Effect of temperature and humidity on dielectric and impedance properties of K(Nb$_{0.8}$Ta$_{0.2}$)$_{0.99}$Mn$_{0.01}$O$_3$ electroceramics

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Abstract

We report the effect of humidity and temperature on the dielectric and impedance properties of lead-free potassium tantalum niobium oxide (KTN). It illustrates large dielectric constant ~4500 at 1 kHz, low tangent loss in dry condition, which drastically changes under humidity condition. The nature and magnitude of dielectric constant and tangent loss were moderately different in both heating and cooling conditions. A series of phase transitions from rhombohedral to orthorhombic (below room temperature), and orthorhombic to tetragonal (~185 °C) and tetragonal to Cubic (390 °C) have been obtained respectively over a wide range of temperature with a significant change in magnitude and nature in transition temperature during cooling mode. A detail transport properties have been carried out based on Impedance spectra, Modulus spectra, Nyquist Plot, and ac conductivity to establish a microstructure-property relation. The activation energy of the charge carriers determined that mainly electronic charge carriers contribute to transport properties in the low-temperature range while oxygen vacancies and cations near the high-temperature ferroelectric phase transition. The effect of moisture on room temperature capacitance, tangent loss, and impedance have been discussed.

Introduction

A large number of researchers from various scientific communities are searching for a novel ferroelectrics material with significantly large dielectric constant, low tangent loss, large polarization, large piezoelectric coefficients, and low coercive field due to their potential applications as memory elements, sensors, actuators, transducers, dielectric filters, oscillators, ultrasonic wave generators, positive and negative temperature coefficient devices, microwave appliances, etc [1–4]. The choice of the material for device fabrication is driven by their unique physical and chemical properties such as dielectric constant, tangent loss, resistance, capacitance, conductivity, and microstructural relation over a wide range of temperature and frequency. The optimized calcination and sintering temperatures of electroceramics offer the controlled growth of the domain and domain walls, which is essential for the sensing application and shows the required transport properties [5, 6]. In general lead-based ceramic possesses high dielectric constant as well as low dielectric loss so that it is the natural choice for the device application. Pb(Zr$_{1-x}$Ti$_x$)O$_3$ (PZT) is one of the most suitable and widely accepted choice having a maximum number of above mentioned physical properties [7–10]. Due to the toxic and health hazardous nature of Lead, the European Union and most of the developed countries phased out lead-based materials and devices with lead-free ferro/piezo-electric materials.

To cope with the latest development and discovery of novel lead-free materials, many theoretical and experimental approaches have been employed to develop suitable and desirable materials with ABO$_3$ crystal structure [11]. Most of the investigated materials contain the transition metals at the octahedral site or B site of...
the ABO₃ crystal structure, such as Ti⁴⁺, Nb⁵⁺, Zr⁴⁺, Ta⁵⁺ with the monovalent, divalent and trivalent cations at the A site such as Na⁺¹, Sr⁺², Ca⁺², La⁺³, K⁺¹. These systems provide the eightfold and twofold coordination existence for the oxygen environment. A number of lead-free ceramics with large piezoelectric coefficients (d₃₃) and enhanced polarization are reported in literature such as: K₀.₅Na₀.₅NbO₃-LiNbO₃ [12], CaTiO₃-BaTiO₃ [13], BaZrO₃-BaTiO₃ [14, 15]. The scientific community is also continuously trying to fabricate the multifunctional ferroelectric thin films for possible above mentioned applications [16–19]. Among the various perovskites, K(Nb₀.₅Ti₁₋ₓ)O₃ and its solid-solution found special attention due to nontoxicity, comparatively moderate polarization, and dielectric constant concerning lead-free perovskite systems [20, 21].

In the case of ceramic materials, the CIS technique is a potent non-destructive method to examine the microstructure-electronic property relationship. This method established the effects of grains, grain boundaries, and electrode-electrolyte interface on electrical transport [22]. It facilitates to explain the electrical conduction mechanism and detail charge, hoping under the application of the ac electric signal in the wide range of frequency. The dielectric relaxation time and ionic charge hoping of the ferroelectric material, can be explained using the CIS technique. The bricklayer model [23] can be employed to get an equivalent electrical circuit for the description of transport properties, such as impedance, capacitance, inductance, and constant phase factor [24–28].

