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Effect of NiO substitution on the structural and dielectric behaviour of NaNbO₃

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The structural and dielectric properties of NiO substituted NaNbO₃ ceramics are reported. The orthorhombic (*Pmna*) crystal structure of NaNbO₃ transforms to a lower symmetry monoclinic phase (*Pbma*) after the dilute dispersion of NiO. X-ray photoelectron spectroscopy reveals pentavalent “Nb,” monovalent “Na,” and divalent “Ni” states along with the signatures of non-local screening effects. The antiferroelectric to paraelectric transition (T_{AFE}) accompanied by a structural change from the orthorhombic to the tetragonal phase shifts by 55 °C toward the low-temperature side, whereas the morphotropic phase boundary ($T_{\text{O-M}}$) moves toward a higher temperature by 28 °C for nominal substitutions ($x \leq 0.10$). The generalized Lyddane-Sachs-Teller expression $\left(\frac{\epsilon_0 - \epsilon_\infty}{\epsilon_\infty}\right) = \left(\frac{\omega_l}{\omega_t}\right)^2$ and thermodynamic free energy models are employed to explain the anomalous behaviour of the temperature dependence of relative dielectric permittivity ($\epsilon_r(T)$) across T_{AFE} and $T_{\text{O-M}}$. The frequency dependence of ac-conductivity $\sigma_{ac}(\omega)$ follows the Jonscher power law ($\sigma_{ac} = \sigma(0) + A\omega^b$), suggesting the dominance of the phonon-assisted hopping mechanism, whereas the frequency independent term ($\sigma(0)$) was explained by Funke’s Jump-Relaxation Model. Published by AIP Publishing. <https://doi.org/10.1063/1.5013643>

I. INTRODUCTION

In the coming years, lead and lead-based ceramics will be gradually expelled from many commercial applications and materials owing to concerns regarding their toxicity.^{1–3} Among various lead-free materials, alkaline niobates (NaNbO₃ and KNbO₃) and their composites have drawn immense attention due to their promising applications in modern microwave electronic devices, sensors, piezoelectric actuators, etc.^{4–7} In 2004, Saito *et al.* reported the enhanced piezoelectric charge coefficient $d_{33} \sim 400$ pC/N in the Li and Ta doped K_{0.5}Na_{0.5}NbO₃ system which is competitive with that of the Pb(Zr_xTi_{1-x})O₃ system.¹ Among the above two alkali niobates, NaNbO₃ and its composites have drawn considerable attraction due to their wide range of applications including high-density optical data storage, hologram recording materials, and radio-telephone engineering.^{8–13} NaNbO₃ is the only perovskite that undergoes the most complicated temperature and pressure driven structural phase transitions which are not completely understood till date. The structural and dielectric behaviours of NaNbO₃ have been refined several times following the improvement of the characterization techniques for both single and polycrystalline samples.^{14–19} The low-temperature powder neutron diffraction measurements revealed the coexistence of ferroelectric and antiferroelectric phases over a wide temperature range and the anomalous smearing of dielectric permittivity over the temperature range (12 K $\leq$ T $\leq$ 350 K), consistent with the competing ferroelectric and antiferroelectric interactions.¹⁴

Recently, Almeida *et al.*²⁰ reported the population accumulation effect of silicate glasses containing NaNbO₃ nanocrystals useful for the optical limiting behaviour which finds applications in laser power regulation devices and stabilization of signal levels in optical data transmissions.²¹ The incorporation of In₂O₃ within the NaNbO₃ matrix exhibits enhanced photocatalytic activity which makes them a promising candidate for hydrogen fuel cells.²² Raevski *et al.* reported the diffuse first-order phase transition near 423 K in 9 at. % of Gd doped NaNbO₃ with a significant decrease in the domain size across this transition which is tunable by incorporating the Gd ions; also, dipoles of Gd ions contribute significantly to the frequency dependence of dielectric permittivity.^{23,24} However, the single crystals of 0.9NaNbO₃–0.1Gd_{1/3}NbO₃ exhibit different prehistories and dielectric aging in the low-frequency ranges with a smeared phase transition whose frequency dependent characteristics are different as compared with the standard relaxor ferroelectrics.²⁵ Titov *et al.* reported a dramatic decrease in the mean size of twin domains in (1– x)NaNbO₃ + x Gd_{1/3}NbO₃ with an increasing Gd content (x) as observed using the Metripol microscope system.²⁶ When x exceeds a certain threshold value $x_c \approx 0.11$, an abrupt drop occurs in the permittivity maximum $\epsilon(T)$ by more than 100 K. These authors also noticed that the dielectric permittivity maximum ($\epsilon_r \geq 1600$) diffuses markedly with an increase in the value of “ x ” due to the difference in the sizes of Na⁺ and Gd³⁺ ions.²⁶ In the case of (1– x) NaNbO₃ – x BiCrO₃ ceramics, a mixed phase consisting of both perovskite and the pyrochlore lattice was noticed by Hsiao *et al.*²⁷ Increasing the heat treatment conditions from 1223 K (for 5 h) to 1523 K (for

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3 h) reveals that there is a reduction in the pyrochlore content in the mixed phases for the compositions between 0.1 and 0.4.²⁷ For $x=0.4$, a very high ($\sim 10^4$) magnitude of ϵ_r with less dissipation (<1) values was observed across 323 K in the NaNbO_3 - BiCrO_3 composites.²⁷

