Investigation of surface scaling, optical and microwave dielectric studies of Bi$_{0.5}$Na$_{0.5}$TiO$_3$ thin films

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ABSTRACT

Herein, we have investigated the optical and microwave dielectric properties of Bi$_{0.5}$Na$_{0.5}$TiO$_3$ (BNT) thin films grown under different oxygen pressure (PO$_2$) using the pulsed laser deposition technique. The X-ray diffraction measurements confirm the single phase of BNT and the secondary phase and a further reduction in the secondary phase and increase in the BNT phase with PO$_2$, which signifies the close relationship between the crystal structure and oxygen content. The shift of Raman-active TO$_1$, TO$_2$, and TO$_3$ modes towards higher wavelengths and increase in mode intensity with PO$_2$ indicating the degree of the film of crystallinity. The local roughness ($\sigma_{loc}$) of all films obtained as $\sim$ 0.85 and the interface width ($\omega$) and lateral correlation length ($\xi$) of films vary with PO$_2$. Also, the films exhibit an increase in refractive index and reduction in the optical bandgap due to improvement in crystallinity and reduction in the oxygen vacancies. The microwave dielectric properties show that a strong PO$_2$ depends on the higher dielectric constant ($\varepsilon_r = 336$) with lower loss ($\tan\delta = 0.0093$) at 5 GHz, which shows the potential applications in high-frequency devices.

1 Introduction

The study of ferroelectric perovskite oxides in condensed matter research has renewed scientific interest owing to their technological applications such as capacitors with tunable capacitance, ferroelectric non-volatile dynamic random-access memory, radio-frequency identification cards, piezoelectric sensors, actuators, and pyroelectric devices [1–5]. Particularly, the lead-based ferroelectric materials like Pb(ZrTi)O$_3$ (PZT), Pb(ZnNb)O$_3$ (PZN), Pb(MgNb)O$_3$ (PMN), Pb(NiNb)O$_3$ (PNN) have been receiving much attention due to their excellent dielectric, ferroelectric, piezoelectric, and pyroelectric properties for the applications mentioned above [6–10]. In the last decade, many research efforts on the lead-free
piezoelectric materials such as BaTiO$_3$ (BT), (Ba,Zr)TiO$_3$ (BZT), (Ba,Ca)TiO$_3$ (BCT), (Ba,Sr)TiO$_3$ (BST), (Bi$_{0.5}$Na$_{0.5}$)TiO$_3$ (BNT), (Bi$_{0.5}$K$_{0.5}$)TiO$_3$ (BKT), and (K$_{0.5}$Na$_{0.5}$)NbO$_3$ (KNN) replace the PZT because of its toxicity [11–17]. The rapid progress in the BNT and its solid solutions was identified as high-performance lead-free ferroelectric and piezoelectric materials.

BNT was first discovered by Smolenskii et al., which is a ferroelectric material with the random distribution of Bi$^{+3}$ and Na$^+$ ions at A-site of ABO$_3$ type perovskite structure [18, 19]. At room temperature (RT), it has a rhombohedral ferroelectric perovskite structure with R3c space group, which exhibits high Curie temperature ($T_C$) ~ 320 °C, high dielectric constant ($\varepsilon_r$) ~ 692 @1 kHz, low dielectric loss (tan$\delta$) ~ 0.046, and large remnant polarization ($P_r$)- ~ 38 µC/cm$^2$ at high coercive field ~ 73 kV/cm resultant poor in piezoelectric coefficient ($d_{33}$) ~ 80 pC/N because of polling difficulties [16, 20–22].