The present study deals with the effect of environmental conditions on dielectric and structural phase transition properties of KTN ceramics. Effect of grains and grain boundaries on electrical transport properties near the ferroelectric to paraelectric phase transition temperature has been investigated using impedance, modulus, and conductance spectroscopy.

Methods

The niobium rich potassium tantalate K(Nb₀.₈Tₐ₀.₂,ₙ₉%Mn₁₀.₀)O₃ was synthesized by solid-state reaction technique. The high-quality ingredients such as potassium carbonate (K₂CO₃), niobium pentoxide (Nb₂O₅), tantalum pentoxide (Ta₂O₅), and manganese dioxide (MnO₂) were used to synthesize the KTN ceramic. The used chemicals were purchased from Alpha Assar LTD with a purity of more than 99.9%. A small amount (0.01%) of manganese was added to improve the stability and crystalline quality of the composition. An appropriate stoichiometry green powder of KTN is physically mixed in a pestle mortar. The homogeneous solution of the integrands was prepared by the physical mixing in liquid alcoholic medium (IPA). The obtain mixture (physically only) was calcined at the optimized temperature 900 °C (+/− 5 °C) in the box furnace. The calcined powder was thoroughly ground with a small amount of PVA as a binder to make the pellet. The 10 mm circular diameter pellets were pressed using the hydraulic press and die-punch to achieve at least 90% to 95% of theoretical density. The KTN pellets were sintered at an optimized temperature of 900°C (± 2 °C) for 2 h with the temperature ramp 5 °C min⁻¹. The sintering temperature higher than calcination temperature leads to pyrochlore, impurity phase, and sometimes pellet melting above 950 °C. Apart from phase purity, we have optimized 900 °C sintering temperature for controlled porosity (10%–12%), which was favorable for the application point of view (Humidity Sensing) [29].

The sintered pellet was characterized by the x-ray diffraction (XRD) technique with the monochromatic Cu-Kα, radiation source (Rigaku Ultima IV) over the large Braggs angle range of 20° ≤ 2θ ≤ 60°. The XRD patterns were scanned with a speed of the 2° min⁻¹ with a step sized of 0.02°. The Archimedes principle method was employed for the calculation of the experimental density of the sintered pellet. The scanning electron microscopy (SEM) technique (Zeiss EVO MA–10) was used to record the image of grains and grain boundaries for the analysis of surface morphology. The Energy-dispersive X-ray spectroscopy (EDX) technique was used to obtain the elemental compositions. The smooth and flat surfaces of the pellets were painted with high-quality conductive silver paste (SPI Conductive silver paint) and dried at 250 °C (for 2 h) to form the capacitor structure for electrical measurement. Conducting silver paint is used for electrode due to its high work function and low cost compared to high work function expensive platinum and gold conducting paint. The dielectric constant (ε), tangent loss (tanδ), ferroelectric hysteresis (PE Loop), and other various electrical measurements were performed on a silver-coated parallel plate capacitor. The dielectric measurement was performed in the frequency range 100 Hz ~ 1 MHz using the LCR meter (HIOKI 3532–50 LCR Hi-TESTER). The temperature-dependent polarization-electric fields (PE-loop) measurements were performed by the Radiant ferroelectric tester.

Theory

Four parameters, Impedance, phase angle, parallel plate capacitance, and tangent loss were measured as a function of temperature and frequencies. The dielectric constant of a substance is defined as the ratio of the amount of capacitance or stored energy by the substance to the capacitance or stored energy when the same
potential difference is applied to a same dimensional vacuum capacitor.

\[ \varepsilon_r = \frac{E_{\text{material}}}{E_{\text{Vacuum}}} \]  

(1)

The stored energy is defined as \[ E = \frac{1}{2} \varepsilon_r \varepsilon_0 \left( \frac{V}{d} \right)^2 \], where \( V \) is the applied voltage, and \( d \) is the thickness of the capacitor \[ 30 \]. The real \( Z' \) and imaginary part \( Z'' \) of the impedance was obtained using the following relation

\[ Z' = Z \cos \delta \]  

