 compositions, b variation of Raman modes with composition, c variation of Raman modes with composition, and d variation of Raman modes with composition
an increase in the Ca and Mn substitution (Fig. 8b). The FWHM increased while the intensity decreased with Ca and Mn substitution increase. This mode is associated with the vibration of A-site atoms. Such redshift of Raman mode agrees with the decrease in the binding energy of Na-1s.

The second mode, \( E(1) \) at \( \sim 151 \text{ cm}^{-1} \) continuously blueshifted with an increase in the Ca and Mn substitution (Fig. 8b). The mass of Ca is less than the mass of Bi, which decreased the total mass, and hence the blueshift was observed. The FWHM of this mode decreased for \( x = 0.03 \) and further increased continuously for \( x = 0.06 \) and \( x = 0.12 \). This could be associated with the variation of \( A_3-O \) and \( A_2-O \) bond lengths.

The mode \( A(2) \) and \( E(2) \) at \( \sim 239 \) and \( \sim 283 \text{ cm}^{-1} \) continuously redshifts with an increase in the substitution (Fig. 8b). These modes are due to the complex vibrations of the \( BO_6 \) octahedra involving angular twisting of the O-cage and central motion of the B-site atoms [25]. The FWHM of these modes increased for \( x = 0.03 \), decreased for \( x = 0.06 \), and increased for \( x = 0.12 \) compositions. Such variations agree with the interpretations of the bond length of the long B–O bond.

Mode \( A(3) \) at \( \sim 331 \text{ cm}^{-1} \) redshifted continuously with an increase in substitution (Fig. 8b). These modes are due to a different twisting of \( BO_6 \) octahedra, respectively. The dominance of \( Ti^3+ \) with an increase in substitution is notable. \( Ti^3+ \) is bigger than \( Ti^4+ \). Hence the B–O bond length increases, thereby weakening the bond strength. This could be the probable reason for the redshift observed in this mode. The FWHM of these modes decreased for \( x = 0.03 \), increased for \( x = 0.06 \), and further decreased for the \( x = 0.12 \) composition. Such variation could be associated with modifying the short B–O bond length and long O–B–O bond angles.

The modes \( E(3) \) and \( E(4) \) at 526 and 574 \text{ cm}^{-1} \) are associated with modifying B–O bonds and the horizontal compression of \( BO_6 \) octahedra (Fig. 8c). These two phonon modes vary similarly. A continuous redshift for \( x = 0.03 \) and \( x = 0.06 \) and a blueshift for \( x = 0.12 \) is observed. The FWHM of the \( E(3) \) mode increased for \( x = 0.03 \) and decreased for \( x = 0.06 \) while again increased for the \( x = 0.12 \) composition. An exactly opposite trend was observed for the \( E(4) \) mode. Such coexistence of compressive and tensile strain is due to a similar modification in the B–O bond lengths and O–B–O bond angles.

The three modes centered at \( \sim 765, \sim 828, \) and \( \sim 866 \text{ cm}^{-1} \) present in the 700–900 \text{ cm}^{-1} \) range show the Raman shift similarly (Fig. 8d). The Raman mode was redshifted for \( x = 0.03 \) and blueshifted for \( x = 0.06 \), and redshifted for the \( x = 0.12 \) composition. Such variation is associated with the modification in the long B–O bond strength.

Some modes are present that are not theoretically predicted but present in all the NBT-based samples. A Raman mode present at \( \sim 479 \text{ cm}^{-1} \) is redshifted for \( x = 0.03 \) and \( x = 0.06 \) and blue-shifted for \( x = 0.12 \). The mode at \( \sim 610 \text{ cm}^{-1} \) blue-shifted for \( x = 0.03 \) and further red-shifted for \( x = 0.06 \) and again blue-shifted for the \( x = 0.12 \) composition. Most probably, these are correlated to the modifications of the B–O bond strengths as the trends are similar. However, this is not a strong claim in the absence of a definite theoretical estimate.

In the pure NBT sample, the Raman modes are strongest in the 200–400 \text{ cm}^{-1} \) range with very high intensity while moderate intensities are observed for the modes in the broad range in 400–700 \text{ cm}^{-1} \). But with the substitution of \( CaMnO_3 \), the intensity of these two ranges become equally strong and are comparable. The modes in the 200–400 \text{ cm}^{-1} \) range became broader, while the modes in the range 400–700 \text{ cm}^{-1} \) became narrower with an increase in \( CaMnO_3 \) content. An extra mode was observed at \( \sim 412 \text{ cm}^{-1} \) in the \( x = 0.06 \) and \( x = 0.12 \) compositions. This is a \( B_{2g}(3) \) mode associated with the stretching of the \( MnO_6 \) octahedra of orthorhombic (\( Pnma \)) of \( CaMnO_3 \) [46]. A \( B_{1g}(5) \) mode due to the vibration of O-atoms of orthorhombic (\( Pnma \)) \( CaMnO_3 \) was observed at 351 \text{ cm}^{-1} only in the \( x = 0.12 \) composition [46].

