Low frequency dielectric dispersion studies in ferroelectric ceramics of Pb$_{0.77}$K$_{0.26}$Li$_{0.2}$Ti$_{0.25}$Nb$_{1.8}$O$_{6}$

K Sambasiva Rao, P Murali Krishna, D Madhava Prasad, T Swana Latha & C Satynarayana
Centre for Piezoelectric Transducer Materials, Department of Physics, Andhra University, Visakhapatnam 530 003, India.

Received 3 November 2006; accepted 28 February 2008

Temperature and frequency dependence of dielectric constant and conductivity properties of Pb$_{0.77}$K$_{0.26}$Li$_{0.2}$Ti$_{0.25}$Nb$_{1.8}$O$_{6}$ (PKLTNO) ceramics are modeled through universal dielectric response (UDR). Partial substitution of Ti$^{4+}$ in Nb$^{5+}$ increased the B-sites ordering, supported by charge compensation and creation of oxygen vacancies that obeys Kroger-Vink notation. The release of electrons by this reaction are captured by the Nb$^{5+}$ and Ti$^{4+}$ to generate Nb$^{5+}$ and or Ti$^{3+}$. Thus the possibility of the hopping of electrons among Nb$^{5+}$ and Nb$^{3+}$ and Ti$^{4+}$ and Ti$^{3+}$ entering in the crystal structure participate in the conductivity. The dielectric characterization is performed from room temperature to 590°C, in the frequency range of 45 Hz-5 MHz. The measured dielectric constant has been found to fit to Jonscher’s dielectric dispersion relations: $\varepsilon' = \varepsilon_{\infty} + \sin(n(T)\pi/2) (\sigma(T)/\omega_0) (\omega^a(T)^{-1})$ and $\varepsilon'' = \sigma/\omega_i\omega_0 + \cos(n(T)\pi/2) (\sigma(T)/\omega_0) (\omega^b(T)^{-1})$. Cole-Cole plots are found inclined at an angle $(1-n(T))\pi/2$ which obeys the universal material behaviour $\varepsilon_{\infty} + A(T) (\omega^b(T)^{-1})$. The exponent $n(T)$ and coefficient $A(T) = [\sigma(T)/\omega_0]$ has been observed to be minimum and maximum respectively at $T_c \approx$ 425°C. The conductivity studies reveal the conduction in the material arising due to hopping of bound charges.

**Keywords:** Dielectric constant, Space charge, Low frequency dielectric dispersion, Electrical conductivity

Dielectric spectroscopy (DS) is an experimental tool, which has been found to be applicable in wide range of materials. It covers nowadays the extraordinary spectral range from $10^{-8}$ to $10^{12}$ Hz. This enables researchers to make sound contributions to contemporary problems in modern physics. The complex dielectric function describes the interaction of electromagnetic waves with mater and reflects by that the underlying molecular mechanisms. It is known that dielectric study can reveal lot of information of a solid, such as phase transition, defect, and transport properties. A detailed analysis of the frequency and temperature dependence of the ac conductivity and permittivity is necessary in order to characterize the microscopic mechanisms and the accompanied relaxation phenomena of the charge carrier transport. DS is a non-invasive, very sensitive technique to investigate variety of complex systems and also suitable to study biological systems as recently reviewed. For the investigation of relaxation processes and conductivity DS is a frequently used method. Dielectric relaxation spectroscopy (DRS) is a popular and powerful technique that has been shown to provide information about the molecular dynamics of almost any kind of materials and liquid crystals. In particular, dielectric measurements complement dynamic mechanical analysis (DMA), for example, by determining the frequency dependence of the various processes over a wider range of frequencies.

A striking observation is that many systems display a similar frequency dependence conductivity and permittivity namely Jonscher’s universal dielectric response (UDR) found a topic of intense experimental and theoretical interest. At low frequencies the bulk (real) ac conductivity $\sigma(0)$ is frequency independent, but at higher frequencies the ac conductivity increases, following a power law behaviour such that, $\sigma(\omega) \propto \omega^n$. Where $\omega$ is angular frequency and $n < 1.0$. The universality is considered with conventional Debye behaviour of relaxation times and stretched exponential parameter. The power laws are observed in a range of single crystals, polycrystalline and amorphous materials including ceramics, polymers, composites, wet cement, electronic and ionic conductors, it is important that any model must be able to account for the ubiquity of the UDR. In view of the increased interest, in this paper we presented the detailed study of the universal dielectric response.

