Investigation on relaxation and conduction mechanism in Pb$_{0.75}$K$_{0.5}$Nb$_2$O$_6$ new ferroelectric ceramic

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**ABSTRACT**

Using conventional solid state synthesis under air, the sample Pb$_{0.75}$K$_{0.5}$Nb$_2$O$_6$ was prepared in a single-phase TTB structure as indicated from X-ray analysis. Impedance spectroscopy analysis of the dielectric properties of Pb$_{0.75}$K$_{0.5}$Nb$_2$O$_6$ ceramic were investigated in the frequency range, 1 Hz–1 MHz and in the temperature duration from room temperature to 550 °C.

Impedance and modulus plots were used as tools to analyze the sample behavior as a function of frequency. Cole–Cole plots showed non-Debye relaxation. The nature of variation of the electrical conductivity, and value of activation energy of different temperature regions, suggest that the conduction process is of mixed-type (i.e., ionic polaronic and space charge generated from the oxygen ion vacancies). The structural and dielectric results are compared with three others TTB compounds derived from Pb$_{0.75}$K$_{0.5}$Nb$_2$O$_6$ (PKN) family: Pb$_{1.85}$K$_{1.15}$Li$_{0.15}$Nb$_5$O$_{15}$ (PKLN), K$_3$Li$_2$Nb$_5$O$_{15}$ (KLN) and Pb$_{1.8}$Gd$_{0.1}$K$_{1.1}$Nb$_5$O$_{15}$ (PGKN).

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1. Introduction

During the last years considerable attention has been focused on the study of niobates of tetragonal tungsten bronze type ferroelectrics (TTB). This structure is one of the greatest and yet purely studied families of ferroelectric oxides. They are described as a framework of MO$_6$ octahedra (M = metal of transition, in our case M = Nb) sharing corners, which reveals three kinds of tunnels with pentagonal (p), square (c) and triangular (t) sections[1,2]. The first two sites of coordination number respectively 15 and 12 can be occupied by ions of large size while the third one, of coordination number 9, can only be occupied by small size ions[3,4]. One of the most known of these compounds is the lead potassium niobate with general formula Pb$_2$K$_5$Nb$_5$O$_{15}$ derived compounds. The reason for having interest in them is provided by their potential applications as substrate material for Surface Acoustic Wave (SAW) devices[5,6], by their non-linear optical properties and piezoelectric devices[7–10]. Pb$_2$K$_5$Nb$_5$O$_{15}$ has a large electromechanical coupling factor of bulk waves, SAW’s and a small temperature coefficient of small fundamental frequencies, which was first discovered by Yamada and co-workers [11–13]. At room temperature it is isomorphic to ferroelectric PbNb$_2$O$_6$[14] having the space group $Cm2m$ (C$14$2$V$) and unit cell with four formula units[15].

Single crystal growth, structure and dielectric properties of Pb$_2$K$_5$Nb$_5$O$_{15}$ (Pb$_{1-x}$K$_{2x}$Nb$_2$O$_6$, where $x$ = 0.20), has been reported by Nakano and Yamada, and Hossain[13,16]. Because of this great interest and taking into account the standards of environmental protection, and on the basis of our recent work on the effect of the Pb substitution by K on the ferroelectric properties of the solid solution Pb$_{1-x}$K$_{2x}$Nb$_2$O$_6$ ($x$ = 0.1, 0.2, 0.25 and 0.3)[17], we are oriented to explore in details the new representative of PKN samples-Pb$_{0.75}$K$_{0.5}$Nb$_2$O$_6$ (called further as PKN25, Pb$_{1-x}$K$_{2x}$Nb$_2$O$_6$ where $x$ = 0.25) with less Pb and investigate their electrical properties. In this paper, we report the X-ray structural characterization and frequency-dependent dielectric and ac-conductivity measurements. We apply the phenomenological models in order to treat the results of dielectric and impedance spectroscopy experiments and to compare them with those for other TTB compounds such as PKLN[18,19] (to show the effect of Li$^+$ insertion) and PKGN [20] (to show the effect of the Gd$^{3+}$ insertion).