(2)

\[ Z'' = Z \sin \delta \]  

(3)

The cell capacitance can be calculated from impedance spectrum data with the help of given formula in equation No. 4, which also establishes the relationship between the imaginary part of dielectric constant and impedance \[ 31, 32 \].

\[ \varepsilon' = -\left( \frac{1}{C_{\text{Vacuum}}} \right) \left( \frac{1}{\omega} \right) \left( \frac{Z''}{(Z')^2 + (Z'')^2} \right) \]  

(4)

where \( \omega = 2\pi f \) is defined as the angular frequency of the applied AC electric field. In general, the raw impedance data of the material contains capacitive, resistive, and inductive components. The representation of impedance on the Nyquist \((-Z'\) in the y-axes and the \(Z'\) on the x-axes concerning frequency spectrum) plot looks like a semicircle. The arc, radius, double semicircle, and cutting edge on the real axis explain the behavior of the dielectric properties. In general, the polycrystalline sample possesses the grains and grain boundaries. The frequency-dependent electronic performance of these grains to electrode or electrolyte can be explained using the Nyquist plot. In this article, an equivalent electrical circuit has been proposed for the impedance analysis to understand the frequency-dependent impedance. The complex impedance is converted into the complex modulus data using the following relation

\[ M^\prime = i\omega C_0 Z = i\omega C_0 (Z' - Z'') = M' - iM'' \]  

(5)

\[ M' = \omega C_0 Z'' \text{ and } M'' = \omega C_0 Z' \]  

(6)

**Results and discussion**

**Crystal structure analysis**

The XRD measurement of KTN ceramic pellet was performed at room temperature (296 K), and its Bragg planes were indexed using the JCPDS file no. 71-0946 \[ 33 \]. The Bragg angle positions, peak sharpness, and homogeneous background in XRD patterns show good crystalline quality. The detail discussion on the crystal structure, including Rietveld refinement, is given in our recently published paper and patent, which deals with the effect of relative humidity on resistance/transport properties of KTN (Humidity sensing application) \[ 29, 34 \]. Rietveld refinement revealed that the crystal structure and space group belong to orthorhombic and Ammn2, respectively, with a lattice constant: \( a = 3.9836 \) Å, \( b = 5.6698 \) Å and \( c = 5.7116 \) Å. In the same paper, the scanning electron microscopy image revealed the size of the grains, which looks like the oblate cubicoid size having the dimension of the order of 500 to 1200 nm. These big crystals are decorated with tiny small crystals of the order of 100 nm. The elemental compositions of the KTN pellet were obtained by EDX analysis, which indicates almost similar compositions as taken for precursors, well within the experimental limit (+/- - 10%) of SEM-EDAX data \[ 29 \]. An in-depth critical analysis of crystal structure and microstructure have been reported elsewhere \[ 29 \].

**Effect of humidity on dielectric and impedance properties of KTN**

To investigate the humidity effect on the capacitance, the dielectric measurement was performed in two different conditions; 1. dry condition (Rh ~ 10 ~ 15%), where the KTN pellet was covered by the dark blue silica-gel crystal without physical contact, 2. moist condition (Rh ~ 75 ~ 80%), where the KTN pellet was put on the top of the water-filled beaker. Note that we have taken the full precaution to avoid any physical contact with the water level (1 cm apart). The measured value of the relative humidity in the same conditions by the commercial humidity sensor in dry and moisture condition was in the range of 10%-15% and 75%-80%, respectively. The variation of capacitance and tangent loss in dry and moisture condition is given in the figures 1 (a) and (b). The KTN system absorbed water molecules in a moist condition, which drastically increase the dielectric constant \[ 35 \]. The effect of humidity on capacitance and tangent loss was significant in low-frequency regions. The low-frequency range is sensitive to probe the free mobile charge carriers responsible for a large change in capacitance and tangent loss. The capacitance changes nearly two orders for 100 Hz and near one order for 1 kHz, i.e., 26.62 pF to 5.8 nF and 26.31 pF to 340 pF (figure 1(a)). A remarkable change in capacitance
is also observed at the 10 kHz from \(~26\) pF to \(~44\) pF from dry to moist condition. The full spectrum of capacitance is completely distinguishable in dry and moisture conditions. In the high-frequency range, the difference in capacitance with and without humidity is small. It may be due to the lagging of developed mobile charge carriers against the high probe ac impedance signal [36]. The low value of the tangent loss (\(~0.01\)) in the dry condition supports the presence of very weak electronic charge carriers in the matrix inside grains, grain boundaries, and also among grains and grains boundaries and related interfaces (figure 2(b)). The LCR meter, HIOKI 3532-50 LCR HITESTER has experimental limitation for the measurement of tangent loss (maximum