The doping of transition metals such as Ti, Mn, Co, Ni, or Cu inside the NaNbO_3 matrix has generated great interest because of their ability to alter their band structure and electrical conductivity.^{28–33} Molak *et al.* reported that Mn-doped NaNbO_3 exhibits nine orders change in the resistance (10^{13} – $10^4 \Omega$) without altering its antiferroelectric behaviour.³³ These authors observed the activation energy $E_a = 0.08$ eV in the temperature range of 290 K–400 K and $E_a = 0.5$ eV– 0.6 eV for $T > 450$ K. Such a change in the magnitude of E_a is associated with the energy levels introduced by the Mn dopant and/or due to oxygen vacancies.³³ On the other hand, the two-phase composites of binary transition metal oxides (TMO) can exhibit very high dielectric permittivity, and such systems have seen great interest for gas sensor applications.^{30–35} For example, Wu *et al.* reported giant relative dielectric permittivity ($\epsilon_r > 10^5$) near room temperature in $\text{Li}_{0.05}\text{Ti}_{0.02}\text{Ni}_{0.93}\text{O}$ due to an enhanced grain-boundary layer mechanism across the periphery of the capacitor geometry layers.³⁴ Similarly, some recent studies reported colossal dielectric permittivity in donor-acceptor (Nb, In) co-doped rutile TiO_2 and in (Li, In) doped ZnO .^{36,37} By increasing the Nb doping concentration in TiO_2 ceramics, two different dielectric responses were observed by Li *et al.* in the frequency dependence of dielectric properties which are associated with the space charge polarization and the electron-pinned defect-dipole effect.²⁹ Focusing on the antiferroelectric NaNbO_3 system, very limited literature is available dealing with the doping of TMOs inside NaNbO_3 . Erüinal *et al.* reported that at low sintering temperatures ($\sim 937^\circ\text{C}$), Na_3NbO_4 emerges out as a secondary phase when 0.25 mol. % Cu^{2+} doped in NaNbO_3 . This system exhibits a distinctly diverse stoichiometry with two kinds of mutually compensating defect structures as represented by the Kroger-Vink notation $(\text{Cu}_{\text{Nb}}''' - \text{V}_\text{O}'')$ and $(\text{V}_\text{O}'' - \text{Cu}_{\text{Nb}}''' - \text{V}_\text{O}'')$.³⁸ In this notation, the subscript indicates the lattice site occupied by the defect and the superscript corresponds to the electronic charge of the defect. The $''$ symbol indicates a single positive charge, and the $'$ symbol signifies a negative charge.

The electron paramagnetic resonance studies of $\text{Na}_{0.98}[\text{Nb}_{0.9975}\text{Cu}_{0.0025}]\text{O}_3$ and $\text{Na}(\text{Nb}_{0.9975}\text{Cu}_{0.0025})\text{O}_3$ systems reveal the quartet hyperfine coupling of $S = 1/2$ spin with the nucleus of isospin $I = 3/2$, indicating the $3d^9$ electronic configuration of Cu^{2+} .³⁸ Nevertheless, the two-phase composites comprising antiferromagnetic NiO and antiferroelectric NaNbO_3 have not been investigated till now. Both the systems (NiO and NaNbO_3) exhibit structural transitions above room temperature, one can tune such transitions for the modern electronic applications such as ferroelectric memories and magneto-electronic devices. Such structural transitions are usually accompanied by a change in the long-range ferroic-order (antiferromagnetic/ferrielectric) to a disordered (para-magnetic/para-electric) state.³⁹ In particular, NiO exhibits a high temperature cubic to low temperature rhombohedral phase transition across 250°C , which plays an important role in the development of spin-valve devices, and NaNbO_3 exhibits a series of transitions below 480°C , e.g., orthorhombic to tetragonal

across 480°C and tetragonal to cubic at 370°C .^{39–41} Therefore, an attempt has been made here to study the structural and dielectric behaviours of $(1-x)\text{NaNbO}_3 + x\text{NiO}$ two-phase composites over a wide composition range ($0.05 \leq x \leq 0.95$), which shows some intriguing dielectric properties. Our results show the evidence of the change in the crystal structure of NaNbO_3 from orthorhombic ($Pmna$) to monoclinic ($Pbma$) after the incorporation of NiO in the NaNbO_3 matrix. The frequency variation in the ac-electrical conductivity of NaNbO_3 -NiO composites was explained on the basis of Jonscher's power law of phonon-assisted hopping and Funke's Jump-Relaxation Model. A systematic engineering of the morphotropic phase boundary in the temperature window of 20 – 55°C with NiO doping may open a constructive approach for near room temperature applications including spin-valve devices.

II. EXPERIMENTAL DETAILS

Various compositions of $(1-x)\text{NaNbO}_3 + x\text{NiO}$ ($0 \leq x \leq 1$) samples were prepared by the standard solid state reaction method using a stoichiometric amount of sodium niobate (NaNbO_3) and nickel oxide (NiO). For the synthesis of pure NaNbO_3 , highly pure potassium carbonate (Na_2CO_3 , EMPLURA, $\geq 99\%$) and niobium pentoxide (Nb_2O_5 , SRL Pvt. Ltd., $\geq 99.95\%$) were taken as starting materials. Appropriate amounts of these materials were mixed and blended by the ball-milling method for 5 h with distilled water as the milling medium. The obtained products were heated above 100°C in air overnight to remove the water content and then calcined at 700°C for 4 h in air to obtain pure NaNbO_3 . Stoichiometric amounts of pure NiO powder were added to pure NaNbO_3 for different desired compositions of $(1-x)\text{NaNbO}_3 + x\text{NiO}$ [$0.10 \leq x \leq 0.95$] two phase composites. These mixed powders were pressed into cylindrical pellets of diameter ~ 13 mm using a hydraulic press with a maximum load of 5 ton per cm^2 . All these pellets were finally sintered at 1040°C for 4 h in air.

The phase purity and crystal structure were examined using X-ray diffraction (XRD) measurements using a Rigaku X-ray diffractometer (model: TTRAX-III) with Cu-K_α radiation ($\lambda = 1.54056 \text{ \AA}$), followed by Rietveld refinement of the obtained diffraction patterns by means of the FullProf programme. The microstructure of the samples was examined using a field emission scanning electron microscope (FESEM, Sigma, Zeiss) using a secondary electron mode. For the elemental analysis of the samples, a dual source X-ray photoelectron spectroscope (XPS, Al- K_α at 1486.8 eV and Mg- K_α at 1253.6 eV) from VG Microtech equipped with an ultra-high vacuum (8×10^{-10} Torr) chamber with a pass energy of 100 eV was employed. The XPS spectra were recorded using monochromatized Al- K_α radiation, and the binding energies were calibrated against the advantageous C-1s peak 294 eV. For the dielectric measurements, two sides of the sintered pellet were fashioned into a parallel-plate electrode geometry using silver coating. An impedance analyzer from Solartron (Model SI1260) was used for the dielectric measurements in the frequency range of 100 Hz– 20 MHz with the 100 mV ac peak-to-peak amplitude of the electric field.