Hence the dominance of the \( CaMnO_3 \) modes with the increasing substitution is observed highlighting the strong influence of the \( MnO_6 \) octahedral properties over the TiO6 octahedra in these substituted materials.

### 3.4 Morphology study

The morphology of all the compositions was studied and analyzed using ImageJ software. All the compositions \((x = 0, 0.03, 0.06)\) show a dense honeycomb type morphology (Fig. 9a–c). But, for the \( x = 0.12 \) composition, the edges of each grain became rounded rather than a sharp edge (Fig. 9d). An additional agglomerated morphology was also observed for the \( x = 0.12 \) composition, which could be due to two phases in this composition [47]. The small particle in the surface of samples could be due to the presence of some minor secondary phases. The EDS mapping for this composition is done at several area to check the homogeneity of the dopants on the surface of this composition (Fig. 9a, b). The manganese content is observed to be slightly more at those clusters in comparison to the grains. For a better understanding of the dopant distribution, the EDS is taken at different points (Fig. 9c, d). The cluster shows a high content of manganese and low content of Ca, Bi, and Ti while the grains show dopants contribution like the expected composition. This can be concluded that some minor off-stoichiometry composition is formed which gave rise to such cluster formations which could not be detected from XRD and Raman spectroscopy. These clusters are observed to be embedded in the grains rather than just sitting on the surface.

The \( x = 0.03 \) composition shows the largest grain size of \( \sim 37.78 \pm 7.68 \text{ µm} \) in comparison to the \( x = 0 \)
(15.33 ± 4.61 µm) composition. The other two compositions, i.e., \(x = 0.06\) (8.40 ± 2.89 µm) and \(x = 0.12\) (13.35 ± 6.35 µm), show smaller grain size in comparison to the \(x = 0\). Among all the compositions, the \(x = 0.03\) shows bigger grain size. The grain size is affected due to the lattice strain. The lattice strain affects the grain size in opposite way, that means lesser the strain more the grain size. In this series of materials, the \(x = 0.03\) show least lattice strain in comparison to all other compositions. Such least lattice strain could be associated with less oxygen vacancy and Bi loss which is observed from the XPS data. The Ti\(^{3+}\) content is also more in the modified systems compared to the unmodified one. The Mn\(^{2+}\) content is maximum in the \(x = 0.03\) composition and the ionic radii of the Mn\(^{2+}\) (≈ 0.67 Å) and the Ti\(^{3+}\) (≈ 0.67 Å) is comparable. While for other compositions, the Mn\(^{3+}\) and Mn\(^{4+}\) content is higher, which may induce strain in the lattice due to mismatch of the ionic radii. The reduction of the lattice strain could help the neighboring planes to reorient in the same crystalline plane that resulted in a larger grain [48].

### 3.5 Dielectric study

The room temperature dielectric spectra revealed an enhancement in the dielectric permittivity with an increase in the CaMnO\(_3\) composition (Fig. 10a). The dielectric constant increased for \(x = 0.03\) and further continuously decreased for the \(x = 0.06\) and \(x = 0.12\) compositions. The tan loss also decreased for the \(x = 0.03\) composition but continuously increased for the other two. The Bi loss decreased for the \(x = 0.03\) and continuously increased for the other two compositions. Hence, such a behavior can be correlated to the Bi loss due to the volatile nature of Bi. This is discussed in the XPS section. As dielectric behavior is dependent upon the grain size of the ceramics, hence the \(x = 0.03\) shows the highest room temperature dielectric constant due to its largest grain size [49].

The phase transitions were studied using the temperature-dependent dielectric plot at different frequencies. The phase transition temperature (\(T_c\)) corresponding to the ferroelectric to paraelectric phase was observed in the 50–400 °C temperature range for the \(x = 0\), \(x = 0.03\), and \(x = 0.06\) compositions (Fig. 10b, c) [16]. The \(T_c\) varies nominally with frequency showing a possibility of a relaxor mechanism. At a frequency of 10 kHz, the \(T_c\) continuously shifted to a lower temperature with increasing doping, from 332 °C for the \(x = 0–275\) °C for \(x = 0.03\) and to 254 °C for the \(x = 0.06\) composition. The phase transition was not detected for the \(x = 0.12\) composition (Fig. 10d). This may be due to the near room temperature phase transition of the CaMnO\(_3\) phase [50]. For the \(x = 0.12\) sample, the \(T_c\) may be close to the
room temperature. As these measurements were performed above 50 °C, such a transition was not observed. Note that the XRD and Raman analysis of the $x=0.12$ composition reveals the presence of a mixed phase of $Pnma$ and $R3c$ phases. While the $R3c$ phase shows spontaneous polarization, the $Pnma$ contains a centrosymmetric point group “mmm” for which it is paraelectric. Hence, the phase transition temperature was reduced for the $x=0.12$ near the room temperature.