![Figure 1](image)

**Figure 1.** (a) and (b) shows the variation of the capacitance and tangent loss in dry and moisture condition. Figure 1(c) and its inset image are the Nyquist plot in dry and moisture condition, respectively.
tanδ = 9.9999, hence we observed saturation in a tangent loss under humidity below 20 kHz. The magnitude of tangent loss in the low-frequency range is many orders higher in humidity condition compared to dry condition. The high value of the tangent loss in moisture condition suggests the free flow of the charge carriers inside the matrix. To investigate the conduction mechanism, CIS (Nyquist plot) is chosen to explain conductivity and polarization. The complex impedance spectra in dry and moisture condition were recorded in the frequency range 100 Hz to 1 MHz. Figure 1(c) and its inset image show the Nyquist plot in dry and moisture condition. Completely different impedance spectra in both cases show the different physical mechanism for the capacitance, conductance, and dielectric loss. In low humidity range or dry condition (Rh ∼ 10%–15%) a vertical line parallel to Y-axis appeared (Figure (c)) which shows nearly infinite resistance, negligible charge carriers, and very small value of the tangent loss. In the moisture condition, KTN shows one semicircle with Randles straight line tail (inset figure 1(c)). The experimental data were fitted with a Nyquist plot using an equivalent circuit composed of series resistance, and a parallel combination of the capacitance with a series combination of resistance and Warburg element. The existence of the Warburg coefficient confirms ionic charge conduction in moisture condition. The complex impedance spectra in the dry and moisture condition suggest giant variation in the physical property of the KTN electro-ceramics.

Dielectric spectroscopy
The dielectric spectra of the KTN system were studied as a function of the temperatures and frequencies. The behavior of the dielectric constant with the temperature at variable frequency is given in figures 2(a) and (b) during the heating and cooling method, respectively. The consecutive three structural phase transitions had observed over large temperature window such as rhombohedral to orthorhombic [below room temperature], orthorhombic to tetragonal [∼185 °C] and tetragonal to Cubic [390 °C]. The behavior of tangent loss during the heating and cooling measurement has shown in figures 2(c) and (d), respectively, also supports the structural phase transition. The dielectric anomaly observed around 390 °C suggests ferroelectric to the paraelectric phase transition. The crystal structure is transforming orthorhombic (Amm2) to tetragonal (P4mm) near 185 °C with large dielectric constant due to non-centrosymmetric symmetry in the case of the tetragonal crystal structure.

