

A study of lattice parameters and dielectric properties against temperature and frequency on Ferroelectric Lithium and Titanium modified Lead Potassium Niobate Ceramics.

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Abstract: Ferroelectric Lithium and Titanium modified Lead Potassium Niobate ceramics were prepared by using solid-state reaction method. A single phase formation of the compounds with orthorhombic crystal system was confirmed by X-ray diffraction. The lattice parameters and dielectric behavior were investigated in a range of frequencies (500 Hz-20 KHz) and temperatures (425^oC-505^oC). Substitution of Lithium and Titanium ions does not change the crystal structure, but decreased the lattice parameters and eventually the cell volume. The cell volumes in the Li substitutional composition have been found to be less when compared with the unsubstituted PKN. The phase transition temperatures (T_C) have been observed from real and imaginary parts of the dielectric constant versus temperatures at 1 KHz in each of the composition. High ϵ' and ϵ'' in low frequency region related to space charge polarization.

Key words: Ferroelectric, Lattice parameters, Dielectric properties, Phase transition, PKN ceramics, X-ray Diffraction.

I. Introduction

Ferroelectricity is a phenomenon which was discovered in 1921. Ferroelectricity has also been called Seignette electricity, as Seignette or Rochelle salt was first material found to show ferroelectric properties such as spontaneous polarization on cooling below the Curie point, ferroelectric domains and a ferroelectric hysteresis loop. A huge leap in the research on ferroelectric materials came in the 1950's leading to the wide spread use of Barium Titanate (BaTiO₃) [1-6] based ceramics in capacitor applications and piezoelectric transducer devices. Since then, many other Ferroelectric ceramics including Lead Titanate (PbTiO₃), Lead Zirconate Titanate (PZT), Lead Lanthanum Zirconate Titanate (PLZT), and relaxor Ferroelectrics like Lead Magnesium Niobate (PMN) have been developed and utilized for a variety of applications. With the development of ceramic processing and thin film technology, many new applications [7-9] have emerged. The biggest use of ferroelectric ceramics have been in the areas such as dielectric ceramics for capacitor applications, ferroelectric thin films for nonvolatile memories, piezoelectric materials for medical ultrasound imaging and actuators, and electro-optic materials for data storage and displays. In the past few decades, many books and reviews have been written explaining the concepts of ferroelectricity in materials [10-21]. Perovskite family name of a group of materials and the mineral name of Calcium Titanate (CaTiO₃) having a structure of the type ABO₃. Many piezoelectric (including ferroelectric) ceramics such as Barium Titanate (BaTiO₃), Lead Titanate (PbTiO₃), Lead Zirconate Titanate (PZT), Lead Lanthanum Zirconate Titanate (PLZT), Lead Magnesium Niobate (PMN), Potassium Niobate (KNbO₃), Potassium Sodium Niobate (K_x Na_{1-x} NbO₃) and Potassium Tantalate Niobate [K(Ta_xNb_{1-x})O₃] have a perovskite type structure.