III. RESULTS AND DISCUSSION

A. Phase evolution and micro-structural analysis

Figure 1 shows the XRD pattern of the composites $(1-x)$ $\text{NaNbO}_3 + x$ NiO for different compositions ($0 \leq x \leq 1$) recorded at room temperature. The Rietveld refinement data for these diffraction patterns are shown in the [supplementary material](#) (Fig. s1). For dilute substitution of NiO (" x " < 0.10), all the diffraction patterns are analogous to the orthorhombic crystal structure similar to that of pure NaNbO_3 without any significant deviation in the lattice parameters and bond angles. All these diffraction patterns were corresponding to the space group $Pbcm$ (57). However, with an increase in the composition, a slight increase in the lattice parameters ($a = 5.51 \text{ \AA}$, $b = 5.52 \text{ \AA}$, and $c = 15.58 \text{ \AA}$) was noticed when compared with the standard values of NaNbO_3 ($a = 5.50 \text{ \AA}$, $b = 5.56 \text{ \AA}$, and $c = 15.58 \text{ \AA}$) (Fig. 2). This change in the lattice parameter is expected with the increase in the dopant concentration because the divalent Ni^{2+} ions (ionic radius, $r_{\text{Ni}^{2+}} = 0.69 \text{ \AA}$) are likely to occupy the Nb sites (ionic radius, $r_{\text{Nb}^{5+}} = 0.64 \text{ \AA}$) in the octahedra. As the composition " x " increases, the diffraction peaks corresponding to the rhombohedrally distorted NiO become more prominent (the Miller indices are indexed in red color in Fig. 1); this secondary phase has been refined using the space group $R-3m$ (166). It is interesting to observe that the diffraction peak at the Bragg angle $2\theta \sim 46.55^\circ$ (220) splits into a doublet

FIG. 1. The X-ray diffraction data of $(1-x)$ $\text{NaNbO}_3 + x$ NiO samples for (a) $x = 1.0$, (b) $x = 0.7$, (c) $x = 0.3$, (d) $x = 0.1$, and (e) $x = 0.0$, sintered at 1040°C for 4 h in air. The blue color Miller indices (#) represent the lattice plane of NaNbO_3 , and the red color Miller indices (\$) represent the lattice plane of NiO .

FIG. 2. Variation in the lattice parameters and volume of the unit cell for the $(1-x)$ $\text{NaNbO}_3 + x$ NiO composite with a change in the NiO concentration (x). The inset shows the variation in the density (ρ) of the unit cell with a change in x .

corresponding to the Miller indices (220) and (002) for $x = 0.10$ and $x = 0.30$ (as shown in Fig. 3). Such peak-splitting usually occurs due to the significant distortion from the orthorhombic crystal structure and transfers to a lower-symmetry monoclinic structure due to the cationic displacement.^{42,43} Hence, the threshold between orthorhombic and monoclinic crystal symmetry for the NaNbO_3 - NiO composite lies in between $x = 0.3$ and $x = 0.5$.

Previous studies reported a similar type of peak-splitting across $2\theta \sim 45.7^\circ$ in Li-doped KNbO_3 and NaNbO_3 and Li/Ta co-doped KNbO_3 and NaNbO_3 .⁴⁴ Some other ferroelectric systems such as $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ and $\text{Pr}_{0.5}\text{Eu}_{0.5}\text{MnO}_3$ also undergo such lower symmetry structural phase transitions; in

FIG. 3. Diffraction peak at Bragg angle $2\theta \sim 46.55^\circ$ (220) splitting from (a) $x = 0.0$ to the doublet corresponding to the Miller indices (220) and (002) for (b) $x = 0.1$ and (c) $x = 0.3$.

particular, the tetragonal crystal structure transforms to the monoclinic phase.⁴⁵ In the present case, we observed that the interaxial angle “ β ” deviates from 90.0° to 90.19° as the composition increases from 0.10 to 0.30, along with the decrease in the lattice parameter, which is due to the structural transition from tetragonal to monoclinic. Such distortions were not traceable in these composites for the $x \geq 0.50$ system due to the domination of the rhombohedral NiO phase, and for $x \geq 0.80$, the signature of NaNbO₃ peaks gradually diminishes and completely vanishes. From Fig. 2, it can be noticed that the lattice parameter ‘ a ’ decreases with an increase in x from 0.0 to 0.50, whereas the c -axis increases with a gradual decrease in the volume of the unit cell. Since the ionic radius of the octahedrally occupied divalent Ni²⁺ ion ($r_{\text{Ni}^{2+}} \sim 0.69 \text{ \AA}$) is greater than the ionic radius of the pentavalent Nb⁵⁺ ion ($r_{\text{Nb}^{5+}} \sim 0.64 \text{ \AA}$), one can expect larger unit cell parameters for the current investigated two-phase composites. Using the Rietveld refinement data, we have also calculated the density of the unit-cell for different concentrations of NiO ($0 \leq x \leq 1$) of the $(1-x)$ NaNbO₃ + x NiO two-phase composites (as depicted in the inset of Fig. 2). A significant increase in the unit-cell density from 4.58 gm/cm^3 to 6.42 gm/cm^3 for $x=0$ to 0.50 was noticed due to the incorporation of NiO in the NaNbO₃ matrix. The average grain size (D) and micro-strain (η) have been estimated using the Williamson-Hall (W-H) analysis using the equation $\beta \cos(\theta) = \kappa\lambda/D + \eta \sin(\theta)$, where β is the full width at half maximum (FWHM) of diffraction peak intensity, and the constant “ κ ” represents the shape parameter ($=0.89$ assuming that the particles are spherical), and λ is the wavelength ($=1.5406 \text{ \AA}$) of Cu-K _{α} X-ray

radiation. The average grain size “ D ” (73–490 nm) and micro-strain ($\eta \sim 10^{-3}$) have been obtained from the intercepts and slopes of the W-H plots of $\beta \cos(\theta)$ versus $\sin(\theta)$ (not shown) for different compositions of $(1-x)$ NaNbO₃ + x NiO. As the NiO concentration increases, the FWHM of the diffraction peaks increases, which signifies the contribution of a decrease in the grain size and an increase in the lattice strain in the NaNbO₃-NiO composites, similar to the other systems, e.g., CdO-ZnO and NiO-ZnO composites.^{32,46–50}