It is essential to clarify the physical properties to fabricate BNT suitable in electrical and optical devices for the electrical and optical response. The thin-film materials can be expected to produce good sensitivity, quicker response, and cheaper than bulk ceramics. Therefore, a detailed study on BNT thin films is vital for the fabrication and characterization of electrical and optical properties [23, 24]. To deposit a single phase of BNT, maintaining its stoichiometry and better crystallinity in the thin film is challenging due to the volatile nature of the elements in the present composition. Bi and Na volatilization leads to the formation of secondary phases, oxygen deficiencies, and higher leakage currents resulting in the weak dielectric, ferroelectric, and piezoelectric properties. However, very few reports are available on BNT thin films to the best of the author’s knowledge. In perovskite oxide thin films, the oxygen partial pressure is one of the critical parameters that play an essential role in controlling the growth, high quality of crystalline thin films with optimum PO$_2$. [25–27]

Therefore, the underlying benefits of PLD motivated us to deposit complex oxide BNT films with an excess of Bi and Na with 5 mol% and to investigate the effect of oxygen partial pressure on structural, morphological, optical, and electric properties systematically.

The surface morphology, microstructure, and roughness of thin films play an important role and are strongly dependent on the deposition process and growth conditions such as deposition time (thickness), substrate temperature, and oxygen pressure. The film surface morphology can also control the optical and electrical properties, which affect device performance. Therefore, it is essential to understand the growth mechanism of the deposited thin films. In recent years, the growth behaviour of various thin-film systems was reported for different inorganic materials (metals, semiconductors, and perovskite oxides) [28–30]. The theoretical concepts have been developed to study the growth dynamics of films by atomic force microscope (AFM) measurements. The scaling theory is used to understand the growth dynamics to evaluate the statistical properties from the surface morphology of films. In the past years, many theoretical models were established to study the growth mechanism of films to a set of scaling exponents [31–33]. However, there are no reports available on the growth mechanism of PLD-deposited BNT films using scaling theory and is motivated to pursue this study. In this work, the surface scaling studies of deposited BNT thin films by PLD as a function of oxygen partial pressure are investigated in detail. The microwave dielectric properties of thin films have been widely reported for microwave communication, phase shifters, filters, and resonators [34]. Nevertheless, there are limited studies available involving microwave dielectric properties of BNT films, which suggested studying the influence of oxygen partial pressure on microwave dielectric properties of BNT thin films systematically.

2 Experimental procedures

Researchers have been developed several methods for the synthesis of polycrystalline samples with good purity, homogeneity, and finer particle size, such as solid-state reaction route, sol–gel method, co-precipitation method, and wet (semi-wet) chemical method. The solid-state reaction route method is the most versatile technique and widely used for the synthesis of polycrystalline samples [35]. This technique has many advantages over other techniques, which provide a wide range of selection starting materials (like oxides, carbonates, etc.), thermodynamically stable, environment-friendly, cost-effectiveness, the reaction takes place without any solvents, structurally pure final product, and simplicity. Recently, Shan et al. [36–38] employed a solid-
state reaction route to prepare CaZrO$_3$- and SrTiO$_3$- based materials as a dense diffusion barrier layer for a limiting current oxygen sensor. Therefore, in the present work, we have employed a solid-state reaction route to synthesize the Bi$_{0.5}$Na$_{0.5}$TiO$_3$ (BNT) target to deposit thin films based on its advantages over other techniques. The investigated properties of thin films are strongly dependent on parent or source material. The Bi$_2$O$_3$, Na$_2$CO$_3$, and TiO$_2$ powders (M/s Sigma-Aldrich, USA, 99.99 %) have been used as initial materials. The excess of Bi$_2$O$_3$ and Na$_2$CO$_3$ with 5 mol% is taken to compensate for the loss of volatile elements (Bi and Na) during the sintering of target and deposition process at high temperature. These powders were grounded with ZrO$_2$ balls in a zirconia vessel using a high-energy planetary ball mill (M/s Fritsch GmbH, Pulverisette 6, Germany) for 5 h. The mixed slurry dried at 120 °C for 24 h and further the fine powder calcined at 800 °C for 3 h. The polyvinyl alcohol added as a binder and pressed BNT target at the pressure of 400 MPa by KBr Press (M/s Technosearch Instruments, M-20, India) with 20mm diameter and 4 mm thickness, which is sintered at 1100 °C for 3 h. The BNT films deposited on quartz and Pt(111)/Ti/SiO$_2$/Si substrates by PLD for investigating the optical and electrical properties, respectively. During the film deposition, the deposition parameters such as KrF excimer laser (248 nm wavelength), pulse repetition rate (5 Hz), pulse energy (225 mJ), target to substrate distance (4 cm), and laser fluence (2 J/cm$^2$) and substrate temperature (700 °C) were kept at constant. In contrast, the oxygen partial pressure varied from 1 to 50 Pa. As deposited, BNT/Pt(111)/Ti/SiO$_2$/Si and BNT/quartz films were annealed under O$_2$ atmosphere at 700 °C for 1 h to enhance the crystalline growth. To study electrical properties, Al is deposited on the film surface (Al/BNT/Pt(111)/Ti/SiO$_2$/Si) as electrodes by thermal evaporator (M/s Hind High Vacuum, Lab Coater Auto 500, India).

