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Electricalconductivity and Dielectric Properties of $Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3$ Ceramic Material

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Abstract Solid state reaction route is used by adopting calcination, dry pressing and sintering for the preparation of polycrystalline $Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}$ TiO_3(BNKLT) material. Studies of dielectric and conductivity parameters of the material were studied as a function of frequency(45Hz to 5MHz) and temperature(RT-600°C). At higher temperatures the conductivity curves were found to be merging, due to the effect of release of space charge.The conductivity parameters such as ion-hopping rate (ω_p), fitting parameters (n(T), A(T)) and the charge carrier concentration(K') terms have been calculated using Almond and West formalism.A strong dispersion in both the components of complex dielectric constant, appear to be a common feature in ferroelectrics associated with good ionic conductivity and is referred to as the low frequency dielectric dispersion(LFDD).This offered an opportunity to obtain a good candidate for replacing the lead based ceramics.

Keywords Conductivity, Activation Enthalpy, Carrier Concentration, Dielectric Relaxation

1. Introduction

An increasing amount of attention has been paid to lead-free or low lead- content ceramics in recent years, in consideration of environmentalprotection. Actually, research on lead free dielectric or ferroelectric materials has begun a few decades ago. Unfortunately, the best properties from the currently investigated lead-free ferroelectric materials are still not as good as expected. Since it was discovered by smolenskii et al in 1961[1], $(Bi_{0.5}Na_{0.5})TiO_3$(BNT) has attracted much attention due to its good ferroelectricity. Its piezoelectric and electromechanical properties were greatly enhanced by forming solid solutions with potassium (K), Barium (Ba) and Lithium (Li) kind of dopants[2-5]. $[Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}]TiO_3$ is considered to be a new kind of material for lead-free piezoelectric and many efforts have been made to investigate the fabrication of high-performance piezoelectric with BNT[5-7]. Literature survey revealed that there is no previous research on conductivity, dielectric relaxation properties of BNKLT ceramic materials.

Transport and relaxation properties can be described at higher temperatures with reference to inter particle interaction[8]. The electrical conductivity studies indicate the nature of charge species involved in the conduction on application of electric field. Impedance spectroscopy has appliedsuccessfully in the investigation of ferroelectric materials[5]. The dielectric constant obtained from ac data would be unambiguous and would have a better physical significance than those obtained from capacitance measurements at chosen fixed frequencies.

The factors that mainly influence the magnitude of the ionic conductivity are concentration of mobile ions and their mobility, which in turn depend on the ion-hopping rate. The enthalpy for the ionic hopping process has profound influence on the magnitude of the electrical conductivity. Hence, an attempt was made to study the conductivity and dielectric relaxation behaviourof BNKLT ceramic material. This study reveals clear understanding on the role of the macroscopic parameters such as fitting parameters (n, A), hopping rate(ω_p), activation enthalpy(H_m) and carrier concentration (K') on the conductivity of $Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3$ (BNKLT)ceramic material.The present research on conductivity and dielectric relaxation behaviour of BNKLT is first of its kind in the world.

2. Experimental Work

In the present work, solid state reaction route is used for the preparation of polycrystalline material. $Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3$(BNKLT) ceramic material have been prepared by taking the raw materials of Analar Grade chemicals(oxides and carbonates) Bi_2O_3, Na_2CO_3, K_2CO_3, Li_2CO_3 and TiO_2in the preparation of the composition. The powders were mixed with desired weight ratio with approximately 3% excess Bi_2O_3 and Na_2CO_3, to compensate the weight loss due to their high vapour pressure. The powders were mixed and grounded well in dry and methanol medium before each calcination. The resultant grounded mixture was calcined twice at 850°C for 2hr with intermedi-

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ate grinding. After calcination, the ceramic powder was mixed with polyvinyl alcohol (5%), as the binder and pelletized into discs of 13 mm diameter and about 1-1.5 mm thickness. After binder burnout, at 600℃ for 1 hr, the green discs have been sintered in a closed platinum crucible at 1135℃/2 hr.The measurement of dielectric (ε'), and conductivity (σ) as function of temperature (RT–600℃) and frequency (45 Hz to 5 MHz) have been carried out using computer interfaced LCR Hi-Tester (HIOKI 3532-50, Japan).