The FESEM micrographs [Figs. s2(a) and s2(b) in the [supplementary material](#)] were recorded in the secondary-electron (SE) mode for $x=0.10$ and 0.95 , respectively. These micrographs depict the polygonal shape morphology of average grain sizes $\sim 344 \text{ nm}$ and 380 nm , with clear grain boundaries of widths $\sim 42 \text{ nm}$ and $\sim 53 \text{ nm}$ for $x=0.10$ and 0.95 , respectively. In order to understand the detailed and precise distribution of the grains in $(1-x)$ NaNbO₃ + x NiO ($x=0.10$ and 0.95) two phase composites, a thorough statistical analysis has been carried out. The inset of Figs. s2(a) and s2(b) ([supplementary material](#)) represents the histograms of the particle size distribution of those two-phase composites in which a maximum number of particles lie in the range $350\text{--}400 \text{ nm}$ and $300\text{--}400 \text{ nm}$ for $x=0.10$ and 0.95 , respectively.

B. X-ray photoelectron spectroscopy

The electronic structure of the synthesized composites was investigated by using XPS. The entire XPS spectrum for O-1s, Na-1s, Ni-2p, and Nb-3d core levels was calibrated by

FIG. 4. The core level X-ray photoelectron spectra of (a) Na-1s, (b) Nb-3d, (c) Ni-2p, and (d) O-1s core-level spectra of $(1-x)$ NaNbO₃ + x NiO for $x=0.70$.

using the binding energy (BE) of advantageous carbon (C-1s) orbitals positioned at 284 eV.^{51–54} Figure 4(a) shows the X-ray photoelectron intensity versus binding energy (BE) spectra of the Na-1s core levels for $x = 0.70$. From the figure, we observe that Na-1s spectra exhibit a single peak centered at 1070.22 eV, indicating that “Na” ions have a +1 oxidation state.^{55–57} The 3d-core-level XPS spectra of Nb [Fig. 4(b)] exhibit two peaks associated with the 3d doublet states $3d_{5/2}$ and $3d_{3/2}$ without any signatures of satellite peaks, signifying the presence of pentavalent oxidation of Nb. On the other hand, the XPS spectra of Ni-2p show four peaks between 853.96 eV and 879.05 eV [Fig. 4(c)]. This spectrum is further deconvoluted into five Gaussian-Lorentzian (GL) peaks centered at 845.47 eV, 853.96 eV, 860.35 eV, 871.78 eV, and 879.05 eV, respectively. The two main peaks centered at 853.96 eV and 871.78 eV are associated with the doublets Ni- $2p_{3/2}$ and Ni- $2p_{1/2}$, respectively.^{51–54} The binding energy separation (ΔE) between these doublets ($\Delta E = E_{p_{1/2}} - E_{p_{3/2}}$) is 17.82 eV, signifying the presence of the divalent oxidation state of Ni.^{51–54,58} This binding energy difference is slightly higher as compared with the binding energy of the metallic state of Ni (~ 17.4 eV), however, less than the stoichiometric value of pure NiO (~ 18 eV).^{51–54,58} Along with these two main peaks, we also observed additional three more satellite peaks centered at 845.47 eV, 860.35 eV, and 879.05 eV designated by S1, S2, and S3 in Fig. 4(c), respectively. These satellite peaks are shifted toward the lower binding-energy scale as compared with pure NiO.^{53,59} This shift in the satellite peaks is associated with the non-local screening of Ni²⁺. The charge transfer nature of the valance band states leads to the screening of Ni²⁺, which can be analyzed in terms of a simplified model based on final state effects where photoemission is accompanied by the rearrangement of electrons in the valance band⁶⁰

$$2p^6 3d^8 + h\nu \rightarrow 2p^5 3d^8 + e^-, \quad (1)$$

$$2p^5 3d^8 + e^- \rightarrow 2p^5 3d^9 L + e^-, \quad (2)$$

where “L” represents a hole in the O-2p band. Using this model, the main Ni- $2p_{3/2}$ peak is observed across ~ 853.9 eV associated with the local screening of lattice oxygen along with a satellite peak at 860.3 eV caused by the non-local screening effect.^{59,60} Finally, the O-1s XPS spectrum shown in Fig. 4(d) is partially resolved into three GL peaks centered at 528.93 eV, 530.86 eV, and 533.09 eV, which indicates that oxygen is in a different environment in the NaNbO₃-NiO composites.^{37,38} The main peak centered at ~ 528.93 eV arises due to the oxygen bonded with the cations, i.e., Na⁺, Nb⁵⁺, and Ni²⁺, whereas the second peak at 530.86 eV is related to the surface oxygen presence in the system with a small amount of vacancies.^{61–63} The third peak at 533.09 eV may correspond to the additional oxygen present in the system in the form of a hydroxyl group adsorbed by Na or Ni from the surface.⁶⁴