The phase and crystal structure of BNT films were examined by an X-ray diffractometer (M/s Rigaku, Japan, TTRAX III) with Cu–K$_\alpha$ radiation (1.5406 Å). The films’ scaling behaviour and growth dynamics were studied using surface morphology measurements performed by AFM (M/s Oxford, Cypher). The RT Raman spectra were recorded using the Raman spectrometer (M/s JOBIN YVON, LABRAM HR800) with an Ar-ion laser ($\lambda = 514$ nm). The transmittance spectra were collected by UV–Vis–NIR spectrophotometer (M/s Shimadzu, UV 3101PC; Japan) to study the linear optical properties from the Swanepoel envelope method. The frequency and temperature variation of dielectric properties were measured using an LCR meter (M/s Wayne Kerr Electronics Pvt. Ltd, 1J43100) in the range of 100 Hz–1 MHz. The microwave dielectric properties of the thin films on quartz substrates were measured using a vector network analyzer (ZVA24; M/s Rohde & Schwarz, Columbia, MD) by a split post-dielectric resonator (SPDR) method.

3 Results and discussion

3.1 XRD analysis

Figure 1a–d illustrates the X-ray diffraction (XRD) patterns of BNT thin films deposited on a quartz substrate at various oxygen pressures from 1 to 50 Pa. The films deposited at lower and higher oxygen pressures exhibited the BNT phase and the secondary phase of Bi$_4$Ti$_3$O$_{12}$ (BIT1) and Bi$_2$Ti$_2$O$_7$ (BIT2). The secondary phases were suppressed with the rise in the PO$_2$, and the single phase of BNT was observed at 10 Pa. The oxygen vacancies and interstitials oxygen ions create charge fluctuations that lead to Bi, Na, and Ti ions stoichiometry in BNT. Hence, the secondary phases appeared in BNT thin films grown at lower and higher oxygen pressure. Zhao et al. [39] also observed similar defects in BaTiO$_3$ thin films produced at lower oxygen pressure. Moreover, Debye–Scherrer expression estimates the average crystallite size of deposited thin films at various pressures by the following Eqs. [40–42].

$$D = \frac{k\lambda}{\beta \cos \theta},$$

where $D$ is average crystallite size, $\beta$ is the full width at half maximum of diffraction peak (FWHM), $\theta$ is Bragg angle, $\lambda$ is the wavelength of X-ray (Cu–K$_\alpha$ = 1.5406 Å), and $k$ is shape factor. Since the exact value of $k$ is not known for the present material system, $k = 0.89$ was used, which makes all $D$ calculations as only estimates [40]. The estimated average crystallite size is in the range of 17–25 nm. The film deposited at lower oxygen pressure for 1 Pa having a smaller crystalline size of 17 nm, and it increases to 25 nm upon increasing the oxygen pressure up to 50 Pa. Oxygen partial pressure is one of the crucial
parameters for the growth of oxide films grown by PLD, improving the film quality. It is well known that atomic kinetic energy affects film crystallization and PO$_2$ governs the atomic kinetic energy [43]. The atomic kinetic energy in plasma changes with the rise in PO$_2$ through the collisions with oxygen atoms. The target-ablated species have a large mean-free path at lower oxygen pressure directly impinging to the substrate surface. The adatoms on the surface have maximum kinetic energy because of weak collisions between oxygen atoms and atoms in plasma. The maximum kinetic energy induces backscattering of adatoms and results in weak crystallization in the films. At higher/sufficient oxygen pressure, the atoms in the plasma plume could gain sufficient energy (i.e. smaller mean-free-path and lower kinetic energy) by scattering oxygen atoms, which prompts adatoms to reach thermodynamically stable locations through surface migration. The surface adatoms can migrate fast to look for lower energy sites and form low energy structure, which leads to improvement of the film crystallinity and quality. Hence, the film crystallinity improved with rise in PO$_2$. Wang et al. [44] investigated that the vanadium oxide thin films grown at lower PO$_2$ (0.008 Pa) showed amorphous, and the films become crystallized with rising the PO$_2$. Yang et al. [45] also observed weak crystallization in Ta$_{0.1}$W$_{0.9}$O$_x$ films at low PO$_2$ caused by many defects (oxygen vacancies), which prevent the film crystallization. Therefore, the oxygen pressure strongly influences crystallization, phase, orientation, nucleation, grain growth morphology, and optical and electrical properties of films.