Figure 2. (a) and (b) show the variation of dielectric constant and tangent loss as a function of temperature for different frequencies in heating mode. Similarly, figure 2(c) and (d) also illustrate the variation of dielectric constant and tangent loss in cooling mode. The comparison of heating and cooling measurement at 500 kHz is given in the inset of figures 2(a) and (b).
A kink in the dielectric constant, as well as in tangent loss in both the cases (heating and cooling) is observed at 185 °C, which is more prominent in the cooling mode suggest a clear change in crystal structure towards higher symmetry. A comparatively large value of the dielectric constant, low value of tanδ and sharp kink in dielectric constant has been observed in the temperature range of (30–100)°C in heating mode compared to a cooling process which is mainly due to the highly hygroscopic character of the KTN pellet as shown in figures 2(b) and (d) [29]. The close observation of the dielectric data shows that the second-order ferroelectric phase transition from tetragonal to cubic has occurred at 400°C during the heating process, which shifted nearly 10°C towards the lower temperature region in cooling mode measurement for higher probe frequencies as shown in figures 2(a) and (c). The heating and cooling data show the moderate change in the nature and magnitude of the ferroelectric phase transition temperature (Tc), which may be due to the effect of domains and domain walls and its movement during the heating and cooling process [38]. The variation of dielectric constant and tangent loss at 500 kHz is given in the inset image of figures 2(a) and (b) for close view in the heating and cooling mode, simultaneously. The 10°C shift in Tc towards lower temperature during the cooling process support movement of domains and domain walls. Giant dielectric dispersion was observed as a function of frequency due to the broad dielectric relaxation time and non-Debye type dielectric dispersion [39]. The magnitude of dielectric constant and tangent loss was found five to ten times low at higher frequencies, which may be due to the absence of electronic charge contribution to the dielectric constant for frequency greater than 1 kHz.

Nyquist plot
The Nyquist plot is the graphical representation of the real and imaginary part of the impedance with variable frequency. The Nyquist plot at different temperature and their respected model fitting (Brick Layer Model) are given in figures 3(a) and (b). An equivalent electrical circuit was optimized for the analyses of the impedance data. The realistic physical properties have been tried to explain using an appropriate equivalent circuit (figure 3(b)). The Nyquist plot’s formed a semicircular type arc, and the arc diameter decreases as the temperature increase. The arc was not centered at the real axis, and its center is shifting to the lower value of the Z'; it shows the decrement of the bulk resistance as the temperature increases [40]. In figure 3(b) the contact resistance of the electrode and electrolyte was defined as the value of the Rc, which is of the order of ~50Ω. The admittance CPE can be defined by the formula

\[ \frac{1}{Y_{CPE}}(\omega) = \alpha_0 + \beta(\omega)^n \]

where \( \alpha_0 \) and \( \beta \) are the constant, \( n \) is an integer, and \( Y_{CPE} \) is the admittance of the CPE. \( \alpha_0 \) describes the dispersion and the value of the \( n \) define the capacitive and resistive nature of the material. \( 0 \leq n \leq 1 \) describes the ideal capacitor of the CPE and \( n = 0 \) is for the perfect resistor. In the present study, the value of the \( n \) lies in the range of 0.71 to 0.75 [41]. The fitting of the Nyquist plot was performed by the commercially available software Zview. Various permutation and combination of the electrical circuit have been used to make a suitable equivalent circuit (figure 3(b)). The corresponding overlapped semicircles over the data points are the fitted line of the equivalent circuit. In the equivalent model circuit, two parallel circuits were joined in series: (i) parallel combination of the grain boundary resistance \( R_g \), grain boundary capacitance \( C_g \) (ii) parallel combination of Bulk resistance \( R_b \), bulk capacitance \( C_b \) and one constant phase element CPE as shown in figure 3(b). The series resistance Rs in the proposed equivalent circuit shows the contact resistance of the electrode, which is of the order of 50Ω. The obtained values of all the theoretical parameters satisfy the experimental assessment of the respected temperature. The well-association of the experimental data points with the fitting line assures us for the proposed model.

Frequency-dependent imaginary part of impedance
The variation of the imaginary part of impedance (Z”) with frequency at different temperatures has been shown in figure 4. The analysis of this spectrum was performed by spotting the maximum value of impedance with corresponding frequency. The peak frequency is called relaxation frequency, which is the fingerprint frequency for the respected material. As the temperature increases, impedance value drops suddenly to the low-frequency window side, and again it merges in the high-frequency range. The peak position shifts towards the high-frequency side (figure 4) by increasing the temperature. It shows that the electrical relaxation processes is thermally activated. The merging of the imaginary impedance data of the various temperature in high-frequency range implies the disappearance/relaxation of the space charges [42, 43]. The relaxation time was obtained from Z” fitting using the equation \( \omega_{\text{max}} \times \tau = 1 \). The variation of the relaxation time has been expressed against the inverse of temperature in the inset figure 4. Interestingly a discontinuity was observed in the activation energy (Inset figure 3). It was found that the relaxation time follows the Arrhenius equation \( \tau = \tau_0 \exp \left( \frac{E_a}{k_bT} \right) \), and the slope of the fitted Arrhenius equation was used to calculate the activation energy. In this study, it was found the space charge carrier follows the two different regions of the activation energy. At low temperature, the system
gave low activation energy $\sim 0.29$ eV, i.e., which is corresponding to the energy required for electronic charge conduction. However, in the high-temperature region (in the vicinity of FPT temperature) large value of the activation energy ($\sim 0.76$) indicates that oxygen vacancies/mobile charges are responsible for the electrical conduction process.