C. High temperature dielectric studies

In order to understand the role of NiO on the global dielectric behaviour of NaNbO₃, we measured the variation in

the relative dielectric permittivity ϵ_r as a function of temperature $\epsilon_r(T)$ at different frequencies of the ac-signal for two compositions $x = 0.10$ and 0.95 . Figures 5 and 6 show ϵ_r versus T measured between the temperatures 30 °C and 550 °C for different frequencies (f) in the range 5 kHz–20 MHz for $x = 0.10$ and $f = 100$ Hz–20 MHz for $x = 0.95$, respectively. Two major humps were observed in $\epsilon_r(T)$; the first hump appears across 520 °C and the second hump across 398 °C for $x = 0.10$ at low frequencies. These two transitions are associated with the antiferroelectric to paraelectric transition (T_{AFE}) and orthorhombic ($Pmna$) to monoclinic ($Pbma$) crystal structure transition (T_{O-M}) within the antiferroelectric region, respectively. For low frequencies, the antiferroelectric transition is more prominent than the crystallographic transition (the $\sim 21\%$ increase in the dielectric permittivity was noticed). For the case of undoped NaNbO₃, the above transitions take place at 570 °C and 375 °C, clearly indicating the dominant role of antiferromagnetic NiO, signifying the effect on the antiferroelectric long range ordering. These transitions are strongly dependent on the ac-driving frequency; in particular, T_{AFE} for these composites gradually smeared-off with an increasing frequency from 5 kHz to 1 MHz (indicated by the red color up-arrow in Fig. 5), whereas the structural transition T_{O-M} shifts from 398 °C to 345 °C as the measuring frequency increases from 5 kHz to 1 MHz.

It is interesting to note that a feeble anomaly close to 170 ± 5 °C was observed for the $x = 0.10$ composite (Fig. 5). A similar type of anomaly was reported previously by Shirane *et al.* in NaNbO₃ with a small amount of ferroelectric KNbO₃.⁴⁰ Raevski *et al.* reported such a weak anomaly across 150 °C in $\epsilon_r(T)$ of single crystals of NaNbO₃, (Na,Li)NbO₃, and (K,Na)NbO₃ solid solutions. From the temperature dependence of lattice parameters [$a(T)$, $b(T)$, and $c(T)$], these authors concluded that such an additional phase transition in the vicinity of second-order transition is due to the rhombohedral

FIG. 5. Temperature dependent relative dielectric permittivity $\epsilon_r(T)$ measured at various frequencies ($5 \text{ kHz} \leq f \leq 1 \text{ MHz}$) for NaNbO₃ + 0.10 NiO with very closely spaced temperature intervals ($T = 3$ °C) and temperature ranging from 30 °C to 550 °C. The inset shows the temperature dependence of dissipation factor $\text{Tan} \delta$ recorded for the same range of frequencies. The encircled region shows the feeble anomaly that emerged at $T \sim 170$ °C.

FIG. 6. Log-scale representation of temperature dependent relative dielectric permittivity $\epsilon_r(T)$ measured at various frequencies ($100 \text{ Hz} \leq f \leq 20 \text{ MHz}$) for $\text{NaNbO}_3 + 0.95 \text{ NiO}$ with very closely spaced temperature intervals ($T = 2^\circ \text{C}$) and temperature ranging from 50°C to 550°C . The inset (i) shows the variation in the same in linear scale. The inset (ii) shows the temperature dependence of dissipation factor $\text{Tan} \delta$ recorded for the same range of frequencies.

distortion of the perovskite structure (1% lattice hysteresis between $a(T)$ and $b(T)$ across 150°C with a change in the interaxial angle $\Delta\beta \sim 0.3$).^{65,66} On the other hand, the temperature dependence of loss tangent ($\text{Tan} \delta$ vs. T) shows a cusp like feature across 279°C and increases continuously beyond this temperature (inset of Fig. 5); across the same, ϵ_r starts rising. For $x = 0.95$, the giant values of $\epsilon_r(T)$ were noticed for all the frequencies with a very broad maximum in $\epsilon_r(T)$ [inset (i) of Fig. 6] where a major contribution from NiO is anticipated. Moreover, the transitions pertaining to NaNbO_3 ($T_{\text{O-M}}$ and T_{AFE}) were untraceable in Fig. 6, and the global dielectric behaviour is dominated by NiO. Interestingly, a shoulder-like feature is evident between 250°C and 320°C [indicated by the arrow mark in the inset (i) of Fig. 6], which is linked with the antiferromagnetic to paramagnetic transition of NiO; such a change in the magnetic ordering is usually accompanied by the structural change from the rhombohedral to high temperature cubic crystal structure of NiO. In the case of undoped NiO (with perfect stoichiometry), such a transition usually occurs across $253 \pm 6^\circ \text{C}$.^{30,67} The temperature dependence of loss tangent for $x = 0.95$ [inset (ii) of Fig. 6] exhibits a giant frequency independent peak centered at 314°C associated with the change in the crystal structure and magnetic ordering as discussed above. Nevertheless, the additional phase transition noticed across 170°C for lower compositions ($x \leq 0.10$) is very feeble in the $x = 0.95$ system due to the dominance of the antiferromagnetic NiO.

The divergence of $\epsilon_r(T)$ across the ferroelectric phase transition is directly connected with the softening of the phonon mode and can be explained by the Lyddane-Sachs-Teller (LST) relation. The generalized LST relation contains all the dielectric dispersion terms

$$\left(\frac{\epsilon_0 - S'}{\epsilon_\infty} \right) = \left(\frac{\omega_l}{\omega_t} \right)^2, \quad (3)$$

where ϵ_0 and ϵ_∞ are static and high frequency dielectric permittivities, respectively, and S' is the strength of the permanent dipole moments.⁶⁸ As the ferroelectric transition is approached, the suppression of long-range harmonic modes occurs and a short-range anharmonic ordering takes place, leading to the softening of optical phonon frequencies ($\omega_l \rightarrow 0$).⁶⁸ Under these circumstances, the high frequency dielectric permittivity (ϵ_∞) attains its maximum value. Such a singular behaviour of “ ϵ_r ” can also be understood from the thermodynamic free energy model: the nonlinear free energy expression contains the terms polarization P and temperature T in the form ($F(T, P) = F_0(T) + AP^2 + BP^4 + CP^6$), where A , B , and C are the phenomenological coefficients.⁶⁸ According to the theoretical description given by Landau and Lifshitz, the coefficients “ A ” and “ T ” are linked to the dielectric constant as given by the following relation:⁶⁹

$$\epsilon = \frac{1}{\left(\frac{\partial^2 F}{\partial T^2} \right)_{P=0}} = \frac{1}{2A}. \quad (4)$$

Across the phase transition, coefficient “ A ” $\rightarrow 0$ leads to the divergence in dielectric constant.⁶⁹ Although the validity of the above equation is for a second-order phase transition, even for a first-order phase transition, the magnitude of “ A ” significantly drops from its maximum value but does not vanish completely.