The NBT is a well-known relaxor-type material. The relaxor nature increased with an increase in the CaMnO$_3$ content. This is due to the increase in diffuseness of the material that may have originated from the random distribution of multiple cations at different atomic sites [16]. The dielectric stability improved significantly over a broad temperature range with CaMnO$_3$ substitution, implying the applicability of these materials as stable capacitors [51]. The $\varepsilon/\varepsilon_{\text{max}}$ vs. $T/T_{\text{max}}$ depicts the relaxor nature and stability of the prepared compositions (Fig. 10f).

### 3.6 Magnetism study

The M–H plot of $x=0$ (Na$_{0.5}$Bi$_{0.5}$TiO$_3$) showed an anti-S-shaped curve which results from the diamagnetic and weak ferromagnetic signals (Fig. 11a). It is well known that the diamagnetism of pure Na$_{0.5}$Bi$_{0.5}$TiO$_3$ originates from the empty state of Ti$^{4+}$ cations. In contrast, the weak ferromagnetism may create by vacancies (e.g., Ti$^{4-}$ and Na$^+$) or be related to the surface effect [14, 52]. Zhang et al. predicted that perfect Na$_{0.5}$Bi$_{0.5}$TiO$_3$ is non-magnetic, while Na or Ti vacancies could induce magnetism rather than the Bi or O vacancies [53]. Ju et al. reported that Na vacancies at the surface were possibly introduced to a non-zero magnetic moment [54]. It is also discussed that the magnetic hysteresis for a Na deficient NBT system showed two distinct behaviors: weak bulk ferromagnetism at low fields (below 800 Oe) and diamagnetism at areas above 800 Oe [17]. In the present work, the XPS revealed the presence of $\sim$49% of Ti$^{3+}$ in the B-site. Also, Ca$^{2+}$ at the Na$^+$ site creates Na deficiency in the lattice [24]. Such self-defects induced weak ferromagnetism in the pure NBT system.

The M–H plots indicated that the solid solution of CaMnO$_{3-\delta}$ in the host Na$_{0.5}$Bi$_{0.5}$TiO$_3$ materials produced a complex magnetic behavior (Fig. 11b–d). Some reports suggest that defects at the Bi$^{3+}$, Na$^+$, and Ti$^{4+}$ sites produce a non-zero magnetic moment while oxygen vacancies produce a zero magnetic moment. The reduction of Ti$^{4+}$ to Ti$^{3+/2+}$ induces magnetic moment in the NBT-based systems. The incorporation of CaMnO$_3$ reduced the diamagnetism component in the modified systems. The magnetic moment is relatively the same $\sim$0.028 emu/g for $x=0.03$ to $\sim$0.03 emu/g for $x=0.06$ and further improved to $\sim$0.10 emu/g for $x=0.12$ compositions at 30 kOe field. The M–H plots show an unsaturation of magnetization with an applied magnetic field, possibly due to the competing effect among the ferromagnetic, paramagnetic, and...
antiferromagnetic components that give rise to the total magnetic moment of all the compositions [24]. The $x = 0.03$ composition shows a mixed behavior of paramagnetism and very weak ferromagnetism (Fig. 11b). Such existence of weak ferromagnetism could be due to a handful of different possible interactions. From the XPS analysis, it was observed that there is a presence of Mn$^{2+}$, Mn$^{3+}$, and Mn$^{4+}$ in this composition. The amount of Mn$^{2+}$ is ~50% while Mn$^{3+}$ is ~35% and Mn$^{4+}$ is ~15%.

The interaction of Mn$^{2+}/3+$ through oxygen vacancies ($V_O$) called the F-centre exchange interaction induced the ferromagnetism in this system [55]. This ferromagnetic ordering is due to several favorable Mn$^{2+}/3+$–($V_O$)–Mn$^{2+}/3+$ configurations. With the substitution of Ca$^{2+}$ for Na$^+$ at the A-site, charge compensation demands the introduction of Na-vacancies. These vacancies influenced ferromagnetism. Also, the Ti$^{3+}$ defects induce ferromagnetism. As Ti$^{3+}$ is ~53% in this system calculated from the XPS analysis, some ferromagnetism could be due to the Ti$^{3+}$ states. The presence of paramagnetism was possibly related to the isolation of Mn cations, which favored the paramagnetic property in this material [56].