Niobates with tungsten-bronze structure have attracted much scientific and commercial attention because of their wide potential applications as ferroelectric, piezoelectric, pyroelectric and nonlinear optical materials. The tetragonal tungsten
bronze (TTB) unit cell can accommodate metal ions in five different sites designated A₁, A₂, C, B₁ and B₂. The structure basically consists of a complex array of distorted BO₆ octahedra sharing corners in such a way that there are three different types of interstices between them which are available for cation occupation. The unit cell may be described as \((A_1)_4 \,(A_2)_2 \,C_4 \,(B_1)_7 \,(B_2)_3\)O₃₀, where A₁ and A₂ sites may be substituted by Na, K, Cs, Ca, Sr, Ba, Pb, Bi and rare earths. The much smaller C site by Li, Be, Mg and Al. B₁, B₂ sites by Mg, Fe, Ti, Zr, Sn, Nb, Ta and W. However, they must be made in such a way that the valency charges of ions occupying the A, C and B sites balance those of the O²⁻ ions and maintain overall electrical neutrality.

PKN has a large electromechanical coupling factor of bulk waves and a small temperature dependence of small fundamental frequencies, which was first discovered by Yamada. It is recognized to be important material for surface acoustic wave (SAW) devices by their non-linear optical properties by others. However, the utilization of PKN single crystal is largely limited due to PbO loss resulting from the high temperature growth and to formation of cracks when cooling through the Curie temperature. PKN belongs to space group \(C_{2v}^{14} - C_{m2\bar{m}}\) and its unit cell contains four formula units.

The elaboration, control of stoichiometry and dielectric spectroscopy analysis of PKN was reported by Zigao et al. Impedance spectroscopic analysis and piezoelectric properties on \(Pb_{0.4}K_{0.6}Nb_2O_6\) has been reported by Rao et al. Influence of lanthanum substitution on impedance, dielectric and electromechanical properties of \(Pb_{(1-x)}K_{x}2Nb_2O_6\) for \(x = 0.23\) has also been reported by Rao et al. Effect of simultaneous substitution of \(Li^+\) and \(Ti^{4+}\) in ceramics of \(Pb_xKNaB_2O_5\) on structure, dielectric, modulus, impedance and conductivity properties have been characterized by Rao et al. Structure, dielectric and piezoelectric strain coefficient of \(Pb_{0.25}K_xM_{3-x}^\varepsilon\)Nb₂O₆ ceramics, where \(M= La\ or\ Bi\) and \(x = 0.1 < x < 0.4\) has been reported by Neurgaonkar et al. Present material, \(Pb_{0.77}K_{0.26}Li_{0.25}Ti_{0.25}Nb_{1.8}O_6\) (PKLTON) belongs to the formula type \(A_xC_yB_{10}O_{30}\), where all A-sites and C-sites are filled, which is called completely filled structure.

Previous reports indicate, the dielectric spectroscopy characterization of substitutional solid solution based on \(Pb_{0.7}K_{0.3}Nb_2O_5\) in which \(K^+\) is replaced by other monovalent ions \(Li^+\) and \(Nb^{5+}\) by tetravalent \(Ti^{4+}\) have not been studied for so far.

The objective of the present study is to investigate the space charge influence on dielectric properties and to observe the critical behaviour of the pre factor \(A(T)\) and exponent \(n(T)\) in Jonscher’s expression \(A(\text{io})^n\) in para electric/ferroelectric transition region.