2. Synthesis, structure analysis and experimental details

Polycrystalline lead potassium niobates PKN ($x$ = 0.25) has been synthesized by solid state reaction route, using high purity (99.9%) carbonates and oxides; PbO, K$_2$CO$_3$ and Nb$_2$O$_5$. These ingredients (carbonates and oxides) were mixed in a desired stoichiometry, and 3% of PbO was added to compensate the loss caused by its volatility, the mixture was grounded in ethanol medium for an hour with agate mortar with pestle before each thermal treatment. The obtained powder was calcined at 900 °C/4 h. The process has been repeated three times to achieve homogenous state with single phase powder. The formation of the single phase compound was confirmed via X-ray powder diffraction (XRD). The granulated powder was compacted under a hydraulic press with 250 MPa pressure into discs of 13 mm diameter and of 1 mm thickness approximately. Then the obtained pellets were placed into alumina crucible and sintered at 1100 °C/1 h. The obtained sintered ceramic samples were crack-free.

The experimental density $\rho_{\text{exp}}$ was determined as the ratio of the mass of the pellet sample over the volume of the pellet sample. The measured density $\rho_{\text{exp}}$ was compared with the theoretical density $\rho_{\text{theor}}$ determined from X-ray measurements using the formula:

$$\rho_{\text{theor}} = \frac{\sum A/N}{V} (\text{g/cm}^3)$$

where $\Sigma A$ is the sum of the atomic weights of all the atoms in the unit cell, $N$ the Avogadro’s number and $V$ is the volume of the unit cell in cm$^3$.

The X-ray measurements were performed with a Siemens D5000 advanced diffractometer. The room temperature XRD pattern is shown in Fig. 1a. A good agreement of a cooper radiation with $\lambda_{K\alpha 1} = 1.5406(0)$ Å and $\lambda_{K\alpha 2} = 1.5444(3)$ Å was found between the observed and calculated interplanar
spacing. Profile adjustment calculation of Bragg reflections using the Fullprof software [21] revealed to be coherent for the orthorhombic structure with the space group Cm2m symmetry.

The lattice parameters and cell volume obtained for PKN25 are $a = 17.683 (7)$ Å, $b = 17.858 (7)$ Å, $c = 3.919 (2)$ Å and $V = 1237.553 (6)$ Å$^3$. They can be compared with the values reported on Pb$_2$KNb$_5$O$_{15}$ by Rao et al. $a = 17.721$ Å, $b = 17.983$ Å, $c = 3.892$ Å and $V = 1240.291$ Å$^3$ density = 6.10 g/cm$^3$ [22] and $a = 17.723$ Å, $b = 17.987$ Å, $c = 3.890$ Å and $V = 1241.662$ Å$^3$ density = 6.12 g/cm$^3$ [23]. Recall that the ratio $a/b$ in our case is close to that reported in Ref. [22] since its value is 1.0104 when compare with reported 1.014 in Ref. [22].

The theoretical density of PKN25 $\rho_{\text{theor}} = 6.12 (4)$ g/cm$^3$ is comparable with 6.1 g/cm$^3$, reported in Ref. [22], while the experimental density is $\rho_{\text{exp}} = 5.72 (2)$ g/cm$^3$. The compactness defined as the ratio between the experimental density $\rho_{\text{exp}}$ and the theoretical density $\rho_{\text{theor}}$ was estimated as 93%. It reveals that PKN25 compound has a good quality.

The SEM micrograph of PKN25 is shown in Fig. 1b. The surface morphology indicates the existence of polycrystalline microstructure comprising good grain growth with shape anisotropy. The grains are homogenously and uniformly distributed over the entire volume of the sample and show a good crystallization with certain degree of porosity. The average grain size of ($d = 1–4$ μm).