### 3.2 Raman studies

Figure 2a shows the Raman spectra of BNT films deposited on a quartz substrate at different PO$_2$ measured from 50 to 1200 cm$^{-1}$. BNT has 13 Raman-active modes based on group theory: $\Gamma_{\text{Raman}} = 4A_1 + 9E$, where $A_1$ and $E$ modes are Raman and IR active [21]. The whole BNT Raman spectra can be categorized into four frequency regions (A, B, C, and D) which are shown in Fig. 2a. The Raman-active $A_1$ (TO$_1$) modes located at 88.59–123.83 cm$^{-1}$ are associated with the Bi–O and Na–O vibrations. The Raman-active $E$ (TO$_2$) modes located at 159.66–409.63 cm$^{-1}$ are associated with the Ti–O vibrations. The TO$_3$ modes located at 481.94–637.10 cm$^{-1}$ are related to TiO$_6$ octahedral vibrations. The LO$_3$ modes located at 719.06–885.41 cm$^{-1}$ correspond to the overlapping of $A_1$ (LO) and $E$ (LO) modes. In Fig. 2b, the TO$_1$, TO$_2$, and TO$_3$ modes are shifted to the higher wavenumber, and the intensity of all the modes increased with an increase in PO$_2$ from 1 to 10 Pa, which indicates improvement in the crystalline quality of films with PO$_2$. The rise in Raman bands is due to the...
improvement in crystallinity in line with XRD studies and previous reports [40]. In the case of a film deposited at 50 Pa, all modes shifted to a lower wavelength, whereas the BNT modes are suppressed due to the existence of a secondary phase. However, the Raman spectrum of the film deposited at 10 Pa is similar to that of the BNT target and earlier reports [16, 46].

3.3 Scaling behaviour and growth mechanism

The surface morphology of BNT thin films was investigated by AFM, which gives insight into the surface microstructure, scaling behaviour, and growth dynamics of the films. The AFM 3D, 2D images, and their height profiles of BNT thin films deposited on quartz substrate at various oxygen partial pressures from 1 to 50 Pa over a scan area of 5 μm × 5 μm are shown in Fig. 3. The AFM images are indicating the homogenous distribution of grains within the film surface. The root-means-square (RMS) surface roughness of the films is in the range of 8.6–11.2 nm, estimated by WSxM 5.0 software. At lower pressure (1 Pa), the RMS roughness is 8.6 nm and is increased to 11.2 nm for the film deposited at 10 Pa. Further, it is slightly decreased to 10.6 nm for the film deposited at 50 Pa. Thus, the obtained RMS roughness of deposited films is in line with crystallite sizes.