D. Frequency dependence of ac-conductivity

In order to understand the frequency ($1.5 \text{ kHz} \leq f \leq 13 \text{ MHz}$) dependence of the charge transport mechanism in the present composite system, we measured the ac-conductivity σ_{ac} at various temperatures with 100 mV constant peak-to-peak driving potential of varying frequency. The scattered symbols shown in Figs. 7(a) and 7(b) are the frequency dependence of σ_{ac} values obtained experimentally for both $x = 0.10$ and 0.95 . In the present case, $\sigma_{ac}(f)$ was plotted only for selected temperatures between 30°C and 540°C . In Fig. 7, solid lines represent the best fit of the experimental data with Jonscher’s universal power law (JPL) ($\sigma_{ac} = \sigma(0) + A\omega^s$).^{70,71} In this equation, the quantity $\sigma(0)$ is the frequency independent conductivity, the coefficient “ A ” is the dispersion parameter, and the dimensionless frequency exponent “ s ” represents the measure of the degree of the interaction and is a temperature dependent parameter. For ceramics and high- k dielectric composites, the above-mentioned power law is extensively used to understand the frequency dependent behavior although different models are available in the literature.^{34,67,72} For the general case, the value of “ s ” should lie between 0 and 1, popularly known as the “universal dielectric response” (UDR).^{71,73,74} Some systems also follow the double power law behaviour with $s > 1$.^{75–77}

From Fig. 7, it can be observed that for both the compositions, ac-conductivity σ_{ac} increases with an increase in the frequency, signifying the trapping of localized charge carriers. The origin of the frequency dependence of conductivity lies in the relaxation phenomena arising due to the mobile

FIG. 7. The log-log plot of ac-conductivity (σ_{ac}) against angular frequency (ω) measured at various temperatures for (a) $x=0.10$ and (b) $x=0.95$. The inset shows the variation in the frequency exponent “ s ” calculated from Jonscher’s universal power law.

charge carriers. Generally, at low frequencies, there exists a frequency independent plateau region [i.e., dc-conductivity $\sigma(0)$]; however, for $x=0.10$, the frequency independent $\sigma(0)$ plateau region is not clearly visible since the measurements were performed between the frequencies 1.5 kHz and 1 MHz [for many polycrystalline systems, $\sigma(0)$ is dominated for $f < 1$ kHz (Ref. 78)] At low frequencies [the plateau region in Fig. 7(b)], the charge conduction process occurs through infinite paths via long-range translational motion of the charge carriers. This behaviour can be explained using the jump relaxation model. According to this model, the electrons undergo successful hopping to its neighbouring vacant site at low frequencies for a long time period and lead to the long range translational motion of charge carriers which contributes to the dc-conductivity $\sigma(0)$.

On the other hand, in the frequency dependence region, the charge transport occurs mainly by hopping of the charges. In the present case for $f > 7$ kHz, two competing relaxation processes occur; (i) successful hopping where the charge carriers relax into its neighborhood site and (ii) unsuccessful hopping where the charge carrier jumps back to its initial position. The ratio of successful hopping over unsuccessful hopping creates the dispersion in conductivity at high frequencies, and the term $A\omega^s$ dominates. In most polycrystalline samples, two different dispersion regimes can be observed in $\sigma_{ac}(T)$. Such regions are associated with the grain boundaries

(low-frequency dispersion) and grains (high-frequency dispersion) which can be explained by the double power law

$$\sigma_{ac} = \sigma(0) + A_1\omega^{s_1} + A_2\omega^{s_2}. \quad (5)$$

In the above equation, the second term $A_1\omega^{s_1}$ ($0 \leq s_1 \leq 1$) is assigned to the low frequency dispersion region ($2 \text{ kHz} \leq f \leq 3 \text{ MHz}$) corresponding to the short-range hopping process, whereas the contribution of the third term $A_2\omega^{s_2}$ ($0 \leq s_2 \leq 2$) is significant in the high frequency region ($f > 3 \text{ MHz}$) which is associated with the hopping of charge carriers back and forth between the localized states. From the linear fitting analysis ($\sigma = A\omega^s$), we obtained the values of “ A ” and “ s ” for the two compositions, and these values are listed in Table I. The temperature dependence of the experimentally determined “ s ” values can be used to examine the validity of charge transport by a specific hopping model for the current system.^{79–82} For example, if the transport is through the variable range hopping mechanism, the magnitude of the exponent $s \sim 0.8$ is expected which is consistent with the current result $0.838 \leq s \leq 0.974$ for $x=0.10$.^{30,80} Nevertheless, a significant deviation is often observed from the standard power-law behaviour ω^s for $x > 0.10$, which is associated with the feeble frequency dependence of the exponent s .^{79,80}

The variation in “ s ” as a function of temperature for both the compositions is shown in the inset of Figs. 7(a) and 7(b). Generally, the conduction behavior exhibits a remarkable relationship with the obtained exponent “ s .” The temperature independent behaviour of “ s ” suggests that the charge transport process is mainly dominated by tunneling of the charge carriers by thermal energy.⁷⁶ Previous reports on the frequency and temperature dependent ac-conductivity studies of the NaNbO_3 system reveal that the “ s ” values derived from the power law lie between 0.15 and 0.44.⁷⁶ These values signify that the charge conduction mechanism is dominated by the small and large polaron hopping process with a high effective mass of electron m_e^* due to the localization of electrons.⁷⁶ For small polaron hopping conduction, the value of “ s ” increases with temperature, while for large polaron hopping, “ s ” decreases with an increase in the temperature. For $x=0.10$, we noticed three different regions in the $s(T)$ curve [inset of Fig. 7(a)]: from 30°C to 60°C (Region-I), from 60°C to 310°C (Region-II), and from 310°C to 520°C (Region-III). It is clearly evident that in the plateau region-II, “ s ” is almost independent and decreases to 0.83 on either sides of the temperature window. From this analysis, we conclude that the conduction mechanism below 60°C is mainly dominated by the hopping of small

TABLE I. The list of measured parameters “ A ” and frequency exponent “ s ” obtained from Jonscher’s power law analysis for $x=0.10$ and $x=0.95$.