**Experimental Procedure**

**Material**

Ceramic composition of lead potassium lithium titanium niobate \(Pb_{0.7}K_{0.26}Li_{0.25}Ti_{0.25}Nb_{1.8}O_6\) (PKLTON) has been synthesized by solid state reaction as follows:

\[
0.77PbO+0.13(K_2CO_3)+0.1(Li_2CO_3)+0.25(TiO_2) +0.9(Nb_2O_3)\rightarrow Pb_{0.7}K_{0.26}Li_{0.25}Ti_{0.25}Nb_{1.8}O_6+0.23CO_2
\]

Initially stoichiometric mixture of, AR grade powders of oxides, carbonates and titanates of PbO, Li₂CO₃, Nb₂O₅, TiO₂ and K₂CO₃ have been weighed and grounded well mechanically in an agate mortar in methanol medium. K₂CO₃ has been heated at 300°C before weighing to reduce its hygroscopic nature. Subsequently, the grounded mixture has been taken for thermal treatment. The powders were carline thrice at 900°C for 4 h to achieve single phase with a well grounding at each stage. A weight check confirmed a total decomposition of the carbonate. The fine homogeneous calcined powder then granulated using organic binder poly vinyl alcohol (PVA) to provide strength and flow ability of granules and to reduce the brittleness of the sample. The granulated powder compacted under a hydraulic press with 580 MPa uniaxial pressure and made into discs of 11 mm diameter and 3 mm thickness approximately. The pellets placed on a platinum foil and calcined powder was sprinkled on the surface of the sample, to compensate the loss of lead and closed with inverted alumina crucible. The pellets have been burned at 600°C/1 h to eliminate the binder followed by sintering at 1070°C for 60 min in a linear programmable furnace. The experimental density has been obtained in PKLTONO is 5.63 g/cc, reveals ceramic samples are observed to be crack free.

In PKLTONO, A-sites are occupied by \(Pb^{2+}\) and \(K^+\), C-sites are occupied by \(Li^+\). B-sites are occupied by \(Ti^{4+}\) and \(Nb^{5+}\). Further, the total number of cations available in the octahedral positions of B-sites are 10. But, in the present composition under investigation partial substitution of \(Ti^{4+}\) in \(Nb^{5+}\) increased the B-sites by 0.25. These excess B-cations give a possibility for admixture phase, and are associated in
charge compensation of the compound. With the replacement of Nb$^{5+}$ ions with Ti$^{4+}$ at lattice site B—there is a strong possibility of creation of oxygen vacancies. These oxygen vacancies are created in order to maintain the localized charge neutrality$^{25,27}$. In the present case, the ceramic samples have been sintered at high temperature $>$1000°C, a slight amount of oxygen loss occurs according to Kroger-Vink notation,

$$V_0 \rightarrow V_0^\prime + e^\prime,$$
$$V_0^\prime \rightarrow V_0^\prime\prime + e^\prime\prime,$$

these electrons might bonded to Ti$^{4+}$ in the form of

$$\text{Ti}^{4+} + e^\prime \rightarrow \text{Ti}^{3+}.$$

Where, $V_0$ is the oxygen vacancy, $V_0^\prime$ and $V_0^\prime\prime$ are single and double ionized oxygen vacancies respectively and $e^\prime$ is the electron released or captured. Since, Nb can exists in +3 and +5 states and Ti can exists in +3 and +4 states, there is a possibility to release of electrons in the above reaction and these may be captured by the Nb$^{5+}$ and Ti$^{4+}$ to generate Nb$^{3+}$ and or Ti$^{3+}$. Thus there is a possibility of conduction arising due to the hopping of electrons among Nb$^{5+}$ and Nb$^{3+}$ and Ti$^{4+}$ and Ti$^{3+}$. At low frequency conductivity may arise due to short range translational hopping of electrons among Nb$^{5+}$ and Nb$^{3+}$ and Ti$^{4+}$ and Ti$^{3+}$. At high frequencies, the conductivity arise due to localized orientational hopping (back and forth hopping) among Nb$^{5+}$ and Nb$^{3+}$ and Ti$^{4+}$ and Ti$^{3+}$ states.

Low frequency spectroscopy measurements

The well sintered cylindrical samples were carefully polished to eliminate possible inhomogenity due to exchanges with sintering atmosphere. Then, silver paste was used for making electrode on sample surfaces. The measurement of dielectric constant, conductivity as a function of temperature [from room temperature (RT) to 600°C] and frequency (45 Hz-5 MHz) recorded simultaneously at 67 frequency points using computer interfaced HIOKI 3532-50 LCR Hi-Tester, Japan. A constant heating rate of 5°C/min was maintained with an offset temperature 0.2°C and time period of 0.5 min for making the above property measurement.