3. Results and Discussion

3.1. Electrical Conductivity

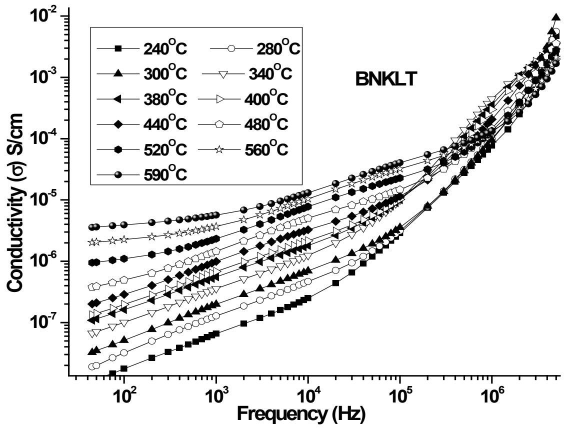


Figure 1(a). Variation of conductivity with frequency at different temperatures

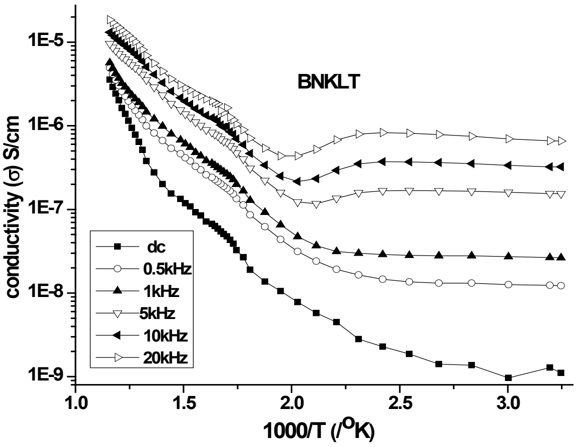


Figure 1(b). Variation of d.c and a.cConductivity versus 1000/T

The mechanism of ionic conductivity in solids has been generally discussed in terms of the conventional hopping formalism[9]. The conductivity of an ionic conductor is determined by both the concentration of the mobile ions and the rate at which they are able to hop from site to site in the material.Fig.1(a) shows the a.c conductivity BNKLT polycrystalline material as a function of frequency(45Hz to 5MHz) at different temperatures.

At RT and low frequency region, the observed plateau region in the studied materials represents (Fig.1(a)) the d.c. conductivity, it may be related to the response of the electrons and oxygen vacancies to the applied external field. This over all behaviour has been found for many ionic conductors and has been reported by many researchers[10-15].As the temperature is increased thermal fluctuation may dissociate oxygen vacancies into single and double ionized oxygen vacancy with the release of electrons and is given by Kroger-Vink(1956) notation[16].

$$O_0 = V_o'' + 2e' + \frac{1}{2}O_2$$
$$V_o \to V_o' + e'$$
$$V_o' \to V_o'' + e' \qquad (1)$$

Where V_o' is single ionized oxygen vacancy having one negative charge and V_o'' is double ionized oxygen vacancy having no net charge on it.The creation of oxygen vacancies may help in production of Ti^{3+} ions at the centers of the octahedra. The hopping mechanism, which plays an important role in the conduction process according to the relation $Ti^{4+} + e^- \leftrightarrow Ti^{3+}$. It is reported that titanate based perovskite oxide materials contain Ti^{3+} that are formed because of capture of electron released during the process of formation of oxygen vacancies by Ti^{4+}. The polaronic conduction of 3d electrons on Ti^{3+} with low mobility must be predominant at low temperature. Thesepolaronic states are thermally dislocated,residual carriers and 3d electrons are strongly scattered by thermal phonons at high temperature, resulting in high electronic conductivity[17].