To understand the dynamic scaling behaviour and growth mechanism of films, the height–height correlation function (HHCF) is fitted with a suitable theoretical model to estimate the growth parameters: local roughness ($\sigma_{loc}$), RMS roughness (interface width) ($\omega$), and lateral correlation length ($\xi$) are calculated from AFM images using HHCF $H(r, t)$, which can describe the scaling and growth mechanism. It is a statistical average of the mean square of height difference between pair points ($x, y$) and ($x', y'$).
where $h(\mathbf{r} + \mathbf{r}', t)$ and $h(\mathbf{r}', t)$ are the heights of a surface at a point $(x, y)$ and $(x', y')$. The HHCF can be estimated by spatial averaging over one or many regions of a large extent, and it should be much larger than $r$ to avoid edge effects. It can also be defined by an exponential correlation model that satisfies the condition for self-affine surface and manifests anisotropic scale invariance by following equation [47]:

$$H(r) = 2\sigma^2 \left[ 1 - \exp \left( -\left( \frac{r}{\xi} \right)^{2\zeta} \right) \right],$$

where $\sigma$, $\xi$, and $\zeta$ are parameters related to the surface roughness.

### Fig. 3

AFM 3D (left side) and 2D (centre) images of BNT films for a 1 Pa, b 5 Pa, c 10 Pa, and d 50 Pa. The height profile of each image is shown on the right side of the respective images.
The HHCF exhibits two distinct behaviours depending on the relative magnitude of \( r \) and lateral correlation length \( (\xi) \) as follows:

For \( r \ll \xi \), \[ H(r < \xi) = 2\omega^2 \left(\frac{r}{\xi}\right)^{2z}, \] (4)

For \( r \gg \xi \), \[ H(r > \xi) = 2\omega^2, \] (5)

where \( \omega \) is the RMS roughness (interface width), \( z \) \((0 \leq z_{\text{loc}} \leq 1)\) is the local roughness scaling exponent, which represents the short-range roughness of a self-affine surface, and \( \xi \) is the lateral correlation length. The log–log plot of HHCF versus distance \( r \) and fitted curve by Eq. (3) of BNT thin films for various oxygen partial pressures from 1 to 50 Pa is shown in Fig. 4a. The oscillatory behaviour is observed for the film deposited higher pressures for \( r \gg \xi \) signifying the formation of the mounded surface [32, 47]. The \( H(r, t) \) is shifted upward as oxygen pressure \( (P) \) increases with the growth rate, which indicates the enhancement in RMS roughness. The \( z_{\text{loc}}, \omega, \xi \) parameters are extracted from HHCF for the film deposited at different pressures to understand the scaling behaviour and growth dynamics. The variation of \( z_{\text{loc}}, \omega, \xi \) with \( P \) is shown in Fig. 4b–d. The \( z_{\text{loc}} \) value of all the deposited films is found to be \( 0.85 \pm 0.08 \), between 0 and 1. The smaller and larger value of \( z_{\text{loc}} \) indicates a locally rough and locally smooth surface, respectively. The value of \( \omega \) increases from 7.9 to 11.5 nm for the film grown at various pressure from 1–10 Pa which confirms that the film is roughening during the growth process and is reduced (10.7 nm) for the film deposited at high pressure (50 Pa). The high value of \( \omega \) is attributed to various non-local effects such as shadowing, high stickiness of substrate, bulk diffusion of incoming particles. The \( \xi \) value is increased from 90 to 156 nm with the rise in \( P_{\text{O}_2} \) from 1 to 10 Pa, and beyond that, it decreases to 94 nm for 50 Pa, which signifies the lateral growth of the islands varies with pressure. It indicates that the islands grow vertical and lateral as the pressure increases and the entire film turns rough. The lateral growth is due to improved nucleation of more incoming flux and the enhancement in crystallite size with \( P_{\text{O}_2} \). The sudden decrease in \( \xi \) at higher pressure (50 Pa) might be due to the appearance of the second phase can be seen in XRD results, where the film growth orientation shifts from (110) to (117). During the nucleation and growth stage, only vertical growth takes place. In contrast, with an increase in oxygen pressure (> 10 Pa), the vertical growth of the secondary phase dominates over the lateral growth.
and the RMS roughness slightly decreases, as shown in Fig. 4d [48].