The $x = 0.06$ composition shows a mixed behavior of paramagnetism and weak antiferromagnetism (Fig. 11c). Generally, the bulk CaMnO$_3$ is known to show G-type antiferromagnetism. Mn$^{3+}$ has a configuration of $t_{2g}^3 e_g^1$, while Mn$^{4+}$ has a $t_{2g}^3$ configuration. G-type antiferromagnetism originates from the hopping of $e_g$ electron from Mn$^{3+}$ to O$^{2-}$ and then from O$^{2-}$ to Mn$^{4+}$. In the case of G-type antiferromagnetism, both the interplanar and intraplanar coupling are antiferromagnetic [22, 57]. From the XPS studies, it is revealed that this composition contains Mn$^{3+}$ and Mn$^{4+}$ where the Mn$^{3+}$ is ~35% while Mn$^{4+}$ is ~65%. However, the Mn$^{4+}$ cation incorporated for the Ti$^{4+}$-site resulted in the antiferromagnetic interaction of the Mn$^{4+}$–O$^{2-}$–Mn$^{4+}$ pair creating the superexchange interaction [58]. Also, this composition contains ~60% Ti$^{3+}$, which could result from the interaction of Ti$^{3+}$O$^{2-}$–Ti$^{3+}$, hence the antiferromagnetic property.

The $x = 0.12$ composition shows a weak ferromagnetic behavior (Fig. 11d). The XPS study reveals the presence of Mn$^{2+}$ (~31%), Mn$^{3+}$ (~51%), and Mn$^{4+}$ (~18%) in this composition. Also, the Ti$^{3+}$ is ~70% in this composition. The increase in Ti$^{3+}$ is due to the change of Ti$^{4+}$ cations due to
the influence of oxygen vacancies which also contributes to the source ferromagnetism because of the conversion of an empty 3d shell to an occupied 3d shell in Ti$^{3+}$ cations [14]. Here, the oxygen vacancy enhanced the F-centre exchange interaction between the Mn$^{2+/3+}$–V$^{O}$–Mn$^{2+/3+}$. There is also some presence of antiferromagnetism in all the CaMnO$_{3-x}$ modified compositions. In addition to the above-discussed possibilities, such behavior could also be due to the interaction between the polaron of Mn$^{2+/3+}$–V$^{O}$–Mn$^{2+/3+}$ that arises from the non-uniform incorporation of Mn ions into the parent lattice [24]. The ferromagnetism behavior in the samples is represented in Fig. 12a, b. The other magnetic contributions, like paramagnetic and diamagnetic were subtracted from the M(H) loop to extract the ferromagnetic contributions for all the compositions. The remnant magnetization and the saturation magnetization were calculated from the ferromagnetic loop to understand its variation with the composition. The remnant magnetization ($M_r$) was observed to be decreased continuously up to the $x=0.06$ composition while it increased for the $x=0.12$ composition, and a similar variation was also noted for the saturation magnetization ($M_s$) as well (Fig. 12c). In addition to the above discussed ferromagnetic exchange interactions, the Ti$^{3+/4+}$ and Mn$^{3+/4+}$ double exchange interactions mediated via the O$^{2-}$ ion (Ti$^{3+}$–O$^{2-}$–Mn$^{3+}$, Ti$^{3+}$–O$^{2-}$–Mn$^{4+}$, Ti$^{4+}$–O$^{2-}$–Mn$^{3+}$, Ti$^{4+}$–O$^{2-}$–Mn$^{4+}$) also contribute to the ferromagnetism in CaMnO$_3$ modified samples [59, 60].

The B–O–B bond angle plays a vital role in deciding the type of magnetism in a material [61]. In this series of compositions, the $x=0$ to $x=0.06$ composition shows an $R3c$ structure while the $x=0.12$ shows a mixed phase of rhombohedral $R3c$ and orthorhombic Pnma structure. In the $R3c$ structure, the B–O–B bond angle continuously increased from 157.70 for $x=0$ to 164.08 for $x=0.06$ and decreased to 157.21 for the $x=0.12$ composition. For d$^5$ Mn$^{4+}$ cations in octahedral coordination, G-type antiferromagnetic superexchange is favored by 180° transition metal–oxygen–transition metal bond angles and is weakened as the B–O–B angle deviates from this angle [62, 63]. The deviation from this angle continuously decreased from $x=0$ to $x=0.06$ (lowest deviation) and increased for the $x=0.12$ composition. This indicates the introduction of antiferromagnetism in the $x=0.03$ and $x=0.06$ while the antiferromagnetism is highest in the $x=0.06$ composition.