T (°C)	$x=0.10$		$x=0.95$	
	s	$A \times 10^{-11}$	s	$A \times 10^{-11}$
50	0.932	29.768	0.81	13.13
100	0.974	16.485	1.04	0.460
304	0.971	34.759	1.32	0.013
500	0.845	340.17	1.41	0.006

polareons. In the present system (for $x = 0.10$), the formation of small polareons occurs due to the incomplete d -orbital of Nb^{4+} caused by the oxygen vacancies above room temperature, reducing Nb^{5+} to Nb^{4+} . With an increase in the temperature ($> 310^\circ\text{C}$), these small polareons dissociate into residual carriers and interact with the positive ions present in the system. Such an interaction between the lattice and charges leads to the formation of large polareons whose mobility is inversely proportional to the square root of temperature ($\propto T^{-1/2}$). Due to this interaction, the slope of the $s(T)$ curve decreases significantly. For a very high composition, $x \geq 0.95$ [inset of Fig. 7(b)], we observed the UDR behaviour in Region-I from 50°C to 100°C (with “ s ” values between 0.81 and 1.04), whereas the double power law behaviour was noticed in three different temperature regimes: Region-II from 100°C to 280°C (1.04 to 1.15), Region-III from 280°C to 450°C (1.15 to 1.36), and Region-IV from 450°C to 540°C (1.36 to 1.61). Normally, the ac-component of $\sigma(\omega)$ in JPL exhibits a weaker temperature dependence than the $\sigma(0)$ dc part, which often follows a thermally activated Mott’s variable-range-hopping process.^{79,80} Recent studies dealing with the temperature and frequency dependent ac-conductivity of KNbO_3 based composites reported the dominance of Mott’s variable range hopping of charge carriers between Nb^{5+} and Nb^{3+} ions.⁶⁷

Figures 8(a) and 8(b) show the temperature dependence of ac-resistivity $\rho_{ac}(T)$ measured at various frequencies ($1.5\text{ kHz} \leq f \leq 1\text{ MHz}$) for $x = 0.10$ and for frequencies

FIG. 8. Temperature variation in ac-resistivity [$\rho_{ac}(T)$] for (a) $x = 0.10$ and (b) $x = 0.95$ for frequency ranging between 1.5 kHz and 13 MHz.

($126\text{ kHz} \leq f \leq 13\text{ MHz}$) for $x = 0.95$, respectively. For $x = 0.10$, the system exhibits a large value of resistivity $\rho_{ac} \sim 10^5\ \Omega\text{m}$ at room temperature for $f = 1.5\text{ kHz}$. As the temperature increases, ρ_{ac} starts to decrease and exhibits a sudden drop across 350°C [as shown by the arrow mark in Fig. 8(a)] due to the phase-transition from the monoclinic to the orthorhombic crystal structure of NaNbO_3 . Additionally, a small hump across T_{AFE} was noticed, which is associated with the antiferroelectric to paraelectric transition of NaNbO_3 .⁸³ For the higher compositions ($x \geq 0.95$), the $\rho_{ac}(T)$ curves exhibit a hundred fold drop across 210°C due to the intermixture of antiferromagnetic domains of NiO with the morphotropic phase boundary of the NaNbO_3 matrix.^{30,67} In order to understand the charge conduction mechanism in these composites, we further analyzed the temperature dependence of ac-resistivity data in detail. Figure 9 shows the plots of $\ln(\rho_{ac})$ against $T^{-1/4}$ for selected frequencies for both the compositions $x = 0.10$ and 0.95 . The linear behaviour of these curves provides the signature of Mott’s variable-range hopping of charge carriers; this result supports the frequency dependence of σ_{ac} analysis discussed above. According to this model, the charge conduction mechanism should follow the relation $\rho = \rho_0 e^{(T_0/T)^n}$, where ρ_0 is the pre-exponent factor, “ n ” is the exponential factor, and T_0 is the characteristic temperature

FIG. 9. Logarithmic variation in ac-resistivity [$\ln(\rho)$] versus $T^{-1/4}$ for (a) $x = 0.10$ and (b) $x = 0.95$ for few selected frequencies.

coefficient. These parameters were extracted from the intercepts and slopes of the logarithmic plots shown in Fig. 9.^{30,84}

The variation in the exponential factor “ n ” in the above equation decides the nature of the hopping process and the validity of the variable-range hopping mechanism in which the value of “ n ” should be approximately -0.25 .^{85,86} In order to confirm this, we have plotted the double logarithm curves of (ρ/ρ_0) as a function of $\ln(T)$ (shown in Fig. 10). Consequently, the magnitude of the slope obtained from the above graphs was found to be ~ -0.25 , affirming the validity of equation $\rho = \rho_0 e^{(T_0/T)^n}$ and thus providing substantial evidence to variable-range hopping of charge carriers for both the systems $x = 0.10$ and 0.95 . Usually, the formation of localized charge carriers (generated by the defects such as oxygen vacancies and interstitial Ni^{3+} ions) plays a major role in the hopping conduction mechanism.^{30,65} These localized charge carriers accumulated across the Fermi level and provide a finite number of electronic states near the Fermi level. The density of electronic states ($N(\xi_F)$) near the Fermi level depends upon the characteristic temperature T_0 (obtained from the slope of Fig. 9) which is given by the relation $N(\xi_F) = 16 \alpha^3/k_B T_0$. In this relation, the decay length α^{-1} signifies the spatial extension of the wave function $e^{-(\alpha R)}$. Moreover, using the magnitude of $N(\xi_F)$, we have calculated the average hopping length r_h and hopping energy ϵ_h using the expressions^{30,67}

$$r_h = \left[\frac{3}{2\pi\alpha N(\xi_F) k_B T} \right]^{1/4}, \quad (6)$$

$$\epsilon_h = \left[\frac{3}{4\pi\alpha N(\xi_F) r_h^3} \right]. \quad (7)$$

All the calculated values of $N(\xi_F)$, r_h , and ϵ_h are listed in Table II. For $x = 0.10$, the average hopping length (r_h) decreases from 1.78 nm to 1.68 nm as the frequency increases from 1.5 kHz to 1 MHz. On the other hand, the addition of NiO significantly increases the average hopping length from 1.78 nm to 3.00 nm for $x = 0.10$ and 0.95 , respectively.