### 3.4 Optical properties

Figure 5a shows the optical transmittance spectra of BNT thin films deposited on quartz substrates at various PO$_2$ in the wavelength range from 200 to 2500 nm. The oscillations in the spectra due to multiple reflections are between air to film and film to substrate interfaces. The spectra of all the films are found to be 50 to 85% of transmission in the visible region, which is relatively high transmittance that confirm the low surface roughness and better homogeneity of films. A sharp drop in optical transmission at the wavelength of 300–400 nm region corresponds to strong absorption, which is the fundamental absorption of the film. It can be seen that the transmittance of deposited films is decreased, where the transmittance spectra shifted to a higher wavelength in the absorption region with increasing oxygen pressure [49].

The thickness ($t$) and refractive index ($n_f$) of the thin films for different O$_2$ pressures are calculated using Swanepoel’s envelope method by following Eqs. [50, 51]:

$$n_f = \left[ N + (N^2 - n_f^2)^{0.5} \right]^{0.5},$$  \hspace{1cm} (6)

$$N = 2n_f^2 \left( \frac{T_{\text{max}} - T_{\text{min}}}{T_{\text{max}}T_{\text{min}}} \right) + \frac{n_f^2 + 1}{2},$$  \hspace{1cm} (7)

where $n_s$ is the substrate refractive index, $T_{\text{max}}$ and $T_{\text{min}}$ are transmission maximum and minimum at a specific wavelength ($\lambda$), $n_1$ and $n_2$ are refractive indices at two adjacent maximum or minimum at $\lambda_1$ and $\lambda_2$. The estimated $t$, $n_f$, and absorption coefficient ($\alpha$) values are shown in Fig. 5b and c. The $t$ and $n_f$ values are increased from 1067, 1091, and 1349 nm and 1.83, 1.90, and 2.31 with the rise in the PO$_2$ from 1, 5, and 10 Pa. The increase in thickness with oxygen pressure is due to the confinement of plasma, which leads to an increase in the particle flux, consequently a higher deposition rate. The thickness of the film deposited at 50 Pa is very thick, producing over confinement of the plasma, which is limiting the incoming flux impinging on the substrate and hence the decrease in film thickness [52].

![Graph showing optical transmittance spectra](image)

Fig. 5  a Optical transmittance spectra, inset of a optical bandgap energy of BNT films deposited at various pressures. b, c $t$, $\alpha$, $n$, $P_0$, and $E_g$ values as a function of oxygen pressure

Further, the optical packing density ($P_0$) of thin films is calculated by the following expression:

$$P_0 = \left( \frac{n_f^2 - 1}{n_f^2 + 2} \right) \left( \frac{n_b^2 + 2}{n_b^2 - 1} \right),$$  \hspace{1cm} (9)

where $n_b$ is the refractive index of the bulk BNT (2.32) [53]. The estimated optical packing density lies in the range of 73.94–99.52% and is increased with PO$_2$, as shown in Fig. 5c. The improvement in crystallinity, optical packing density, decrease in oxygen vacancies, and change in the phase could be the
reason for larger \( n_t \) and extinction coefficient values at film deposited for 10 Pa.

The optical bandgap energy (\( E_g \)) of BNT thin films can be calculated using the Tauc relation in the strong absorption region for direct bandgap by following expression [54]:

\[
(\alpha h) = A(h - E_g),
\]

where \( A \) is a constant, and \( h \) is the photon energy. The Tauc plot \( h \nu \) vs. \((\alpha h)^2\) is shown in inset of Fig. 5a. The intersection of the tangent line with the X-axis provides the bandgap of films. The \( E_g \) values are slightly decreased from 3.55 to 3.34 eV (Fig. 5c) with the rise in \( O_2 \) pressure from 1 to 50 Pa due to the improvement in crystallinity and reduction in the oxygen vacancies in the films, which turn in a narrowing bandgap. Nevertheless, the obtained bandgap energy values of BNT thin films are close to the reported values deposited by a similar PLD technique [53, 55].