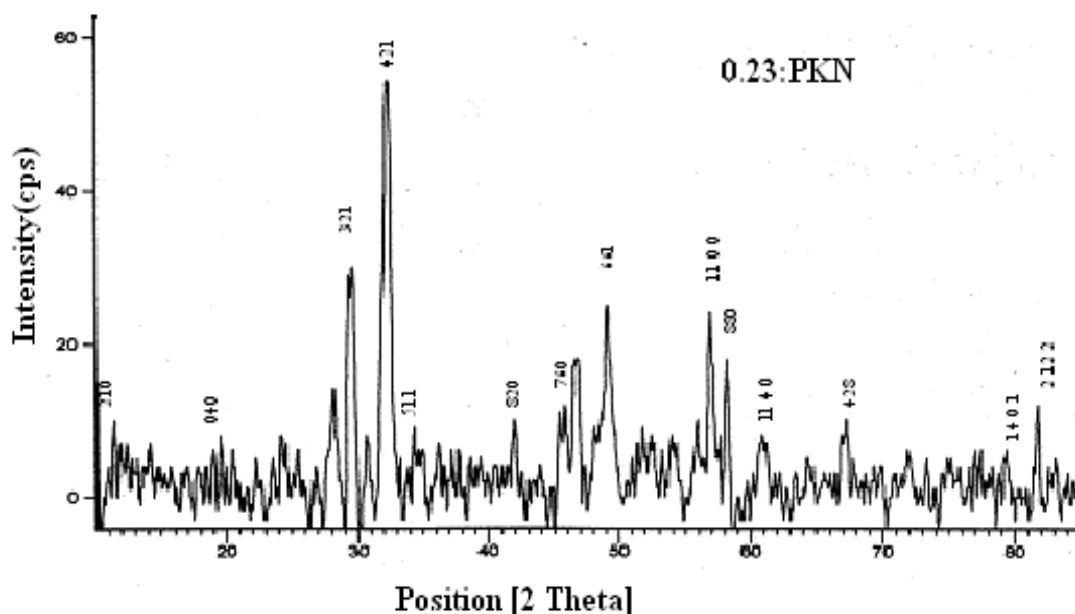
II. Preparation

In the present work the ceramic compositions of modified and unmodified Lead Potassium Niobate, have been prepared by using a high temperature sintering technique. Analar grade chemicals of PbO, K₂CO₃, Li₂CO₂, Nb₂O₅ and TiO₂ have been taken to prepare the compositions like (i). Pb_{0.77}K_{0.46}Nb₂O₆:0.23:PKN, (ii). Pb_{0.77}K_{0.26}Li_{0.20}Nb₂O₆:0.23Li:PKN (iii). Pb_{0.77}K_{0.26}Li_{0.20}Ti_{0.25}Nb_{1.8}O₆:0.23LiTi:PKN. For each composition the weighed raw materials have been grinded in an agate mortar and pestle for more than 8 hours. Calcination of the mixture was done at 900^oC for 4 hours in a platinum crucible covered with a lid. The calcined powder again grinded by adding a binder 5% Polyvinyl Alcohol to bring the particles closer. The powder obtained after grinding with PVA has been pelletized, using a steel die by applying a pressure of (3-5) Tons/cm². The sintered pellets were polished to make the two surfaces parallel and dried over a hot plate. The samples which were electroded having dimensions around 10 mm diameter and 2.3 mm thickness have been used to study the Dielectric properties. The X-ray diffraction technique [22] based on monochromatic radiation has been used for the determination of atomic spacing from the observed diffraction angles. An X-ray diffraction of model PW 1710 based with Cu K α with 1.54056 ^oA has been used. The lattice parameters and

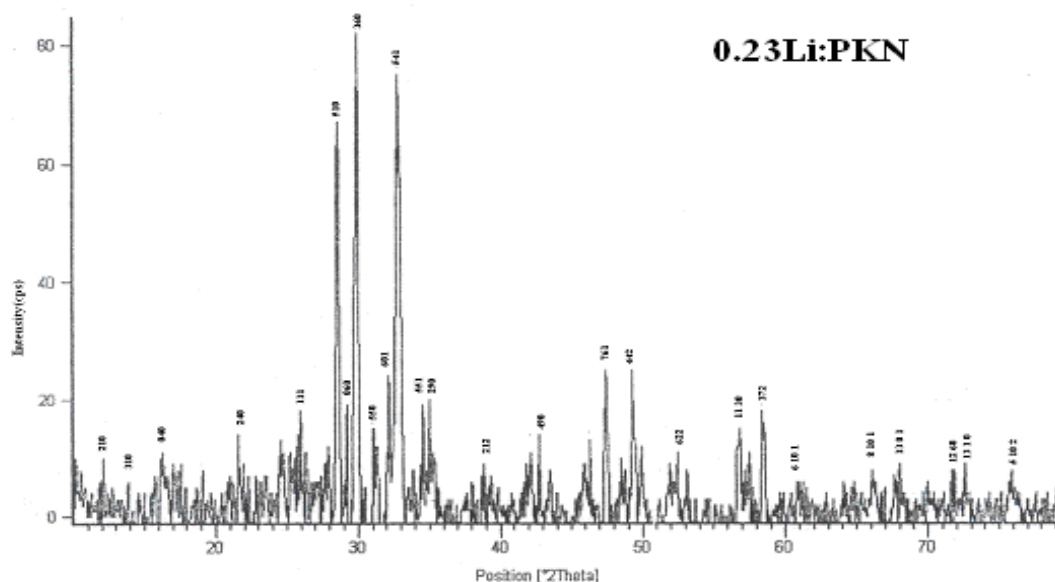
dielectric properties for orthorhombic structure of present PKN and modified compositions have been calculated.