The capacitance, $C_p$ and loss tangent, tan$\delta$ are taken calculating the real dielectric constant ($e^\prime$) and imaginary dielectric constant ($e^{\prime\prime}$) according to the following equation,

$$e' = C_p d/(\varepsilon_0 A), \quad e^{\prime\prime} = e' \tan\delta$$

where, $d$ and $A$ are the thickness and electrode area of the ceramic disc respectively and the $\varepsilon_0$ is the free space permittivity ($\approx 8.854\times10^{-12}$ F/m).

**Results and Discussion**

**Influence of temperature and frequency on dielectric constant**

The temperature dependence of real dielectric constant ($e^\prime$) at various frequencies has been shown in Fig. 1, allowed us to determine the Curie temperature ($T_c$), at 425°C. The values of $e^\prime$ increases with decrease in frequency, is a characteristic feature of the polar dielectric materials. The observed remarks from Fig. 1 are:

(i) $e^\prime$ increases gradually with increase in temperature due to interfacial polarization becoming more dominant as compared to the dipolar polarization and passes through $T_c$ and then, decreases due to phase transition from ferroelectric to paraelectric phase.

(ii) The dispersion of $e^\prime$ in paraelectric phase is mainly attributed to the ionic conductivity. At high temperatures low frequencies another maximum appeared. This phenomenon is strongly related to space charge effects and not to another phase transition.

The frequency independent $e^\prime$ versus $T_c$ in PKLTNO reveals, the material belongs to classical ferroelectrics but not relaxor. It is in good agreement with the fact that the each crystallographic site in the structure is occupied by only one kind of ion.$^{28}$ The

![Fig. 1—Temperature dependence of real part of dielectric constant at various frequencies for PKLTNO ceramic](image-url)
broadness in the dielectric constant versus temperature response may be attributed to the compositional fluctuations caused by the simultaneous substitution of Li\textsuperscript{+} and Ti\textsuperscript{4+} analogues to certain compounds with pervoskite structure\textsuperscript{29}. A sharp decrease in dielectric constant with the increase in frequency can also be explained in terms of interfacial polarization.

Curie-Weiss law has been fitted in paraelectric region and the Curie constant (\(K\)) has been found to be $1.25 \times 10^5$, which is a characteristic feature of oxygen octahedral ferroelectrics\textsuperscript{30-32}. The values of room temperature dielectric constant, \(\varepsilon_{\text{RT}}\), Curie constant (\(K\)) are given in Table 1.

The Arrhenius plot for the influence of temperature on imaginary part of dielectric constant, \(\varepsilon''\) is shown in Fig. 2. An anomaly at a particular temperature has been observed, which is almost coincides with \(T_c\) of material. The dispersion of \(\varepsilon''\) at different frequencies in para region is stronger than that of \(\varepsilon'\). Since, it is directly related to ac conductivity by following well known equation \(\varepsilon'' = \sigma_{\text{ac}}/\varepsilon_0\omega\). The \(\log(\sigma_{\text{ac}}/T)\) curves should have the same shape as \(\log(\varepsilon'') - 1/T\). In Fig. 2 the high temperature behaviour of \(\varepsilon''\) may be described by the Arrhenius law especially at low frequencies. This result suggests that the conduction mechanism predominate in high temperature and low frequency region is thermally activated. The typical complex dielectric constant (Cole-Cole) plots at three different temperatures (para region) are shown in Fig. 3. In the description of dielectric relaxation, a generalized Debye model due to Cole-Cole plots is used with frequency dependent complex permittivity \(\varepsilon^*\) represented by the well-known expression\textsuperscript{11}.

\[
\varepsilon^*(\omega) = \varepsilon_\infty + \{(\varepsilon_{s1} - \varepsilon_\infty)/(1 + \omega \tau_1)^{\alpha_1}\} + \{(\varepsilon_{s2} - \varepsilon_\infty)/(1 + \omega \tau_2)^{\alpha_2}\}
\]

where, \(\omega\) is the measuring frequency, \(\tau_1\) and \(\tau_2\) are the relaxation frequencies, \(\alpha_1\) and \(\alpha_2\) are the characteristics of relaxation time without unit (1\( \geq \alpha \geq 0\)).