The Arrhenius plots for d.c and a.c conductivity versus inverse temperature of BNKLT composition is shown in Fig.1(b). It is observed from the Fig.1(b) that the conductivity shows a temperature independent behaviour at low temperatures for all the frequencies. In high temperature region the conductivity is found to increase with increase of temperature. This rise in conductivity may be due to free as well as bound carriers in the material and hence Arrhenius type change in conduction becomes apparent.

Further, It is evident from the Fig.1(b) that the conductivity of the material from RT to a certain temperature (<150℃) exhibits a decrease in conductivity with increase in temperature indicating a Positive Temperature Coefficient of Resistance (PTCR) behaviour. At moderate temperatures (150-250℃) the conductivity is observed to be independent of temperature but depends on frequency. The PTCR behaviour is intimately connected with the grain boundary[18]. The origin of the PTCR ceramics is usually explained on the basis of the Heywang[19] model, which assumes that the acceptor type states of the grain boundaries create equivalent potential barriers associated with resistive depletion layers near the boundaries. The PTCR is a result of the dependence of barrier heights on dielectric constant of grain or bulk in higher symmetry phase ($T>T_m$). The increase of dielectric constant, as $T<T_m$, leads to a decrease of the barrier heights and to an exponential increase of conductivity. In this region, grain boundary barriers apparently do not play significant role. The decrease of barrier height below T_m is attributed to the compensation of the grain boundary charge by spontaneous polarization[20-25] or the disappearance of the local-

ized states at the grain boundaries in rhombohedral phase.

The conductivity of the material at higher temperatures (250°C-590°C) is found to increase with increase in temperature indicating the Negative Temperature Coefficient of Resistance (NTCR) behaviour similar to semiconductor, which is related to the bound carriers trapped in the sample. At higher temperatures the conductivity curves are found to be merging, which may be due to the effect of release of space charge[26]. Also, as the frequency decreases, oxygen vacancies and other defects mask the growth of ferroelectric phase and hence no clear anomalies appear in this region.

It is seen from Fig.1(b) a change in the slope of the Arrhenius plots has been observed. A slight change in slope may be due to the contributions from different regions in polycrystalline materials (i.e. from grain, grain boundary etc), where appearance of space charge polarization takes place accompanied with the change in activation energy[27] and also it is related to transition temperature(T_m)[28].

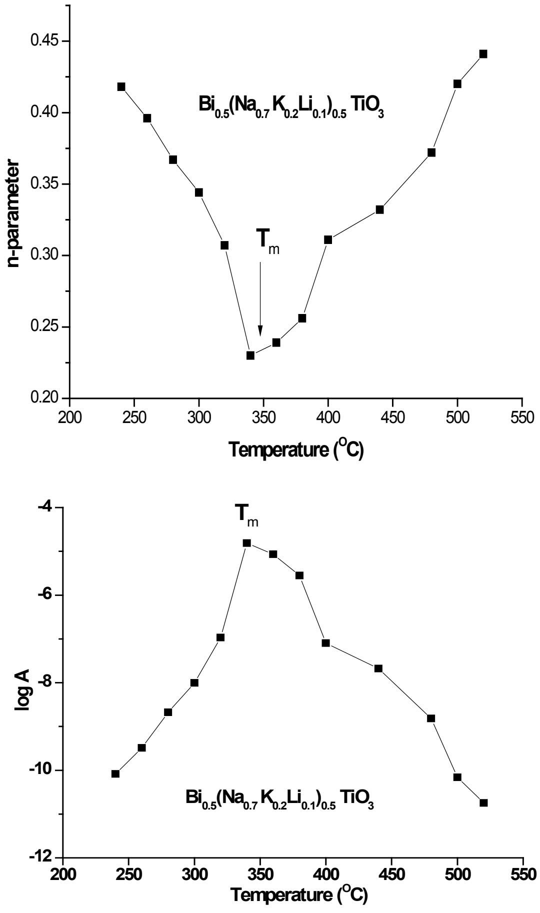


Figure 2. Variation oftemperature dependence Exponential factor(n) and pre-factor (A) as a function of temperature

Table 1. a.c and d.c conductivity activation energies of present studied material