III. Experimental

The X – Ray diffractogram patterns obtained at room temperature on PKN and modified PKN compositions have been shown in the Fig.1 XRD has been studied for $2\theta = 10$ to 80° . The XRD patterns have been indexed by POWD – an interactive powder diffraction data interpretation and indexing program version 2.2 – by E.W.Yu, School of physical Sciences, Flinders University of South Australia, Bedford, SA 5042, Australia. The structure of all the prepared PKN ceramics have been confirmed orthorhombic crystal system from the X- ray diffraction analysis. Almost all the peaks have been indexed. This reveals the single phase formation of the compounds and all the materials are in limit of solubility. The values of **lattice parameters** obtained, a, b and c axial ratio ($\sqrt{10} c/a$), unit cell volume (VA°), experimental density (d_{exptl}), X-ray density (d_{cal}) and percentage of density on the samples have been given in table I. It is evident from the table that there is not much variation in the values of lattice parameters. The values of lattice parameters of 0.23PKN $a=17.787^\circ\text{A}$, $b=18.061^\circ\text{A}$, $c=3.860^\circ\text{A}$ are well matched with reported values. Also, it is evident from the table that there is an increase in the values of lattice parameters with substitution of Lithium and Titanium ion.



(a)



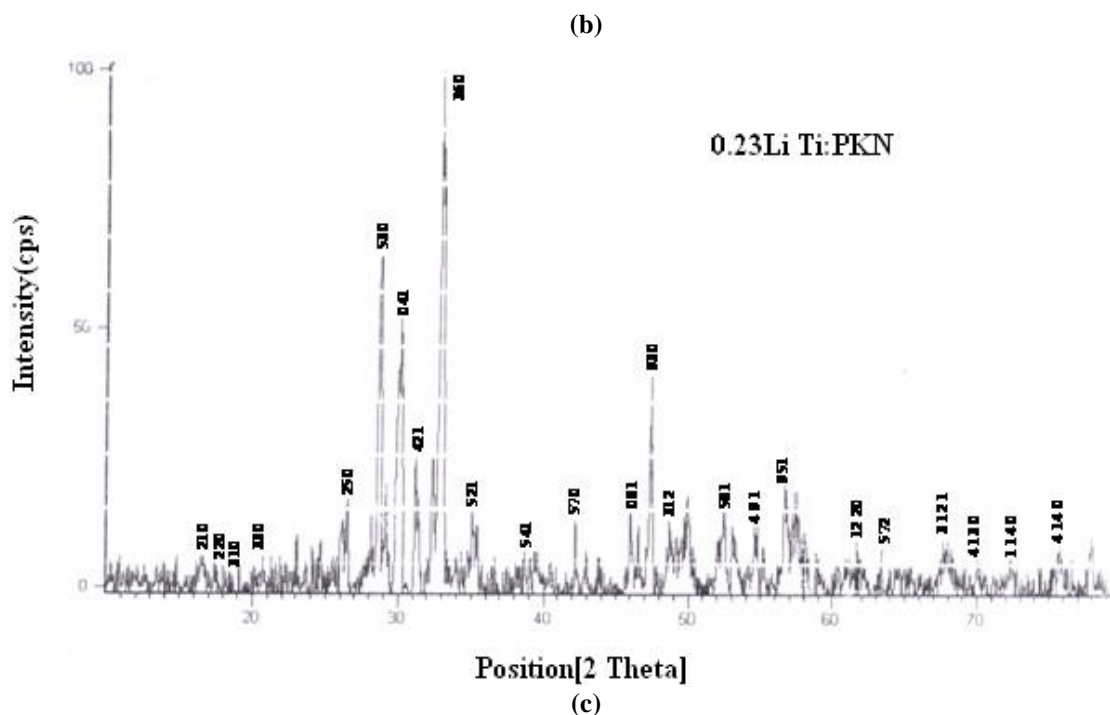


Fig. 1(a,b,c): XRD for 0.23 PKN, 0.23Li:PKN, 0.23LiTi:PKN

Table I: Lattice Parameters

Composition	$\sqrt{10} c/a$	Lattice parameters			Cell Volume	Density (gm/cm ³)		
		aA°	bA°	cA°	V A°	d _{exp}	d _{cal}	%
0.23PKN	0.686	17.787	18.061	3.860	1240.16	5.64	6.14	91.8
0.23Li:PKN	0.691	17.998	18.163	3.937	1287.26	5.92	6.12	95.4
0.23:Li Ti: PKN	0.674	18.245	18.297	3.894	1299.92	5.65	5.70	95.4

The change in the axial ratio lies between 0.674 and 0.691. As the change in axial ratio is not much, distortion in the crystal structure is too small. Also evident from the same table that the cell volume (VA⁰) of 0.23PKN, 0.23Li: PKN and 0.23LiTi: PKN increases with substitution of Li in PKN. It is obvious (Table I) a minimum density 5.64g/Cm³ has been noticed in 0.23PKN, which 91.8% to that of the XRD density 6.14g/Cm³. The high density may be