Silver paste was deposited manually on the circular faces of the ceramic to get the capacitor shaped samples. Dielectric measurements were carried using the Solartron SI-1260 spectrometer in the frequency range of 1–10$^6$ Hz. A source of 1 V was applied to the silver electroded pellet ceramic sample having 1 mm of thickness. The temperature variation was performed using a Linkam TS 93 hot stage with a temperature stability of ±0.1 K.

**Fig. 1.** X-ray diffraction patterns of Pb$_{0.75}$K$_{0.5}$Nb$_2$O$_6$ ceramic showing the observed, the calculated, their difference, and Bragg reflexions (a) and SEM image Pb$_{0.75}$K$_{0.5}$Nb$_2$O$_6$ (b).
3. Results and discussion

3.1. Dielectric analysis

The temperature dependences of the real and imaginary parts of dielectric permittivity $\varepsilon_r' = \varepsilon_r' - j\varepsilon_r''$ at various frequencies are shown in Fig. 2a and b. It follows from Fig. 2a that the temperature dependence of $\varepsilon_r'$ exhibits a diffuse peak that reaches a maximum at Curie temperature $T_C = 409^\circ$C. The height and the diffuse character of the peak decreases when frequency increases. Independence of the peak position on frequency indicates that this phenomena is not related with relaxor-type behavior. Most likely that the observed diffusion is caused by the domain walls or topological defects motion in the nucleating ferroelectric phase [24,25].

The dielectric permittivity at room temperature $\varepsilon_r'(RT) = 647$ presented relatively weak dependence on frequency. At the same time the dielectric permittivity at $T_C$ changes as: $\varepsilon_r'(T_C) = 3400, 2923$ and $2614$ at 1, 10 and 100 kHz, respectively. At low frequencies (<1 KHz), the dielectric constant is very high at $T_C$ and keeps ascending that implies a high concentration of space charge at elevated temperatures [26].

![Fig. 2. Temperature dependence of real part $\varepsilon_r'$ (a) and of imaginary part $\varepsilon_r''$ (b) of dielectric permittivity on heating.](image)
The same behavior was observed for KGN [20] and KLN [27] ceramics in which the phase transition was masked by the effect of ionic conduction at low frequencies. As follows from Fig. 2b the value of \( \varepsilon'_r \) increases with increase of temperature at studied frequencies.

We have recapitulated the different dielectric properties of PKN25 in comparison with PKGN [20] and PKLN [18] in Table 1. The insertion of Li leads to increase the maximum of the permittivity \( \varepsilon'_r \) and \( T_C \) that is estimated to be roughly equal to 20 °C. On the other side, the insertion of Gd leads to high decreasing of \( T_C \) from 409 °C to 310 °C and also of \( \varepsilon'_r \).

Fig. 3a and b shows the frequency variations of \( \varepsilon'_r \) and \( \varepsilon''_r \) for several temperatures respectively. Both dependencies demonstrate the strong dispersion at low frequencies. This behavior is attributed to the

![Fig. 3. Frequency dependence of \( \varepsilon'_r \) (a) and of \( \varepsilon''_r \) (b) in log–log scale at several temperatures.](image)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>( \varepsilon'_r ) (RT)</th>
<th>( \varepsilon'_r) max (100 KHz)</th>
<th>( \varepsilon'_r) max (1 MHz)</th>
<th>( T_C ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PKN25</td>
<td>647</td>
<td>2614</td>
<td>2600</td>
<td>409</td>
</tr>
<tr>
<td>PKLN</td>
<td>668</td>
<td>3299</td>
<td>3130</td>
<td>430</td>
</tr>
<tr>
<td>PKGN</td>
<td>500</td>
<td>2250</td>
<td>1650</td>
<td>310</td>
</tr>
</tbody>
</table>
low-frequency space charge accumulation effects. Such low frequency dielectric dispersion (LFDD) of both components of the complex dielectric permittivity is a common feature of ferroelectrics, having an ionic conductivity [28,29]. A detailed study of this phenomenon was reported by Jonscher et al. [30]. The dispersion of \( \varepsilon'' \) is stronger than that of \( \varepsilon' \) which implies the influence of the dc conductivity. The low frequency slope of the log–log frequency plot of \( \varepsilon''(\omega) \) (close to \(-1\)) indicates the predominance of the dc conduction in this frequency region.