**Modulus mechanism**

The study of modulus formalism is a potent technique to analyze the capacitive behavior of the insulating, conducting, and semiconducting materials. By using the complex modulus spectroscopy, a very small fluctuation of the capacitance can be detected, which arises across the grain boundary or the interface of the grain and electrode. The detail conversion formula of the electrical modulus has been given above in equations (4) and (5). The frequency-dependent imaginary electric modulus ($M''$) at variable temperature is given in figures 5(a) and (b) during the heating and cooling process. The frequency at which the maxima of the $M''$ curve occurred is relaxation frequency. On the base of peak position, the spectra can be divided into three regions. In low-frequency regions where $M''$ increases, in the middle-frequency region where $M''$ becomes constant and again, it started to increase in high-frequency regions and reached to it’s on the maximum value. Such behavior of $M''$ shows the existence of two relaxations frequency in the full spectrum. The mobile charge carrier travels the large distance in the low-frequency range. In the middle frequency range, where $M''$ is a

![Figure 3.](image-url)
constant mobile charge carrier move over the short-range due to the trapping in the potential wall. The relaxation peak in the spectrum divides the mobile charge carrier mobility between the long-range order and short-range order [44, 45]. The constant value of $M''$ in the mid-frequency range is clear in the cooling mode,

**Figure 4.** The imaginary part of the impedance as a function of frequency. The inset data show the variation of the relaxation time as a function of inverse temperature.

**Figure 5.** (a) and (b) illustrate an imaginary part of the electric modulus as a function of frequency at different temperatures in heating and cooling mode, respectively.
which shows more authenticity of data when it is recorded in cooling mode. Here all values of $M'$ can be resolved at each temperature, which signifies the relaxation of the conductivity (mobile charge carrier).

### A. C. conductivity

An in-depth study of frequency-dependent electrical conductivity is significant in explaining the electrical transport property of the materials. The dependency of frequency-dependent A.C. conductivity on dielectric data can be calculated from the empirical formula

$$\sigma_{ac} = \omega\varepsilon_0\varepsilon_r\tan \delta$$  \hspace{1cm} (7)

where $\tan \delta$ - tangent loss, $\varepsilon_0$—the permittivity of free space, $\varepsilon_r$—dielectric constant, $\omega$—angular frequency, and $\sigma_{ac}$—A.C. conductivity. Figures 6(a) and (b) shows the variation of the A.C. conductivity as a function of frequency at variable temperature with heating and cooling method. The A.C. conductivity values increases as the frequency increases, and the spectra show the dispersion in the full range of frequency. It also increased with the increment in the temperature; this phenomenon suggests the occurrence of negative temperature coefficient behavior of the KTN material, which is more prominent in the cooling method experiment. Initially, Jonscher’s power law $\sigma_{ac}(\omega) = \sigma_{dc}(0) + A\omega^n$ was fitted to explain the conduction mechanism. Where the $\sigma_{dc}(0)$ is the DC conductivity and $A$ is AC coupling coefficient or exponential factor, which is temperature-dependent and related to polarization strength. The ‘$n$’ is the frequency-dependent parameter and changes as $0 \leq n \leq 1$, which signifies the interaction of the mobile ions with fixed lattice present over there [46]. Here it has been found that the Jonscher power law is not following the experiment data point accurately. The reason for the disagreement may be the contribution of the different types if the charge carriers over the grain/grain boundary. Further, double power-law or modified power low has been applied to explain the conductivity spectrum (equation (7)) [47, 48].