Temperature region (°C)	BNKLT: Conductivity Activation Energies (eV)					
	0.5kHz	1kHz	5kHz	10kHz	20kHz	dc
580-470	0.37	0.30	0.20	0.18	0.18	0.46
470-370	0.17	0.17	0.18	0.15	0.16	0.19
370-300	0.16	0.16	0.17	0.11	0.10	0.18

The change in the slope of the curve reflects a change in conductivity phenomenon. The plot is divided into three regions (i) 580-470°C (ii) 470-370°C and (iii) 370-300°C. At lower temperature, the complexes formed may be immobile and the orientation effect is suppressed and does not contribute much to the conductivity. As the temperature increases the impurity defect complex start dissociating, there by contributing to the conductivity. At higher temperatures the temperature dependence becomes strong and variation of conductivity with frequency is small. Further at higher temperatures the measured conductivities at all frequencies become equal and also nearly equal to dc conductivity. The activation energies have been calculated for the BNKLT material and the values are given in table1.

The a.c. ionic conductivity, excluding electrode and intergranular effect is found to be dispersive in the material. Typically it varies with frequency as shown in fig.1(a) and can be fitted by the equation

$$\sigma(\omega) = \sigma + A\omega^n \tag{2}$$

Where σ is the d.c conductivity, A is a temperature dependent pre-factor and n is the exponential factor.

At low temperatures, especially below 150°C, the conductivity increases with increase in frequency with a characteristic ω^n dependence. At high temperatures and low frequencies conductivity shows a flat response while it has a ω^n dependence at high frequencies. The value of n has been determined from slope of conductivity curves at high frequency region.

The hopping rate is given by

$$\omega_p = \left(\frac{\sigma_{dc}}{A}\right)^{\frac{1}{n}} \tag{3}$$

$$\log A = log\sigma_{dc} - nlog\omega_p \tag{4}$$

The computed values of n and logA have been plotted as a function of temperature and is shown in fig.2.The temperature dependent fitting parameters, pre-factor A(T) and exponential factor n(T) which generally varies between 0 and 1 depending on temperature. The exponential factor n(T) represents the degree of interaction between mobile ions with the lattice around them. The Pre-factor A(T) determines the strength of polarizability. The present studied material (BNKLT) has been obeyed the above mentioned universal power law. Interesting features of fig.2 are two linear regions are observed which corresponds to the paraelectric and ferroelectric states. A linear relation of the exponential factor with temperature has also been found in some ion conduction systems[29-31]. The value of n(T) decreases with increase in interaction. The observed minimum in the vicinity of T_m shows a large extent of interaction between the charge carriers and the polarization. The decrease in the value of n(T) with decrease in temperature towards T_m is due to the increase in number of polar nano regions which are absent or negligible at high temperatures. It is obvious from the fig.2 the value of A(T) is found to increase with increase in temperature and showed a maximum value at T_m. Further increase in temperature A(T) value decreases. This critical behaviour of the pre-factor A(T), which determines the strength of the polarizability arising from the diffusive motion of carriers. The obtained values of n(T) and log A at T_m are 0.23 and -4.8 respectively.

Ion hopping rates, ω_p is thermally activated process and is given by the equation