In the $x=0$ (undoped composition) the origin of ferromagnetism is due to the presence of Na vacancy as well as due to the Ti$^{3+}$ presence. But, when the CaMnO$_3$ is incorporated in the lattice, oxygen vacancy reduced for the $x=0.03$ and 0.06 compositions compared to the $x=0$ composition, while multiple oxidation states of Mn were detected. In addition to the presence of Mn, the Ti$^{3+}$ presence consistently increased for all the CMO incorporated compositions. The Mn$^{3+}$ content (~35%) is almost same for the $x=0.03$ and 0.06 compositions. The Mn$^{4+}$ content is more for the $x=0.06$ composition. Such lesser Mn$^{3+}$ content and the higher Mn$^{4+}$ compared to the $x=0.12$ composition favoured antiferromagnetic behaviour in the $x=0.03$ and 0.06, hence less magnetization was observed. In the $x=0.12$ composition ~51% of Mn$^{3+}$, ~70% Ti$^{3+}$, and high oxygen vacancy was observed compared to the $x=0$ composition which contributed to high ferromagnetic behaviour. It can be said that the presence of oxygen vacancy and the Mn$^{3+}$ favoured the F-centre exchange interaction between the Mn$^{3+}$–V$^{O}$–Mn$^{3+}$ which is responsible for ferromagnetism in all the CMO modified compositions. All these contribute to highest magnetization in the $x=0.12$ compositions than the other CMO incorporated compositions.

To achieve proper annealing of the CMO modified samples, the samples were treated at different temperature to attain a comparable density with respect to the undoped one. Although most of the samples from $x=0$ to $x=0.06$ were annealed at ~1100 °C, the $x=0.12$ sample was treated at ~1130 °C. This nominal change in the annealing temperature might have changed the oxygen content for this sample. Hence, the oxidation states of Mn changed for this

![Fig. 12](image-url) a Room temperature ferromagnetism plots after extracting the diamagnetic and paramagnetic contributions for $x=0$, 0.03, 0.06, and 0.12 compositions. b Normalized ferromagnetic contributions for $x=0$, 0.03, 0.06, and 0.12 compositions. c Variation of remnant magnetization and saturation magnetization with composition.
composition which is observed from the XPS data. Thus, the change of magnetization might have its roots in the synthesis.

### 3.7 Magnetodielectric coupling

To observe the effect of the magnetic field on the dielectric properties of each composition, the dielectric constant was measured under different applied magnetic fields (Fig. 13). The tuning of polarization in a magnetic field is governed by magnetodielectric coupling, also called magnetoelectric (ME) coupling \([6, 17]\). It is well known that the ME coupling can be examined from the magneto-dielectric measurement \([8, 64]\). The change in the dielectric permittivity can validate the ME coupling in a material by applying an external magnetic field \([64]\). To investigate the room temperature magneto-dielectric effect in the CaMnO\(_3\) modified NBT compositions, a frequency-dependent dielectric measurement was done at various magnetic fields at room temperature. The capacitance spectra were observed to be varied with an increase in the applied magnetic field for all the compositions. For the \(x=0\), 0.06, and 0.12 compositions, the \(C_p\) was observed to decrease with applying a magnetic field consistently. This proves the coupling between the magnetic field and the dielectric constant of the respective materials. An irregular behavior was observed in the \(x=0.03\) composition, which is a decrease in the capacitance at a lower magnetic field of 2 kGauss and further increased continuously. To understand the coupling in detail, the magnetodielectric constant \(MD\) was calculated using the following equation:

\[
MD\% = \frac{C_p(H) - C_p(0)}{C_p(0)} \times 100, \quad \text{where} \quad H \text{ and } 0 \text{ stand for the capacitance under applied magnetic field and zero applied magnetic field, respectively} \quad [12].
\]

\(MD\%\) is an important parameter to compare the ME coupling in a material \([7, 54]\). It can be observed that with the increase in applied magnetic fields, the \(MD\%\) value decreased for the \(x=0\), \(x=0.06\), and \(x=0.12\) compositions (Fig. S2, Fig. 14a, c, d). But for the \(x=0.03\) composition, it initially decreased to 2 kGauss and further increased for the higher applied fields (Fig. 14b). A similar nature was observed for all the frequencies from 1 kHz to 1 MHz. The \(MD\%\) increased with the increase in the frequency. The higher value of \(MD\%\) at low frequency may be contributed by dc conductivity, leakage current, space

![Fig. 13](image-url)
charge polarization, etc. [64]. In the high-frequency region around 100 kHz, which is considered the intrinsic region, MD% at 5 kGauss was observed to be highest (−3.69%) for the $x=0.06$ composition. All the compositions show a negative ME coupling, while the $x=0.03$ composition showed a mixed negative and positive coupling. This could be associated with the competing effect between the lattice strain and the observed mixed magnetism of paramagnetic, antiferromagnetic, and ferromagnetic in this material. The ME coupling increased with an increase in the CaMnO$_3$ incorporation, while a sudden drop in the coupling percentage was observed for the $x=0.12$ composition. As the $x=0.12$ composition show the presence of mixed phase of rhombohedral (R3c) and orthorhombic (Pnma), the ferroelectric polarization is less in this material due to which less coupling was observed in comparison to the other compositions as ME coupling is best observed in the multiferroic materials [5, 65]. In all the compositions, a hysteresis was observed for the MD% with an upward field and withdrawal of the field. The variation of the dielectric constant with the magnetic field is shown in the Fig. 15. The variation of the dielectric constant ($\varepsilon_r$) and MD% with respect to the magnetic field (low magnetic field to high magnetic field) Is presented in the Fig. S3 and S4 respectively. At low magnetic field that is from 200 to 1000 Gauss, the magnitude of the MD% was observed to be increasing faster than at the high magnetic field. This indicates a strong magneto-electric coupling at lower fields (200–1000 Gauss) than at the higher field (1000–10k Gauss). So, here a negative magnetodielectric coupling is taking place.