3.2. Complex impedance analysis

Polycrystalline ceramic materials have a large variety of frequency dependent effects associated with their heterogeneity. The frequency-dependent impedance spectroscopy can separate the bulk material properties from the grain boundaries and electrode contributions. The principal studied parameters: complex dielectric permittivity \( \varepsilon' \), complex impedance \( Z' \), complex admittance \( Y' \) and dielectric loss \( \tan(\delta) \) are defined by:

\[
\varepsilon' = \varepsilon' - j\varepsilon''
\]

\[
Z' = Z' - jZ'' = 1/j\omega C_0 \varepsilon'
\]

\[
Y' = Y' + jY'' = j\omega C_0 \varepsilon'
\]

\[
\tan(\delta) = \varepsilon'' / \varepsilon' = Z'/Z'' = Y'/Y''
\]

where \( \omega = 2\pi f \) [Hz] \( (f \) is the frequency); \( C_0 = \varepsilon_0 S/e \) is the vacuum capacitance having the same electrodes surface \( S \), the thickness \( e \) and the permittivity \( \varepsilon_0 \).

The variation of the real and imaginary parts of impedance \( Z' \) and \( Z'' \) as a function of frequency within the interval 1 Hz–1 MHz and \( T = 300–500 \) °C is shown in Fig. 4a and b. It follows that the magnitudes of \( Z' \) and \( Z'' \) decrease with increase of the frequency. Such behavior indicates the increasing of the ac conductivity and the frequency dependence of the relaxation time. The large value of \( Z' \) at low frequency is caused by the space charge polarization.

As temperature increases the magnitude of \( Z' \) decreases and the peak \( Z_{\text{max}}' \) shifts towards the higher frequencies that is provided by the increasing of the relaxation time \( \tau \) and the loss of the space charge. The value of \( \tau \) has been calculated from the peak of \( Z'' \), taking into account that the asymmetric broadening of the peak is due to the spreading of \( \tau \) with temperature. From Fig. 4 we note the merging of \( Z' \) and \( Z'' \) and their vanishing above 10 kHz that may be explained by the reduction of space charge effects [31].

Inset in Fig. 4b shows the normalized imaginary part of the impedance \( Z'' / Z_{\text{max}}'' \) plotted as a function of frequency at several temperatures that exhibits slightly asymmetrical peak, indicating a relaxation triggering due to the ionic conductivity at high temperatures. The relaxation time is calculated from the \( Z'' \) peak position \( \omega_m \) using the relation: \( \tau_m = 1/\omega_m \). The relaxation frequency plotted in Fig. 5 as function of \( T^{-1} \) obeys the Arrhenius law in the tow regions ferroelectric and paraelectric:

\[
\omega_m = \omega_0 \exp(E_r/k_B T)
\]

According to Eq. (6) the activation energies \( E_r \) in ferroelectric and paraelectric phase is estimated from the slope of \( \log \omega_m \) vs. \( 1/T \) as 0.315 eV and 0.781 eV, respectively. The lower value of activation energy in the ferroelectric phase may be explained by the contribution of spontaneous polarization.

In paraelectric phase, the activation energy of PKN25 ceramic was determined as 0.72 eV [18], which is nearly lower than that of PKN25 ceramic. This weak difference can be explained by the contribution of \( \text{Li}^+ \) in the conductivity.