$$\omega_p = \omega_e \exp(-\frac{H_m}{kT}) \quad (5)$$

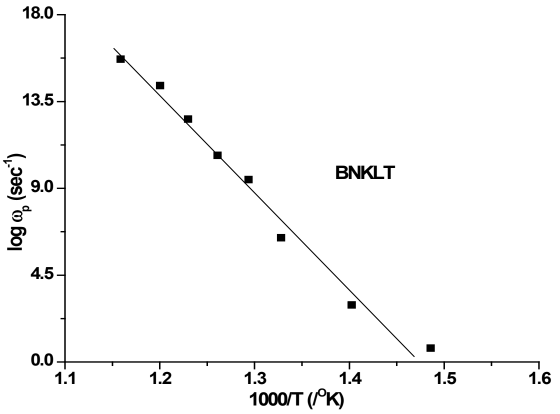


Figure 3(a). The temperature dependence of hopping rate of various materials

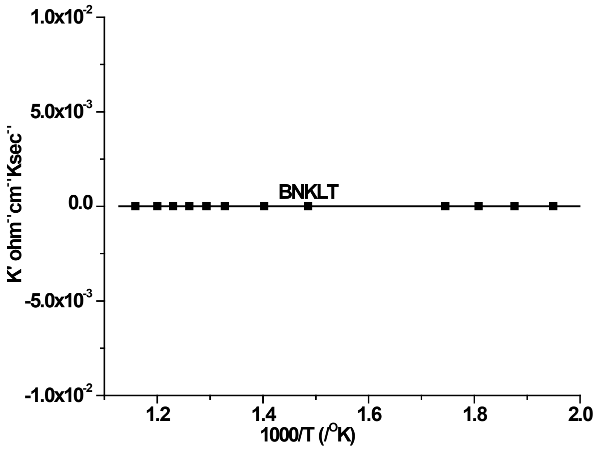
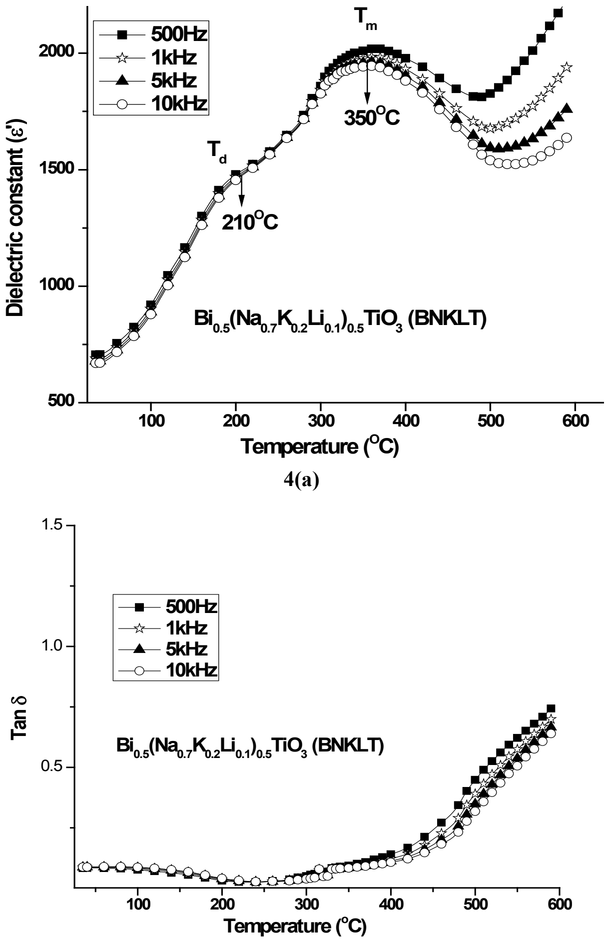


Figure 3(b). Variation of K' with temperature

Where ω_p is the hopping rate, H_m is the activation enthalpy for hopping ions, k is the Boltzmann constant and T is the absolute temperature. The hopping rate ω_p is calculated from equation(3). The Arrhenius format is shown in fig.3(a) by taking the value of slope from (fig.3(a)) and using the equation(5) the values of activation enthalpy was estimated for K^+Li^+ substituted BNT composition and the value is 0.42eV.After the hopping rates have been determined, it is possible to estimate the carrier concentration term K' by using the equation:

$$K' = \sigma T/\omega_p \quad (6)$$

Temperature dependence of the charge carrier concentration term (K') is shown in fig.3(b). It is seen from fig.3(b) that the charge carrier concentration term remains almost constant over entire temperature range in studied sample, which in turn reveals that there is no creation of charge carriers over the entire temperature range. This also suggests that the increase in conductivity with temperature in the present study is mainly due to the increase of hopping rate ω_p with temperature.