The variation of the dielectric constant ($\varepsilon_r$) and MD% with respect to the magnetic field (low magnetic field to high magnetic field) Is presented in the Fig. S3 and S4 respectively. At low magnetic field that is from 200 to 1000 Gauss, the magnitude of the MD% was observed to be increasing faster than at the high magnetic field. This indicates a strong magneto-electric coupling at lower fields (200–1000 Gauss) than at the higher field (1000–10k Gauss). So, here a negative magnetodielectric coupling is taking place.

$$\frac{\Delta \varepsilon}{\varepsilon_0} \times H = \frac{\varepsilon (H) - \varepsilon (0)}{\varepsilon (0)}$$

where the “$E_0$” is the applied electric excitation at 2 V with the sample thickness around ~0.8 mm, and the “$H$” is the applied magnetic field of 5000 Oe. $\varepsilon (H)$ and $\varepsilon (0)$ is the dielectric constant at an applied field ($H$) and no field respectively [8, 66]. The $\chi_{ME}$ was found to be $\sim 0.061$ mV cm$^{-1}$ Oe$^{-1}$, for $\sim 0.058$ mV cm$^{-1}$ Oe$^{-1}$, and $\sim 0.032$ mV cm$^{-1}$ Oe$^{-1}$ the $x=0$, $x=0.03$, and $x=0.12$ compositions respectively. The $x=0.06$ showed a highest $\chi_{ME}$ value of $\sim 0.18$ mV cm$^{-1}$ Oe$^{-1}$ at 100 kHz frequency.
This means with an increase of the spin alignment along the electric field there is a decrease of the electrical polarization along the same direction. This is only possible when the spin influences the charge separation property of the material due to application of electric field. This is direct evidence of magneto-electric coupling. As a hypothetical explanation, one can provide the scenario of the ferromagnetic interaction in a $\text{Mn}^{3+}$–$\text{V}_\text{O}$–$\text{Mn}^{4+}$. When a magnetic field is applied, the spins will be aligned with the magnetic field and dipole moment between the $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$ will be perpendicular to the direction of the alignment. This explains somewhat why the dielectric polarization is lost with magnetic field.

Impedance spectroscopy is an essential tool to distinguish the contributions from grain, grain boundary, and electrode effects [67]. The Nyquist plot (Real $Z$ vs. Imaginary $Z$) for different compositions at various magnetic fields is represented in Fig. 16. This plot consists of two overlapping semi-circles corresponding to different contributions. The grain (bulk) and grain boundary effects are associated with the high and low frequency, respectively. The experimental data were fitted using the circuit shown in Fig. 16a inset. The circuit introduced the constant phase element ($CPE$) due to the deviation from the ideal Debye characteristic [68, 69]. The experimental data were fitted using the EC-lab software. The circuit represents the series combination of two circuits in which one is the parallel combination of grain resistance ($R_g$), $CPE$, and capacitance ($C_{gb}$), and the other one is the parallel combination of grain boundary resistance ($R_{gb}$) and grain boundary capacitance ($C_{gb}$). The radius of the semi-circular arc of the $x = 0, 0.06, 0.12$ compositions increased with an increase in the magnetic field. The grain resistance and grain capacitance at various magnetic fields for all the compositions are tabulated in Table S1. The $R_g$ value increased with an increase in the magnetic field, whereas the $C_g$ value decreased for the $x = 0, 0.06, 0.12$ compositions. This change in bulk resistance and bulk capacitance suggests the existence of ME coupling in the sample. For the $x = 0.03$ composition a mixed increase and decrease in the $C_g$ and $R_g$ value was observed with the variation in the magnetic field.

Fig. 15 Variation of dielectric constant ($\varepsilon_r$) with an applied magnetic field at room temperature for $a$ $x = 0$, $b$ $x = 0.03$, $c$ $x = 0.06$, and $d$ $x = 0.12$ compositions at $10 \, \text{kHz}$; the inset shows variation of $\varepsilon_r$ with an applied field at $100 \, \text{kHz}$.
4 Conclusion