The scaling behavior of \( Z'' / Z_{\text{max}}'' \) clearly indicates that the distribution of relaxation times is nearly temperature independent. Fig. 6 illustrates the plot of \( Z''(\omega, T) \) data in scaled coordinates, i.e., \( Z''(\omega, T)/Z_{\text{max}}'' \) for the PKN25 ceramic measured at different temperatures.

As it can be noted, the \( \omega_m \) corresponds to the frequency of the peak value of \( Z'' \) in the \( Z'' \) vs. \( \log(\omega) \) plots. The entire data of imaginary part of impedance can collapse into one master curve (Fig. 6) [32].
Fig. 7 shows the Argand plot $Z'_{00}$ vs. $Z''_{00}$ at $T = 200–500 \, ^\circ C$ in the frequency range $1–10^6 \, Hz$. At lower temperatures $Z'$ linearly increases with $Z''$. This behavior is proper for the insulating state of the material. Below $300 \, ^\circ C$ a straight-line ohmic response has been observed. When temperature increases the slope of the line decreases and the plots tend to the real axis. When temperature increases the semi-circles become smaller, providing the shift towards lower $|Z|$. This indicated a reduction of grain and grain boundary resistance and negative temperature coefficient of resistance (NTCR) like in semiconducting materials [33–35].

The semi-circles are not perfect but skewed (inclined) with their centers depressed below the real $Z'$-axis by an angle $(\pi/2 - \alpha)$, where $0 < \alpha < 1$ [36], that indicates the presence of non-Debye type relaxation phenomena caused by a distribution of relaxation time.

To separate the dielectric properties of grains from grain boundaries and electrode contribution, the ceramic material is usually modeled by a sequence of parallel RC units connected in series. Each element gives the semicircular in complex impedance plane ($Z'_0, Z''_0$). In the complex impedance plane plot, the frequency $\omega$ at which the maximum of semicircular arc occurs is determined by the relaxation time constant $\tau$, and can be described by:

$$\omega_{\text{max}} = \frac{1}{\tau} = \frac{1}{(RC)^{-1}}$$

(7)
The resistances of the grains ($R_g$) and the grain boundaries ($R_{gb}$) could directly be obtained from the intersection with $Z'$-axis. The corresponding capacitances: $C_g$ and $C_{gb}$ can be calculated using the relation $f_{max} = \frac{1}{2\pi RC}$. The angular frequencies $\omega$ can be estimated from the maxima of the semi-circles.

This mathematical model is valid for “ideal” systems, where the Argand plot is composed from semi-circles with the centers on the $x$-axis. However, in most materials, the experimental Argand arc plot is given by distorted nonperfect semi-circle arc, the center of which is located below the real axis by a finite angle, referred as the depression angle ($\alpha$). This behavior indicates a kind of distributing impedance response that is normally associated with a spread of relaxation times. Therefore, the relaxation cannot be described by the classical Debye equation employing a single relaxation time. A constant phase element (CPE) [37,38] can be introduced to replace the capacitor in the RC circuit to account for the shape of the depressed semi-circle. The existence of depressed semi-circles in impedance spectra can be explained by a number of phenomena, depending on the nature of the investigated system. In general, the impedance data can be represented as an equivalent circuit, which consists of
tree parallel of resistance \((R)\) and constant phase element (CPE) in series. This is the one of the most common interpretation of phenomena for polycrystalline having a contribution of bulk grain, grain boundary and electrodes. The equivalent electrical circuit is presented in Fig. 8b. The impedance of constant phase element (CPE) can be described as \([38]\): 
\[Z_{\text{CPE}} = \frac{1}{(i\omega)^p},\]
where \(\omega\) is the angular frequency, \(T\) and \(p\) are constants and \(0 < p < 1\).