4(a)

4(b)

Figure 4. Variation Dielectric Constant (ε') and loss tangent (Tanδ) with temperature on BNKLT material at various frequencies

3.2. Dielectric Relaxation

The value of dielectric constant(ε') increases with increasing in temperature attaining a maximum value at T_m. As a typical behaviour of normal ferroelectrics, dielectric constant increases gradually with increment in the temperature due to interfacial polarization becoming more dominant as compared to the dipolar polarization and passes through a maximum at T_m. The dielectric constant (ε') starts to decrease due to the phase transition from ferroelectric to the paraelectric phase. Two dielectric peaks have been observed in the studied material as it is evident from fig.4. The observed two dielectric peaks can be attributed to the factors caused by the phase transition from ferroelectric to anti-ferroelectric and anti-ferroelectric to paraelectric phase. Here, the transition between ferroelectric phase and anti-ferroelectric phase is called as depolarization temperature (T_d), and the temperature corresponding to maximum value of dielectric constant is named as maximum temperature (T_m).

K^+Li^+ substituted BNT composition showed an increase in both T_d (210°C) and T_m (350°C) compared to BNT(T_d=200°C & T_m=325°C) composition. The Li^+ in the $Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3$ ceramics act as soft additive which affects the dielectric properties. Owing to the ionic radius of Li^+(0.76Å) being smaller than that of Na^+(1.39Å), this substitution will result increasing in polarization, which benefits the increase of both ε'_{RT} and ε'_{T_m}. The values ε'_{RT} and ε'_{T_m} are found to be 689 and 1983 respectively. Decrease in conductivity compared with BNT has been observed in K^+Li^+ substituted BNT; it may also increase the values of both ε'_{RT} and ε'_{T_m} [32]. The calculated Dielectric data have been shown in table2.

A broad dielectric constant versus temperature (fig.4) response has been noticed in the BNKLT composition. They are A-site complex perovskites, with the composition (A'A")BO_3. A complex perovskite has a tendency to be disordered, in that there is no regular long range arrangement of the complex-site ions. This lack of order creates many micro regions of slightly different compositions and thus phase transition temperatures. The presence of these many different phases and thus different transition temperatures lead to a broadening of the overall phase transition temperature of the bulk material. Therefore it is assumed that, in K^+Li^+ modified BNT material the compositional fluctuations and microscopic inhomogenties causes the broadening of peak[33].

The important characteristic of ferroelectric materials is the existence of critical temperature called the Curie point (T_c or T_m). The dielectric constant in most ferroelectric crystals has very large value near Curie point. It can be described by the Curie-Weiss law:

$$\varepsilon = \frac{K}{(T - T_C)} \tag{7}$$

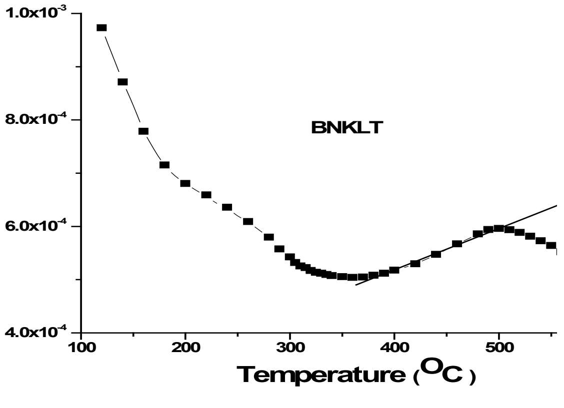


Figure 5. Reciprocal Dielectric Constant (1/ε') Versus Temperature

Where, K is Curie constant, T_C is Curie temperature and T is the temperature in the paraelectricregion.The value of Curie constant has been evaluated in the BNKLT composition by drawing a graph between 1/ε' and temperature (fig.5), using the Curie Weiss law. The Curie constant in the studied composition has observed to be in the order of 10^5 which were consistent with the reported values[34]. Obtained Curie constant (K), 10^5 conforming the studied composition is belong to oxygen octahedraferroelectrics[33].