The prepared \((1-x)\) Na_{0.5}Bi_{0.5}TiO_3-xCaMnO_3 compositions show a Rhombohedral (R3c) phase up to \(x=0.06\) while a mixed Rhombohedral (R3c) and orthorhombic (Pnma) phase for the \(x=0.12\). The rhombohedral cell volume was observed to be decreased with CMO incorporation and while lattice strain decreased for \(x=0.03\) and further increased for the other compositions. The valence state study revealed such variation in the strain is dominated by the Bi loss in the respective compositions. The bond lengths corroborated the Raman shift of all the modes for all the compositions and bond angles observed from the structural analysis. The \(B_{2g}(3)\) mode at \(\sim 412\) \(\text{cm}^{-1}\) originated due to the stretching of MnO_6 octahedra of orthorhombic (Pnma) observed for both the \(x=0.06\) and 0.12 compositions. Another mode called \(B_{1g}(5)\) mode 351 \(\text{cm}^{-1}\) due to the vibration of O-atoms of orthorhombic (Pnma) CaMnO_3 is only present in the \(x=0.12\) composition, confirming the presence of mixed-phase. The grainsize was observed to be highest for the \(x=0.03\) composition. The room temperature dielectric constant and loss were improved for the \(x=0.03\) composition due to less Bi and O vacancy and the largest grain size among all the compositions. The lowering of the ferroelectric to paraelectric phase transition temperature \(T_c\) towards the room temperature was achieved by the incorporation of CMO. The magnetism study revealed a presence of weak ferromagnetism in all the compositions due to the presence of various self-defects like Na-vacancy and Ti^{3+} states. The CMO modified compositions contain ferromagnetism due to the self-defects and the different exchange interactions like F-center exchange between Mn^{2+/3+}-V_O–Mn^{2+/3+} and double exchange interaction between Ti^{3+/4+} and Mn^{3+/4+} mediated by O^{2-} ion. The magnetization was also improved with the CMO incorporation in the NBT lattice. The coupling between the magnetic and dielectric polarization was observed for all the compositions confirming a magnetodielectric coupling. Hysteresis in the Magnetodielectric coupling was also observed with applying and withdrawing the magnetic field for all the compositions. The highest negative \(MD\%\) of 3.69\% at 100 kHz (applied field of 5 kGauss) was observed for the \(x=0.06\) composition making it a promising material for many magnetoelectric device applications.
Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s00339-023-06513-4.

Acknowledgements The authors would like to acknowledge the Sophisticated Instrument Centre (SIC) facilities for providing the FESEM facility at IIT Indore. The authors also acknowledge the Department of Science and Technology (DST), Govt. of India, New Delhi, India, for providing FIST instrumentation fund to the discipline of Physics, IIT Indore, to purchase a Raman Spectrometer (Grant Number SR/FST/PSI-225/2016). The magnetization measurements were performed at the State University at New York (SUNY), Buffalo State. The work at Buffalo State was supported by the faculty start-up fund from the Dean’s Office, School of Arts and Sciences, and Undergraduate Research Office, Buffalo State. A. Mekki, K. Harrabi, and S. Sen gratefully acknowledge the support of the King Fahd University of Petroleum and Minerals, Saudi Arabia, under the DF191055 DSR project. Ms. Koyal Samantaray acknowledges MRHRD for providing Prime Minister Research Fellowship (PMRF). Mr. Ruhul Amin acknowledges DST for INSPIRE Fellowship (No. IF160339).

Author contributions KSS: conceptualisation, data curation, investigation, methodology, writing—original draft writing, formal analysis, visualisation. RA: data curation, formal analysis. SA: formal analysis. AKP: data curation, formal analysis, resources. CH: data curation. AM: data curation, formal analysis, resources. KH: data curation, formal analysis, resources. SS: project administration, supervision, validation, writing—review and editing.

Availability of data The data that support the findings of this study are available on reasonable request from the corresponding author. The data are not publicly available due to privacy and ethical reasons.

Declarations Conflict of interest The authors declare no conflict of interest.