The CPE describes an ideal capacitors with \(C = T\) for \(p = 1\) and an ideal resistor with \(R = 1/T\) for \(p = 0\). Therefore, \(p\) can be used to represent the degree of perfection of the capacitor and represents a measure of arc distortion below the real impedance axis. The parameter \(p\) is related with the depression angle as follow: 
\[\alpha_d = \left( \frac{1}{C_0} \right)^{1/p} p^2.\]

The complex impedance \((Z')\) of each element (CPE/R) is given by:
\[Z' = RT / (1 + (j\omega\tau)^p)\]  \(\text{(8)}\)

where \(\tau_p = RT\)

Now, Eq. (7) can be modified as:
\[\omega_{\text{max}} = \tau^{-1} = (RT)^{-1/p}\]  \(\text{(9)}\)

A good fit of the experimental data was obtained in the whole frequency range using the constant phase element (CPE) as shown in Fig. 8a. It is important to note that the modified equivalent RC circuit model with CPE yields to a Argand relaxation type plot. Such relaxation is commonly used to analyze the behavior of ionic conductors \([36]\). The resistance \(R\), and the parameters \(p\) and \(T\) of the CPE were obtained for each temperature. The values of \(p\) are found to lie close to unity (between 0.95 and 0.99). The constant time \((\tau)\) of grain and grain boundary relaxation were then obtained using the relationship given in Eq. (9). The temperature dependence of the effective grain and grain boundary parameters \(R_g\), \(R_{gb}\) as well as of the relaxation times \(\tau_g\) and \(\tau_{gb}\) are shown in Fig. 9. When temperature increases the \(R_{gb}\) is found to be smaller than \(R_g\), which means that conductivity occurs through the grains boundaries.

It is also natural that relaxation times \(\tau_g\) and \(\tau_{gb}\) decrease with increasing of the temperature. Plots of \(R_g, R_{gb}\) vs. \(T^{-1}\) yield the Arrhenius law. The collected in Table 2 slopes of these plots give the conduction of the material and the relaxation activation energy for grains and grains boundaries. It follows that conduction mechanism is dominated by grains boundaries.
Fig. 8. Argand plot at 500 °C showing impedance deconvoluted curves (a) and equivalent circuit used for fitting the experimental (b).

Table 2
Activation energy values for conduction and relaxation of grains and grain-boundaries in PKN25 paraelectric phase.

<table>
<thead>
<tr>
<th></th>
<th>Grain conduction activation energy, $E_g$ (eV)</th>
<th>Grain-boundary conduction activation energy, $E_{gb}$ (eV)</th>
<th>Grain relaxation activation energy, $\epsilon_g$ (eV)</th>
<th>Grain-boundary relaxation activation energy, $\epsilon_{gb}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.440</td>
<td>0.563</td>
<td>0.696</td>
<td>0.434</td>
</tr>
</tbody>
</table>

Fig. 9. Temperature dependence of the resistance and the time relaxation of grain (g) and grain boundary (gb) in Pb$_{0.75}$K$_{0.5}$Nb$_2$O$_6$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
3.3. Electrical modulus response

Electrical response of the material can also be analyzed by the complex modulus formalism, which provides an alternative approach based on polarization analysis. Hence, the use of the function $Z$ is particularly appropriate for the conductive analysis, whereas $M^\prime$ and $\varepsilon^\prime$ formalisms are suitable when localized relaxation dominates. The complex modulus $M^\prime$ was defined in terms of reciprocal complex permittivity $\varepsilon^\prime$ given by equations:

$$M^\prime(\omega) = M^\prime + jM'' = 1/\varepsilon^\prime = j\omega\varepsilon_0 Z^\prime$$

$$M^\prime = \varepsilon^\prime/(\varepsilon^\prime_0 + \varepsilon^\prime_0); \quad M'' = \varepsilon''/(\varepsilon^\prime_0 + \varepsilon^\prime_0)$$

Frequency dependencies of $M^\prime$ and $M''$ are shown in Figs. 10a and b at different temperatures. At high frequencies the real part of the modulus $M^\prime$ tends to the constant value $M^\prime_\infty$ whereas $M''$ exhibits a peak of the amplitude $M''_{\text{max}}$. The value of $M''_{\text{max}}$ increases and shifts towards higher frequencies with increasing temperature. This shift indicates a relaxation of conductivity in the material [39].