### 3.5 Dielectric and microwave dielectric properties

The frequency variation of dielectric constant (\( \varepsilon_r \)) and dielectric loss (\( \tan\delta \)) of BNT thin films deposited at various \( O_2 \) pressures and measured at RT are shown in Fig. 6a and b. The \( \varepsilon_r \) values decrease with an increase in frequency due to a decrease in the net polarization in the films, i.e. frequency dispersion behaviour. The \( \varepsilon_r \) and \( \tan\delta \) values of deposited films are in the range of 295–454 and 1.13–0.140 @ 1 kHz, respectively. The \( \varepsilon_r \) values of BNT thin films enhanced, and \( \tan\delta \) values decreased with an increase in \( O_2 \) pressure from 1 to 10 Pa, as shown in Fig. 6c. The film deposited at 10 Pa exhibited the higher \( \varepsilon_r \) (454) and lower \( \tan\delta \) (0.140) at 1 kHz. The improvement in the dielectric properties is observed with an increase in the pressure due to reduction in oxygen vacancies, conductivity, improvement in the crystallinity, enhanced dipole and interfacial polarizations, and the stabilization of the BNT phase [56, 57]. Further, the obtained single-phase BNT thin films deposited at 10 Pa are carried out to study the temperature variation of \( \varepsilon_r \) and \( \tan\delta \) at different frequencies from 1 to 100 kHz as shown in Fig. 6d. The \( \varepsilon_r \) and \( \tan\delta \) values are found to be decreased with an increase in frequency with temperature. It also revealed the two structural phase transitions: (i) Ferro-to-anti-ferro transition, which corresponds to rhombohedral-to-tetragonal transition, i.e. depolarization transition temperature (\( T_d \) \( \sim \) 225 °C), and (ii) anti-Ferro-to-para transition which corresponds to tetragonal-to-cubic transition, which is called as Curie transition temperature (\( T_c \) \( \sim \) 296 °C). These results are similar to that of bulk BNT ceramics and agree with the previous reports [21, 58].

The microwave dielectric properties of BNT thin films deposited on quartz substrates at various oxygen pressures are investigated by the SPDR technique [59, 60]. The SPDR is a familiar, non-destructive, and accurate technique for measuring the microwave dielectric permittivity and loss tangent of thin films at a spot frequency in the microwave region of 5 and 10 GHz. The dielectric resonators use a specific resonant mode with a specific resonant frequency, depending on the SPDR permittivity and its dimensions. The electric field in the SPDR film is parallel to the interface of the film. Resonators operate in the TE\(_{01\delta}\) mode that has only an azimuthal electric field component. Accordingly, the electric field remains continuous on the test interfaces and is insensitive to air gaps perpendicular to the z-axis of the fixture [59]. The microwave dielectric permittivity and loss tangent of substrate and film depends on resonant frequency and quality factors. Figure 7a shows the substrate and BNT thin film (10 Pa) measured at 5 GHz. The resonant frequency and quality factor of the empty resonator (\( f_{01}, Q_{01} \)) and resonant frequency and quality factor of the substrate (\( f_0, Q_0 \)) are measured as shown in Fig. 7c. There is a shift in resonant frequency when the thin film is placed in SPDR. The shift of resonant frequency and its quality factor (\( f_s, Q_s \)) of the film is measured and is shown in Fig. 7b. The resonant frequency unloaded Q-factor, and other parameters are estimated by the Rayleigh–Ritz method. The real part of dielectric permittivity and loss tangent of deposited films are determined from the measured resonant frequency, quality factor, and film thickness by following equations:

\[
\varepsilon_r = 1 + \frac{(f_0 - f_s)}{hf_0k_s(\varepsilon_r, h)},
\]

\[
\tan\delta = \frac{Q_c^{-1} - Q_D^{-1}}{P_{es}},
\]