IV. SUMMARY

In summary, the incorporation of NiO inside the NaNbO_3 matrix ($x \geq 0.05$) leads to a significant lattice distortion from an orthorhombic ($Pmna$) to a monoclinic ($Pbma$) crystal structure at room temperature, which is associated with the off-center displacement of cations. The electronic structure and elemental analyses of these composites were studied by means of XPS, which provides evidence of pentavalent and monovalent nature of “Nb” [$3d_{5/2}$ (206.1 eV) and $3d_{3/2}$ (208.7 eV)] and “Na” [$1s$ (1070.2 eV)], respectively. However, the Ni-2p XPS spectra exhibits a doublet with binding energy separation ~ 17.82 eV, signifying the presence of a divalent state of Ni together with the satellite peaks centered at 853.96 eV and 879.05 eV. The temperature dependence of relative-dielectric permittivity $\epsilon_r(T)$ exhibits two cusps across 520°C (T_{AFE}) and 398°C ($T_{\text{O-M}}$) for lower compositions of NiO ($x \leq 0.10$). The first transition, T_{AFE} , is associated with the antiferroelectric to paraelectric transition, and the second one, $T_{\text{O-M}}$, is associated with the orthorhombic to monoclinic crystal structure transition. Along with these two major transitions, we noticed a feeble but lucid anomaly across 170°C in low-frequency $\epsilon_r(T)$ curves which accompanies the second-order transition. Such an anomalous change in $\epsilon_r(T < 200^\circ\text{C})$ is in-line with the previously reported ϵ_r vs. T data of undoped NaNbO_3 and NaNbO_3 mixed with a tiny amount of KNbO_3 .⁴⁰ For higher compositions of NiO ($x \geq 0.95$), all the above two transitions are merged into a single giant hump with ϵ_r as high as $\sim 10^7$.

Our results demonstrate that frequency dependent ac-conductivity $\sigma_{ac}(f)$ follows the JPL [$\sigma_{ac} = \sigma(0) + A\omega^s$], and the frequency independent term ($\sigma(0)$) behaviour was explained by using Funke’s Jump-Relaxation Model. For high frequencies ($f \geq 7$ kHz), a dispersive nature of σ_{ac} was observed mainly due to the competition between two different relaxation processes related to successful and unsuccessful

FIG. 10. The double logarithmic variation of (ρ/ρ_0) as a function of $\ln(T)$ for few selected frequencies for (a) $x = 0.10$ and (b) $x = 0.95$.

TABLE II. Listed below are parameters: density of states [$N(\xi_F)$], average hopping length (r_h), and average hopping energy (ϵ_h), obtained from VRH analysis for $x = 0.10$ and $x = 0.95$.

f ($\times 10^3$ Hz)	$x = 0.10$			$x = 0.95$		
	$N(\xi_F)$ ($\times 10^{39} \text{ J}^{-1} \text{ cm}^{-3}$)	r_h (nm)	ϵ_h (meV)	$N(\xi_F)$ ($\times 10^{39} \text{ J}^{-1} \text{ cm}^{-3}$)	r_h (nm)	ϵ_h (meV)
1.5	8.22	1.780	32.0	2.25	2.58	38.0
500	9.27	1.727	31.2	1.15	3.05	30.7
1000	10.40	1.678	30.4	0.94	3.21	48.3

hopping of charge carriers. Moreover, the temperature dependence of the frequency exponent “ s ” obtained from the JPL analysis provides two different phonon-assisted charge transport mechanisms applicable for the current systems: (i) the formation of small polarons in the range $40^\circ\text{C} \leq T \leq 60^\circ\text{C}$ due to incomplete d -shells of Nb^{4+} and (ii) the formation of large polarons due to the interaction of residual charge carriers with the positive ions (charge–lattice interaction) at high temperatures. Conversely, for $x \leq 0.95$, we observed the double power law behaviour between 100°C and 540°C ($1.04 \leq s \leq 1.61$) and the dominance of universal dielectric response between 50°C and 100°C ($0.81 \leq s \leq 1.04$). From the logarithmic variation of ρ_{ac} versus $T^{-1/4}$ and $\ln[\ln(\rho/\rho_0)]$ versus $\ln[T]$ plots, we demonstrated Mott’s variable range hopping of polarons between the localized states.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for Fig. s1, which shows the X-Ray diffraction pattern together with the Rietveld Refined data for $x = 0, 0.1$, and 0.3 , measured at room temperature. All these X-ray diffraction patterns are well matched with the orthorhombic crystal structure having space group $Pbcm$. Figures s2(a) and s2(b) show the FESEM micrographs recorded in the secondary-electron (SE) mode for $x = 0.10$ and 0.95 . These micrographs depict the polygonal shape morphology of average grain sizes $\sim 344\text{ nm}$ and 380 nm , with clear grain boundaries of widths $\sim 42\text{ nm}$ and $\sim 53\text{ nm}$ for $x = 0.10$ and 0.95 , respectively. In order to understand the detailed and precise distribution of the grains in $(1 - x)\text{NaNbO}_3 + x\text{NiO}$ ($x = 0.10$ and 0.95) two phase composites, a through statistical analysis has been carried out. The inset of Figs. s2(a) and s2(b) represents the histograms of the particle size distribution of those two-phase composites in which a maximum number of particles lie in the range $350\text{--}400\text{ nm}$ and $300\text{--}400\text{ nm}$ for $x = 0.10$ and 0.95 , respectively.

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