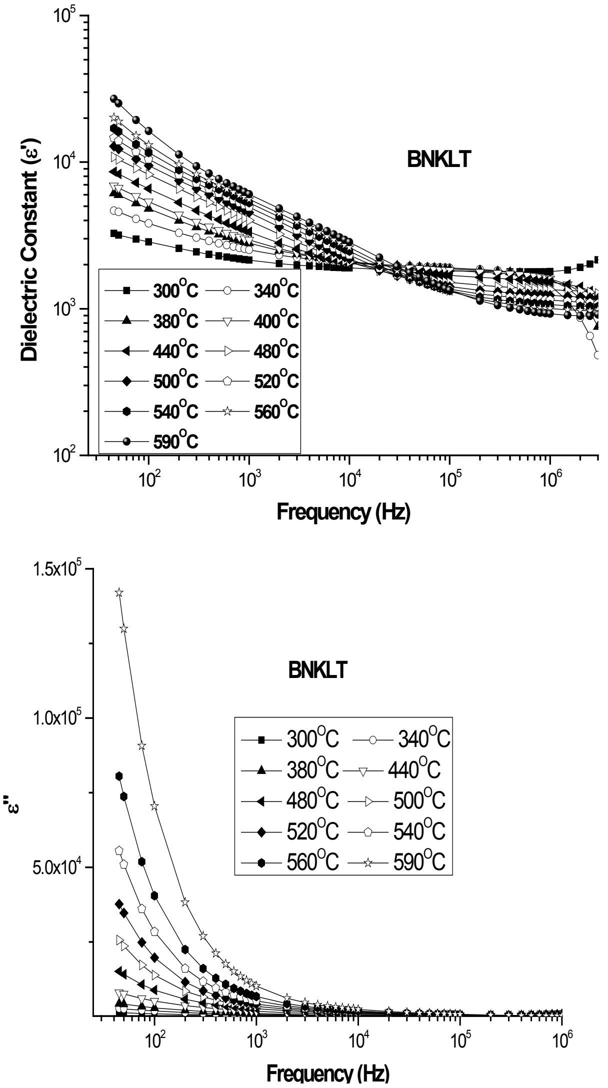


Figure 6. Frequency dependence of dielectric constants, ε' and dielectric loss ε"

The dielectric loss as a function of temperature for BNKLT is shown in fig.4(b). The room temperature tanδ value has been found to be the order of 10^{-2} in studied material indicating low loss material. However, slight increase in the magnitude of Tan δ at RT has been found in BNKLT, it may be due to space charge polarization. The source of dielectric loss in insulating ceramics is the space charge polarization/domain wall relaxation[35]. The presence of defects like oxygen vacanciesV_0'' which act as space charge and contribute to the electrical polarization of perovskite materials, can thus be related to the dielectric loss.

Table 2. Dielectric data of BNKLT ceramic material

Composition	Dielectric constant (ε') at (1kHz)		T_d 1kHz (°C)	T_m 1kHz (°C)	Tan δ at (1kHz)		Conductivity (σ_{RT} - 1kHz) x10^{-8} (S/cm)	Curie Constant ($X10^5$) °K
	ε'_{RT}	ε'_{T_m}			RT	T_m		
BNKLT	689	1983	210	350	0.08	0.09	2.64	2.58

The observed dielectric data in the studied material reveals that high dielectric constant with low dielectric loss(tan δ) in the BNKLT material may be useful as capacitor materials in the electronic industry.

The real part of the dielectric constant (ε') versus frequency response at different temperatures is shown in fig.6. It can be seen from fig.6, that the values of ε' and ε" are found to decrease with rise in frequency in the studied material. The higher values of dielectric constant found at low frequency is due to the presence of all types of polarization (atomic, electronic, space charge etc.) mechanisms. At higher frequencies ε' and ε" arefound to decrease, as it is arise due to the contribution from electronic polarization, other contributions becoming insignificant and also fall in dielectric constant arises from the fact that polarization does not occur instantaneously with the application of the electric field because of inertia[21]. This takes place at the contacts or in the bulk of the material at the grain boundary. Charge is able to accumulate at these interfacial sites and thereby able to contribute to the total capacity or dielectric constant. A strong Dielectric dispersion in both ε' and ε" has been observed at low frequency in studied material. Such a strong dispersion in both the components of complex dielectric constant, appear to be a common feature in ferroelectrics associated with good ionic conductivity and is referred to as the lowfrequency dielectric dispersion(LFDD)[36-38]. The Debye formula giving the ε' and ε" related to the free dipole oscillating in an alternating field and is given by

$$\varepsilon = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1+i\omega\tau} \qquad (8)$$

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1+(\omega\tau)^2} \qquad (9)$$

Where ε_s and ε_∞ are the low and high frequency values of ε', ω=2πf and τ is the relaxation time.