![Fig. 10. Frequency variation of real part of electrical modulus $M^\prime$ (a) and imaginary part of electrical modulus $M''$ (b) and the Arrhenius plot of relaxation frequency (inset).](image)
Arrhenius plot (see Eq. (6) and inset in Fig. 10-b) exhibits a linear dependence of angular frequency versus inverse temperature in the ferroelectric and paraelectric regions.

The values of activation energy in ferroelectric and paraelectric regions are 0.401 eV and 0.586 eV, respectively. There are weakly different from that obtained in Eq. (6) of previous section. This difference may be explained by the presence of different conduction mechanisms (ionic, electronic, polaronic, etc.) [40].

The scaled behavior of each $M''$ by $M''_{\text{max}}$ and each frequency by $\omega_m$ for different temperatures is illustrated in Fig. 11. As it can be observed, the temperature–frequency is electric modulus dependent. It is known as modulus master curve and presents the scaling behavior of sample electric modulus. The coincidence of all curves/peaks at different temperatures exhibits temperature independent behavior of the dynamic processes.

The frequency $\omega_m$ (corresponding to $M''_{\text{max}}$) gives the most probable relaxation time $\tau_m$ from the condition $\omega_m \tau_m = 1$.

Going further in the description of experimental data, the variation of normalized parameters $M''/M''_{\text{max}}$ and $Z''/Z''_{\text{max}}$ as a function of logarithmic frequency measured at 500 °C for the PKN25 ceramic are shown in Fig. 12. Compared with the impedance and electrical modulus data allows the determination of the bulk response in terms of localized, i.e., defect relaxation or non-localized conduction, i.e., ionic or electronic conductivity [41]. The Debye model is related to an ideal frequency response of localized relaxation. In reality the nonlocalized process is dominated at low frequencies. In the absence of interfacial effects, the non-localized conductivity is known as the dc conductivity. However, for the present system the $M''/M''_{\text{max}}$ and $Z''/Z''_{\text{max}}$ peaks overlap suggesting the components from both long range and localized relaxation. In order to mobilize the localized electron, the aid of lattice oscillation is required. In these circumstances electrons are considered not to move by them but by hopping motion activated by lattice oscillation (Fig. 12). In addition, the magnitude of the activation energy suggests that the carrier transport is due to the hopping conduction [42].

3.4. Conductivity

Fig. 13(a) illustrates the temperature variation of the ac conductivity at different frequencies of the PKN25 compound. The Curie points obtained from AC conductivity measurements are in full agreement with the $T_C$ values found from the temperature dependency of the real dielectric constant of PKN25. It can be clearly observed that the conductivities at different frequencies increase and appear to be approaching each other at higher temperatures. The change in slope of curve will reflect a change
in the conductivity phenomenon in paraelectric and ferroelectric regions. The changes in slopes observed in conductivity plots suggest that it can be broadly divided into three regions, which are (i) 540–310 °C, (ii) 300–150 °C and (iii) 140–40 °C. The curve shows a slope change at about 410 °C. This may be due to ferroelectric transformation occurring at this temperature.

It is obvious that at low temperature region the AC conductivity depends significantly on the frequency, which was observed in this type of materials [43,44]. At lower temperatures and higher frequencies it is observed to be independent of temperature in PKN25. However, with the increase in temperature the dielectric relaxation takes place and the dependency of the conductivity on frequency gets reduced.