where \( h \) is the thickness of the film, \( f_0 \) and \( f_s \) are the resonance frequency of the substrate (quartz) and film (BNT), \( K_s \) is a function of \( \varepsilon_r \) and \( h \). \( Q \) is an unloaded quality factor of resonator having the thin
The estimated $\varepsilon_r$ and $\tan\delta$ of deposited thin films at various pressures are displayed in Table 1. The $\varepsilon_r$ values of BNT thin films gradually improved with the rise in the PO$_2$ from 1 to 10 Pa. It is due to an increase in the optical packing density, crystallinity, refractive index, and stabilization of the BNT phase with PO$_2$. It is also observed that the $\varepsilon_r$ values of BNT thin films decreased with a rise in the frequency from 5 to 10 GHz due to a decrease in polarization and an increase in conductivity. The loss tangent of thin films deposited at lower PO$_2$ exhibited slightly higher than higher pressure due to O$_2$ deficiencies. The loss is found to be decreased with rising in PO$_2$. The improvement in microwave dielectric properties of BNT thin films is obtained due to the depreciation of oxygen vacancies. The higher $\varepsilon_r$ (336 and 264) and low $\tan\delta$ (0.0093 and 0.0015) values are obtained at 5 and 10 GHz frequencies for the film deposited at 10 Pa pressure which are promising for tunable microwave applications and high-frequency devices.

4 Conclusion

In oxide materials, the oxygen content is one of the critical parameters that play an essential role in controlling the stoichiometry and crystalline quality of thin films to investigate the structural and physical properties. In this work, the influence of oxygen partial pressure on structural, surface morphological, optical, and microwave dielectric properties of BNT thin films are presented in detail. The single phase of BNT films obtained at film deposited at 10 Pa pressure which is confirmed from XRD and Raman spectroscopic studies. The local roughness exponent, $\alpha_{loc}$ (0.85 ± 0.08), corresponds to the locally smooth surface. The
interface width (ω) and lateral correlation length (ζ) increase with pressure indicate roughening, and islands grow in lateral and vertical directions during the growth process. The optical and microwave dielectric properties of BNT films are significantly improved with oxygen pressure due to the reduction in oxygen deficiencies and improvement in crystallinity. The BNT thin films exhibited two structural phase transitions: Ferro-to-anti-Ferro transition ($T_d^* \approx 225 \, ^\circ C$) and anti-Ferro-to-para transition ($T_C^* \approx 296 \, ^\circ C$). The higher $\varepsilon_r$ (336 and 264) and low $\tan \delta$ (0.0093 and 0.0015) values are observed at 5 and 10 GHz frequencies for the film deposited at 10 Pa pressure and are suitable for the applications such as high-frequency devices.

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### References

1. Y. Sun, H. Wang, G. Liu, H. Xie, C. Zhou, G. Chen, C. Yuan, J. Xu, J. Mater. Sci. Mater. Electron. 31, 5546 (2020)
2. S. Takagi, A. Subedi, V.R. Cooper, D.J. Singh, Phys. Rev. B—Condens. Matter Mater. Phys. 82, 19 (2010)
51. S. Ponmudi, R. Sivakumar, C. Sanjeeviraja, C. Gopalakrishnan, J. Mater. Sci. Mater. Electron. 30, 18315 (2019)
52. A.T.T. Mostako, A. Khare, Laser Part. Beams 30, 559 (2012)
53. M. Bousquet, J.R. Duclère, E. Orhan, A. Boulle, C. Bachelet, C. Champeaux (2010) J. Appl. Phys. 107, 104107
54. J. Tauc, Opt. Prop. Solids 277 (1972)
55. A. Joseph, J.P. Goud, S.R. Emani, K.C.J. Raju, AIP Conf. Proc. 1731, 80039 (2016)
56. W. Zhang, X. Zhu, L. Liang, P. Yin, P. Xie, D. Dastan, K. Sun, R. Fan, Z. Shi, J. Mater. Sci. 56, 4254 (2021)
57. L. Sun, L. Liang, Z. Shi, H. Wang, P. Xie, D. Dastan, K. Sun, R. Fan, Eng. Sci. 12, 95 (2020)
58. Y. Zhao, X. Hao, M. Li, J. Alloys Compd. 601, 112 (2014)
59. J. Krupka, J. Eur. Ceram. Soc. 23, 2607 (2003)
60. A. Rambabu, S. Bashaiah, K.C. James Raju, J. Mater. Sci. Mater. Electron. 25, 1172 (2014)
61. J. Krupka, A.P. Gregory, O.C. Rochard, R.N. Clarke, B. Riddle, J. Baker-Jarvis, J. Eur. Ceram. Soc. 21, 2673 (2001)

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