The complex dielectric constant as a function of the frequency ω in accordance with the Jonscher's power law is given by

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\sigma}{i\varepsilon_o\omega} + (a(T)/\varepsilon_o)(i\omega^{n(T)-1}) \qquad (10)$$

Where ε_∞ is the high frequency value of the dielectric constant, n(T), a(T) fitting parameters.

From the equation (10) the real and imaginary parts of the complex dielectric constant are given by the following relations.

$$\varepsilon' = \varepsilon_\infty + \sin\left(n(T)\frac{\pi}{2}\right)\,(a(T)/\varepsilon_o)(\omega^{n(T)-1}) \qquad (11)$$

$$\varepsilon'' = \frac{\sigma}{\varepsilon_o\omega} + \cos(n(T)\frac{\pi}{2})\,(a(T)/\varepsilon_o)(i\omega^{n(T)-1}) \qquad (12)$$

Where the first term in equation(11) determines the lattice response and that in the equation(12) corresponds to the dc conduction part, while the second term in both equations reflects the charge carrier's contribution to the dielectric constant. The carrier concentration term $(\sin\left(n(T)\frac{\pi}{2}\right)(a(T)/\varepsilon_o)(\omega^{n(T)-1}))$ dominates at low frequency and ε_∞ is negligible. Therefore, for a constant n, equation (11) yields a straight line with a slope equal to n-1 in the double logarithmic plot of ε' and frequency. At higher frequencies the charge carriers fail to respond to the external field, therefore the measured dielectric constant is due to the contribution from the lattice polarization. This accounts for a linear decrease in the low frequency region.The determined values of n(T) and a(T) (obtained from conductivity measurements) theoretical values of ε' has been calculated by using equation(11). The experimental and theoretical values of ε' is fitted at different temperatures of BNKLT composition is shown in fig.7. It is seen from the fig.7 at higher temperatures the fitting of theoretical and experimental values of dielectric constant is good.

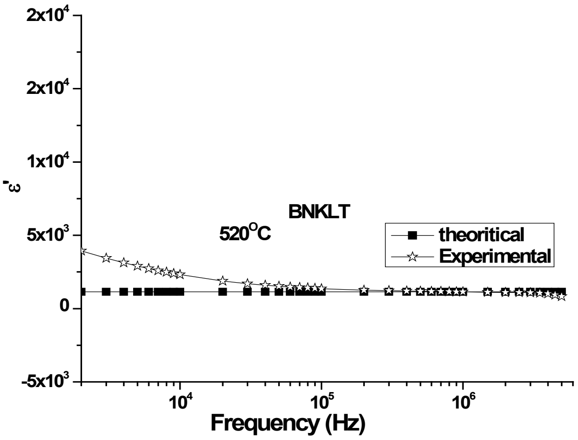


Figure 7. Theoretical and experimental fitting of ε' BNKLT composition

4. Conclusions

The Pollicrystalline BNKLT material has been prepared by solid state sintering method. At higher temperatures the conductivity curves are found to be merging, due to the effect of release of space charge, appearance of space charge polarization takes place accompanied with the change in activation energy. The value of activation enthalpy was estimated for K^+Li^+ substituted BNT composition and the value is 0.42eV. The charge carrier concentration term remains almost constant over entire temperature range studied sample, which in turn reveals that there is no creation of charge carriers over the entire temperature range. K^+Li^+ substituted BNT composition showed an increase in both T_d (210℃) and T_m (350℃) compared to BNT(T_d=200℃ & T_{m}=325℃) composition. The room temperature tanδ value has been found to be the order of 10^{-2} in studied material under investigation indicating low loss material.

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