References

1. W. Eerenstein, W. Eerenstein, N. D. Mathur, J. F. Scott, Nature 442, 759 (2006)
2. M. Bibes, A. Barthélémy, Nat. Mater. 7, 425 (2008)
3. N. Izyumskaya, Ya. Alivov, H. Morkoç, Crit. Rev. Solid State Mater. Sci. 34, 89 (2009)
4. Y. Wang, J. Hu, Y. Lin, C.-W. Nan, NPG Asia Mater 2, 61 (2010)
5. J. Li, Y. Pu, X. Wang, Y. Shi, R. Shi, M. Yang, W. Wang, X. Guo, X. Peng, J. Mater. Sci. Mater. Electron. 31, 4345 (2020)
6. X. Zuo, E. He, Z. Hui, J. Bao, B. Yang, X. Zuo, J. Dai, J. Mater. Sci. Mater. Electron. 30, 16337 (2019)
7. S. K. Samantaray, S. R. Krishna, S. Rayaprol, P. D. Babu, J. Angadi, S. P. Kubrin, B. Angadi, J. Phys. Condens. Matter 32, 425805 (2020)
8. K. Bhoi, S. Dash, S. Dugu, D. K. Pradhan, M. M. Rahman, N. B. Simhachalam, A. K. Singh, P. N. Vishwakarma, R. S. Katiyar, D. K. Pradhan, J. Appl. Phys. 130, 114101 (2021)
9. D. Dung, Y. Dung, N. Q. Hue, N. H. Ham, N. H. Thoan, V. N. Trung, N. D. Quan, D. Sangaa, D. Odkhuu, J. Electron. Mater. 47, 155425 (2006)
10. D. Dung, N. Q. Hue, N. H. Ham, J. Electroceram. 31, 3149 (2012)
11. R. Kumar, M. Kar, Ceram. Int. 42, 6640 (2016)
12. K. Bhoi, H. S. Mohanty, Ravi Kant, M. F. Abdullah, D. K. Pradhan, S. N. Babu, A. K. Singh, P. N. Vishwakarma, A. Kumar, R. Thomas, D. K. Pradhan, Sci. Rep. 11, 3149 (2021)
47. R. Amin, K. Samantaray, S. Ayaz, S.N. Sarangi, I. Bhaumik, S. Sen, J. Alloy. Compd. 897, 162734 (2022)
48. K.R. Hallam, J.E. Darnbrough, C. Paraskevoulakos, P.J. Heard, T.J. Marrow, P.E.J. Flewitt, Carbon Trends 4, 100071 (2021)
49. V.R. Mudinepalli, L. Feng, W.-C. Lin, B.S. Murty, J. Adv. Ceram. 4, 46 (2015)
50. N. Pandey, A.K. Thakur, R.N.P. Choudhary, Indian J. Eng. Mater. Sci. 5, 769–779 (2008)
51. A. Verma, A.K. Yadav, S. Kumar, V. Srihari, R. Jangir, H.K. Poswal, S. Biring, S. Sen, J. Mater. Sci. Mater. Electron. 30, 15005 (2019)
52. D.D. Dung, M.M. Hue, L.H. Bac, Appl. Phys. A 126, 533 (2020)
53. Y. Zhang, J. Hu, F. Gao, H. Liu, H. Qin, Comput. Theor. Chem. 967, 284 (2011)
54. L. Ju, C. Shi, L. Sun, Y. Zhang, H. Qin, J. Hu, J. Appl. Phys. 116, 083909 (2014)
55. J.M.D. Coey, A.P. Douvalis, C.B. Fitzgerald, M. Venkatesan, Appl. Phys. Lett. 84, 1332 (2004)
56. W. Zhou, H. Deng, L. Yu, P. Yang, J. Chu, J. Appl. Phys. 117, 194102 (2015)
57. J.B. MacChesney, H.J. Williams, J.F. Potter, R.C. Sherwood, Phys. Rev. 164, 779 (1967)
58. F. Wang, B.J. Dong, Y.Q. Zhang, W. Liu, H.R. Zhang, Y. Bai, S.K. Li, T. Yang, J.R. Sun, Z.J. Wang, Z.D. Zhang, Appl. Phys. Lett. 111, 122902 (2017)
59. D.V. Azamat, A. Dejneka, J. Lancok, V.A. Trepakov, L. Jastrabik, A.G. Badalyan, J. Appl. Phys. 111, 104119 (2012)
60. R. Hamdi, J. Khelifi, I. Walha, E. Dhahri, E.K. Hlil, J. Supercond. Nov. Magn. 32, 3679 (2019)
61. S. Raghuvanshi, F. Mazaleyrat, S.N. Kane, AIP Adv. 8, 047804 (2018)
62. M.J. Han, E.A. Eliseev, A.N. Morozovska, Y.L. Zhu, Y.L. Tang, Y.J. Wang, X.W. Guo, X.L. Ma, Phys. Rev. B 100, 104109 (2019)
63. D. Bahadur, R.A. Dunlap, Bull. Mater. Sci. 21, 393 (1998)
64. D.K. Pradhan, S. Kumari, P.D. Rack, Nanomaterials 10, 2072 (2020)
65. P. Jain, Q. Wang, M. Roldan, A. Glavic, V. Lauter, C. Urban, Z. Bi, T. Ahmed, J. Zhu, M. Varela, Q.X. Jia, M.R. Fitzsimmons, Sci. Rep. 5, 9089 (2015)
66. H.M. Jang, J.H. Park, S. Ryu, S.R. Shannigrahi, Appl. Phys. Lett. 93, 252904 (2008)
67. A.R. West, D.C. Sinclair, N. Hirose, J. Electroceram. 1, 65–71 (1997)
68. J.T.S. Irvine, D.C. Sinclair, A.R. West, Adv. Mater. 2, 132 (1990)
69. D.K. Pradhan, R.N.P. Choudhary, C. Rinaldi, R.S. Katiyar, J. Appl. Phys. 106, 024102 (2009)

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.