The activation energy values were calculated using the Arrhenius equation (6) or also (12) for the three regions and are given in Table 3:

\[
\sigma_{dc}(T) = \sigma_{dc} \exp(-E/k_B T)
\]  

From Table 3, the AC conduction activation energies at high frequency are found to be lower than that of the low-frequency region. This is due to the fact that at low frequencies the conductivity is taken by mobility or transportation over long distances rather than by relaxation/orientation mechanism. The energy required for relaxation/orientation process is bigger than that required for mobility of charge carriers over longer distances [45,46]. The activation energy values obtained at high temperature are attributed to thermal motion of the oxygen vacancies or the formation of association among the oxygen vacancies and residual cations in the grain boundary [47–49]. The decrease of conductivity in PKYN may be due to decrease in the concentration of oxygen vacancies [50]. The activation energies obtained in the experiment are typical value for an ionic conductor.

Fig. 13 presents the frequency dependence of ac conductivity (\(\sigma_{ac}\)) at several temperatures. It demonstrates a plateau at low frequencies and dispersion at high frequencies. The plateau region corresponding to dc conductivity is found to be extended to higher frequencies when temperature increases. AC conductivity dispersion takes place at a frequency known as hopping frequency that increases with increasing \(T\). This behavior suggests that electrical conductivity occurs via hopping mechanism, which is governed by the Jonscher’s power law [51]:

\[
\sigma_{ac} = \sigma_{dc} + A\omega^n
\]  

where \(\sigma_{dc}\) is the direct current conductivity of the sample, \(\omega\) the angular frequency of measurement. The exponent represents the degree of interaction between mobile ions and with the lattices around them and \(A\) is a constant which determines the strength of polarizability.
The experimental conductivity spectra of the sample are fitted using Eq. (13). The fitting results are presented in Table 4. The nature of the plot (13-b) shows a decreasing trend of \( n \) with increase of temperature. The model based on classical hopping of electrons over barrier predicts a decrease in the value of the index \( n \) with increase in temperature. According to Funke [52] when the \( n \) value is equal to 1, it means that the hopping motion involves a translational motion with a sudden hopping.
and when \( n \) is greater than 1, it means that the motion involves localized hopping without the species leaving the neighborhood. The frequency at which change in slope take place is known as hopping frequency of the polarons (\( \omega_p \)) and is temperature dependent. The ac conductivity follows the Almonde West relation \([53]\) as 
\[
\sigma(\omega) = A\omega_p [1 + (\omega/\omega_p)^n],
\]
where \( \omega_p \) is the hopping frequency and \( n \) is the Jonscher’s constant \([54]\). The literature \([55]\) have reported that 
\[
\sigma_{dc} = A\omega_p,
\]
so the relation takes the form of 
\[
\sigma(\omega) = \sigma_{dc}[1 + (\omega/\omega_p)^n].
\]
The ac conductivity is calculated using the relation \( \sigma = \omega\varepsilon\varepsilon_0\tan\delta \). The plateau region of the conductivity at higher frequency and temperature may be related to the space charge.

This assumption is reasonable since the space charge effect vanishes at higher temperature and frequency. This typical behavior suggests the presence of hopping mechanism between the allowed sites.

4. Conclusion

Polycrystalline ferroelectric \( \text{Pb}_{0.75}\text{K}_{0.5}\text{Nb}_2\text{O}_6 \) (PKN25) ceramic that belongs to TTB type structure has been prepared by mixed-oxide method. X-ray structural analysis confirmed the formation of single-phase material in an orthorhombic system at room temperature. A dielectric peak at \( T_C = 409°C \) has been observed. Dielectric properties analysis confirms a nonrelaxor type behavior. Higher values of dielectric permittivity: \( \varepsilon'_r \) and \( \varepsilon''_r \) in the low-frequency region are related to the space charge polarization. Reduction of the space charge polarization and that of the grain interaction occur above 10 kHz. The dispersion in the high-temperature region indicates the localized ionic conductivity. Complex impedance analysis shows the nonDebye poly-dispersive behavior and highlights the presence of grain, grain boundary and material-electrode interface effects in the material. Using impedance and modulus formalisms, the activation Arrhenius energy in paraelectric region was estimated to be equal 0.781 and 0.586 eV correspondingly.

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References