\(\alpha\) represents the measure of the width of the distribution of the relaxation time. The value of \(\alpha\) estimated from the Cole-Cole plots by measuring the angle between the real part of dielectric constant and radius of the circle. If the centre of the semicircle lie on \(\varepsilon'\) axis \(\alpha\) is zero (Debye type). Otherwise the centre is below \(\varepsilon'\) axis and \(\alpha \neq 0\) (non-Debye type). \(\alpha_1\) and \(\alpha_2\) are empirical “broadness” parameters showing the degree of departure from Debye model. \(\varepsilon_{s1}\) and \(\varepsilon_{s2}\) are the limiting values of permittivity. \(\varepsilon_\infty\) is the high frequency limiting of the dielectric constant.

From Cole-Cole plots (Fig. 3), the universal material behaviour, represented by \(\varepsilon_\infty + A(T)(\omega^{\alpha(T)})\) is obeyed by making a straight line inclined at an angle \([1-n(T)]x\ \pi/2\) and an intercept at \(\varepsilon_\infty\) with the horizontal axis\textsuperscript{33}. Figures 4a and 4b respectively,

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Composition & \(\varepsilon'_{\text{RT}}\) (kHz) & \(T_c\) °C & \(\varepsilon'_{T_c}\) (kHz) & \(\sigma_{\text{RT}}\) S/cm \(\times 10^9\) & Curie constant, \(K\) (\(\times 10^5\)) \\
\hline
PKLTNO  & 64 & 425 & 123 & 1.77 & 1.25 \\
\hline
\end{tabular}
\end{table}

Fig. 2—Arrhenius plot of imaginary part of the dielectric constant at various frequencies for PKLTNO ceramic

Fig. 3—Nyquist plots of the complex dielectric constant at different temperatures for PKLTNO ceramic
show the log-log plots of $\varepsilon'\nu$ versus $\omega$ and $\varepsilon''\nu$ versus $\omega$ for the PKLTNO. The observed variation in $\varepsilon'\nu$ with frequency is ascribed to the formation of a space charge region at the electrode/sample interface, which is familiarly known as $\omega^{(n-1)}$ variation or the non-Debye type of behaviour, where the space charge regions with respect to frequency is explained in terms of ion diffusion. The low frequency region is attributed to the contribution of charge accumulation at the interface. At high frequencies, due to high periodic reversal of the field at the interface, the contribution of charge carriers (ions) towards the dielectric constant decreases with increasing frequency.

Hence, $\varepsilon'\nu$ decreases with increasing frequency. Typical variation of $\varepsilon''\nu$ is shown in Fig. 4b. In the present case, the conduction losses predominate at lower frequencies and hence at all temperatures the $\varepsilon''\nu$ shows the $1/\omega$ dependence on the frequency. Also $\varepsilon''\nu$ is found to increase with increase in temperature and dielectric loss peak has not been observed. In ionically conducting materials, at low frequencies there is an unavoidable electrode polarization effects and the dielectric constant is rather high. The dispersion in $\varepsilon''\nu$ is stronger than that in real part implying that it is influenced by the dc conductivity. The low frequency slope of the curve of $\log \varepsilon''\nu$ versus $\log \omega$ is close to -1 indicating the predominance of the dc conduction in the frequency region.

Figure 5 shows the variation of real part of the ac conductivity as a function of frequency at different temperatures in ferro and para region. The frequency dependence of conductivity in different materials is described by power relation proposed by Jonscher,

$$\sigma(\omega) = \sigma_{dc} + A \cdot \omega^n$$

where, $\sigma(\omega)$ is total conductivity, $\sigma_{dc}$ is frequency independent conductivity, and the coefficient $A$ and the frequency exponent $n$ are thermally activated, material dependent quantities. The term $A \cdot \omega^n$ contains the a.c. dependence and characterizes all dispersion phenomenon. From Fig. 5, there exists a plateau-like region ($\sigma_{dc}$) and subsequently the conductivity increases with increase in frequency, varying approximately as a power of frequency, $\omega^n$ (where $n$ is a function of temperature as well as frequency) at all the temperatures. The exponent $n$ has been found to behave in a variety of forms like a constant, decreasing with temperature and increasing with temperature, but always varies within $0<n<1$. Funk explained that the value of $n$ might have a physical meaning (i.e., $n\leq{1}$ would mean that the hopping motion involved is a translational motion with a sudden hopping). On the other hand, value of $n>1$,
would mean that the motion involved is a localized hopping of the species with a small hopping without leaving the neighborhood.