$$\sigma_{ac}(\omega) = \sigma_{dc}(0) + A_1\omega^{n_1} + A_2\omega^{n_2}$$  \hspace{1cm} (8)

$\sigma_{dc}(0)$ is the dc electrical conductivity which depends on the long-range translation hoping of charge carriers. The second and third factors of equation number 8 correspond to the small-range translation hopping motion.
(low-frequency range) and localized hopping motion (high-frequency range). In the low-frequency region (figure 6) the A.C. conductivity graph contains the frequency-independent plateau which may be due to the large contribution of the DC conductivity \( \sigma_{dc}(0) \). Such a contribution of the DC conductivity is because of the large distance shooting of the mobile charge carrier or its successful pining of the ions to its adjacent ions. The frequency-independent part of the AC conductivity is increasing with increasing the temperature, and this plateau is spread over the vast region during the cooling mode, which reveals the large translation hoping in the cooling method experiment. The obtained value of the exponents \( n_1, n_2 \) has been found within the limit of the theoretical model (equation (8)) which falls in between 0.60 to 0.63 and 1.20 to 1.26 for \( n_1 \) and \( n_2 \), respectively. The obtained parameter of double power-law is in the range of reported value [49]. The fitting of the experimental data shows a good agreement with the modified Jonscher’s power law, which validates the theoretical description of experimental A.C. conductivity data.

**Field dependent polarization**

The P-E loop measurement has performed at different temperature with applied AC frequency 20 Hz and 100 Hz in the normal environment condition (figures 7(a) and (b)). The PE measurement has performed to understand the ferroelectric nature of the KTN electroceramics. At room temperature and 20 Hz applied AC frequency, A well saturated and slim shaped ferroelectric hysteresis with the saturated polarization 7 \( \mu \text{C cm}^{-2} \) for the maximum applied electric field 42.30 kV cm\(^{-1}\). It can be seen that with an increase in temperature from RT to 140 °C, the remnant polarization value increases nearly 4 to 5 times (figure 7(a)), which may be due to enhancement in tetragonality in the crystal structure. The enhancement in polarization is supported by the dielectric data where the system goes structural phase transition from orthorhombic to tetragonal at 185 °C. One can also understand the lossy shape of PE loops for low probe frequency (20 Hz) at higher temperature due to high leakage current. The mobile charge carriers significantly affect the polarization shape and magnitude. The mobile/space charge carriers do not cope up with the high probe frequency, or in other words, these mobile charge carriers leg behind during the high-frequency electric polarization measurement. However, bulk
ferroelectric samples do not provide a polarization-electric field (PE) loops greater than 100 Hz probe frequency. The suitable frequencies for bulk PE loops study are in the range of 1–10 Hz. [50–53]. A well-saturated polarization hysteresis loop for 100 Hz applied frequency are observed and compared with 20 Hz probe frequency. It can be seen from figure 7(b) that the effect of leakage current in the PE loops for 100 Hz applied frequency is too small, which may be due lagging of space charge carriers during the measurement of displacement current.

**Conclusion**

We have successfully probed the effect of environmental conditions on dielectric and impedance properties of KTN electro-ceramics. Near about room temperature, the magnitude and nature of dielectric constant, as well as tangent loss, are significantly different during the heating and cooling measurement due to the hygroscopic nature of the system. There was a small difference (10 °C) in the vicinity of FPT temperature (Tc) while heating and cooling measurement. The difference in Tc may be due to the irreversible motion of domains/domain walls while heating and cooling treatment. The AC conductivity and electrical transport properties have been successfully discussed in detail using the complex impedance spectroscopy. The bricklayer model has been successfully employed and concludes both the grain and grain boundary contribute to the conduction mechanism. Two different values of activation energies were obtained in two temperature regions, which suggest the dominant effect of electronic charge carriers in the low-temperature region and oxygen vacancies near the phase transition temperature in the overall conduction process, respectively. The A.C. conductivity data obeyed the double power law. This study also explains that the cooling mode measurement is more authentic for hygroscopic materials using the complex impedance and dielectric spectroscopy.

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