From Fig. 5, the switch from the frequency-independent \( \sigma_{dc} \) to frequency-dependent \( \sigma(\omega) \) regions, shows the onset of the conductivity relaxation phenomenon and the translation from the long range hopping to the short range ion motion. The dispersion in conductivity at low frequencies may be due to the electrode polarization. The frequency dependence of ac conductivity may arise due to free as well as bound carriers. In the present case, the ac conductivity increases with increase in frequency hence must be related to bound carriers trapped in the sample. In present material PKLTNO, the ion Li\(^+\) mainly exhibit cationic conductivity due to the mobility of Li\(^+\) in the partially filled C-site.

Dielectric dispersion relations and interpretation of the experimental results

Both \( \varepsilon' \) and \( \varepsilon'' \) shows strong dispersions in low frequency region (Fig. 4). Such strong dispersions in both the components of the complex dielectric constant appear to be a common feature in ferroelectrics associated with non-negligible ionic conductivity and is referred to as the low frequency dielectric dispersion (LFDD). Detailed studies of this phenomenon were carried by Jonscher et al. According to the Jonscher’s power law, the complex dielectric constant as a function of the frequency \( \omega \) can be expressed as

\[
\varepsilon^* = \varepsilon' - i \varepsilon'' = \varepsilon_\infty + \left( \sigma/\varepsilon_0 \omega \right) + \left[ a(T)/\varepsilon_0 \right] \left( i \omega^{(n\cdot T)} \right)
\]

where \( \varepsilon_\infty \) is the ‘high frequency’ value of the dielectric constant, \( n(T) \) is the temperature-dependent exponent and \( a(T) \) determines the strength of the polarizability arising from the universal mechanism.

The real and imaginary parts of the complex dielectric constant are given by the following relations

\[
\varepsilon' = \varepsilon_\infty + \sin(n(T)\pi/2) \left[ a(T)/\varepsilon_0 \right] \left( \omega^{(n\cdot T)} \right) \quad \ldots (1)
\]

\[
\varepsilon'' = \sigma/\varepsilon_0 + \cos(n(T)\pi/2) \left[ a(T)/\varepsilon_0 \right] \left( \omega^{(n\cdot T)} \right) \quad \ldots (2)
\]

Where, the first term in Eq. (1), determines the lattice response and corresponding dc conduction part respectively. While the second term in both the equations reflects the charge carrier contribution to the dielectric constant. The temperature and frequency dependencies of the dielectric constant \( \varepsilon' \) (Fig. 4a) could be explained by Eq. (1). The charge carrier term \( [\sin(n(T)\pi/2) \left[ a(T)/\varepsilon_0 \right] \left( \omega^{(n\cdot T)} \right) \] dominates at low frequency and \( \varepsilon_\infty \) is negligible. Therefore, for a constant \( n \), Eq. (1) yields a straight line with a slope equal to \( n-1 \) in the double logarithmic plot of \( \varepsilon' \) and frequency. At high frequencies the charge carriers fail to respond to the external field, therefore the measured dielectric constant is due to contribution from the lattice polarization. This accounts for the linear decrease in the low frequency region and a plateau region at high frequencies (Fig. 4). As \( A(T) = a(T)/L \) increases with increase in temperature, the charge carriers term become more prominent at high temperatures, thereby resulting in the low frequency dielectric dispersion. The exponent \( n(T) \) and the coefficient \( A(T) \) have been determined from plots shown typically in Fig. 4a.

The interaction between the charge carriers participating in the polarization process is characterized by the parameter \( n \) and value of \( n = 1 \), is Debye case, which is attainable at very low temperatures. However, as the temperature increases, the interaction increases, leading to a decrease in \( n \). The value of \( n \) calculated from the high frequency region decreases as the temperature increases and attains minimum at \( T_c \) and subsequently it increases with further increase in temperature. The possible explanation for \( n \) to be minimum at \( T_c \) is due to the strong interaction between the charge carriers and the lattice. Careful analysis of Fig. 4b indicates the existence of slopes corresponding to \( -1 \) in the low frequency region and \( -(1-n) \) in the high frequency region. As the dc conductivity term increases with increase in temperature, the second term of Eq. (2) is totally overshadowed by the first term. So, at low frequencies and high temperatures, the dc conductivity term is dominated and yield a slope of \(-1\) which indeed is consistent with the data shown in Fig. 4b.

Qualitative interpretation of the experimental results

A successful fitting is achieved for the experimental dielectric data to the dielectric dispersion relation given in Eq. (1). Figure 6 shows plot of the theoretically calculated [from Eq. (1)] and experimental values for \( \varepsilon' \) as a function of frequency at 380°C and 540°C. In high temperatures an excellent agreement between experimental and theoretical values of \( \varepsilon' \), has been found, whereas at low temperatures the fitting results are not in good agreement because of intervention of another contribution in the low frequency region.
The lattice contribution $\varepsilon_\infty$, shows a peak at $T_C$. An interesting feature of Fig. 8 is that two linear regions corresponding to the ferro and para electric states. A linear relation of the exponent with temperature has also been found in some ion conducting systems. Near $T_C$, a minimum $n$ is observed. Similar results have been obtained in PKN ceramics. A maximum value of $A$ is observed near the $T_C$. The critical behaviour of the prefactor $A$, which determines the strength of polarizability (or the non-ideal conductivity) arising from diffusive motion of carriers. The results show a strong temperature dependence of these parameters.

The charge carriers induced dielectric constant, $\varepsilon'_{\text{car}}$, is calculated according to second term of Eq. (1) for various frequencies is shown in Fig. 10.

The $\varepsilon_\infty$ value was chosen as the dielectric constant at 1 MHz, as the dispersion is negligible around this frequency range. The temperature dependence of $n(T)$ and $A(T)$ have been determined from the curve fitting (Fig. 4a). Variation of $\varepsilon_\infty$, $n(T)$ and $A(T)$ are shown in Fig. 7—The temperature dependence of high frequency dielectric constant $\varepsilon_\infty$ for PKLTNO ceramic. Fig. 8—Variation of critical exponent $n(T)$ with temperature showing minimum at $T_C$ of PKLTNO. Fig. 9—Temperature dependence of the prefactor $A(T)$ showing a peak at $T_C$ of PKLTNO.
Conclusions

The following conclusions can be drawn from this study:

(i) Dielectric spectroscopy experiments have been performed on dense Pb_{0.77}K_{0.23}Li_{0.2}Ti_{0.25}Nb_{1.8}O_{6} (PKLTNO) ferroelectric ceramic sample (T_{C}=425°C) from 300°C to 500°C in 45 Hz to 5 MHz frequency range.

(ii) The dispersion of ε' versus temperature above T_{C} reveals the ionic conductivity is strongly related to space charge effects. The ε'' dispersion is stronger than that of real part implying the dc conductivity influence in PKLTNO.

(iii) The ac conductivity increases with increase in frequency, reveals the bound carriers trapped in the sample. The dispersion in conductivity at low frequencies shows the electrode polarization effect.

(iv) In Cole-Cole plots (non-Debye type) the universal material behaviour found to obeyed by making a straight line inclined at an angle [1−n(T)x v/2 and an intercept at ε_{∞}. Using Jonscher’s dielectric dispersion relations, deduced the lattice response and the charge carrier contribution to the dielectric constant. Agreement between the experimental and theoretical values of ε’’ has been shown, with some deviation at low frequency and temperature range.

(v) Evaluated the true dielectric constant of PKLTNO at some frequency ranges by separating influence of carrier induced dielectric constant (ε_{c}). The parameters n(T) and A(T) are determined. An anomaly at T_{C} is observed in both the parameters indicating the coupling between the charge carriers and the phonons. The treatment which was adopted is in line to rationalize the dielectric behaviour of PKLTNO ceramics.

References

RAO et al.: FERROELECTRIC CERAMICS OF Pb$_{0.77}$K$_{0.22}$Li$_{0.25}$Ti$_{0.25}$Nb$_{1.8}$O$_6$