due to good stoichiometric relations retained in material preparation and samples are well sintered at optimum conditions. It is clear that, higher densities have been achieved in all prepared samples. The dielectric permittivity and variation of dielectric permittivity against temperature and frequency on prepared materials were obtained from the capacitance value measured using computer interfaced HIOKI 3532 – 50 LCR Hi TESTER.

IV. Results And Discussions

Variation of dielectric constant (ϵ') with temperature at different frequencies (500Hz, 1KHz, 10KHz and 20KHz) on 0.23PKN, 0.23 Li PKN and 0.23 Li Ti PKN compositions have been shown in Fig.2(a, c, e). A phase transition from ferroelectric to paraelectric has been observed at temperature (T_c) 465^oC, 505^oC and 425^oC in 0.23PKN, 0.23 Li PKN and 0.23 Li Ti PKN respectively. Substitution of Li in PKN increases T_c whereas, substitution of Li Ti decreases T_c in PKN. This type of behavior has been reported in different ferroelectric materials [23-28]. Further no shift in the value of the phase transition temperature (T_c) has been observed at different frequencies on 0.23PKN, 0.23 Li PKN and 0.23 Li Ti PKN respectively. It is observed that the value of ϵ' increases gradually with increase in temperature due to interfacial polarization becoming more dominant as compared to the dipolar polarization and passes through at T_c and then, decreases due to phase transition from

ferroelectric to paraelectric phase. The dispersion of ϵ' in paraelectric is mainly attributed to the ionic conductivity. The frequency independent ϵ'_{T_c} versus transition temperature in 0.23PKN, 0.23 Li PKN and 0.23 Li Ti reveal that 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 [29]. Variation of dielectric loss ($\tan \delta$) as a function of temperature for compositions 0.23PKN, 0.23 Li : PKN and 0.23 Li Ti: PKN have been shown in Fig.2(b,d,f). A certain anomaly in $\tan \delta$ versus temperature has been observed, at a particular temperature, which almost coincides with the T_c of the material. The decrease of $\tan \delta$ at T_c is due to reduction in the domain wall contribution to the loss. The dispersive loss at high temperatures probably due to localized ionic conductivity.

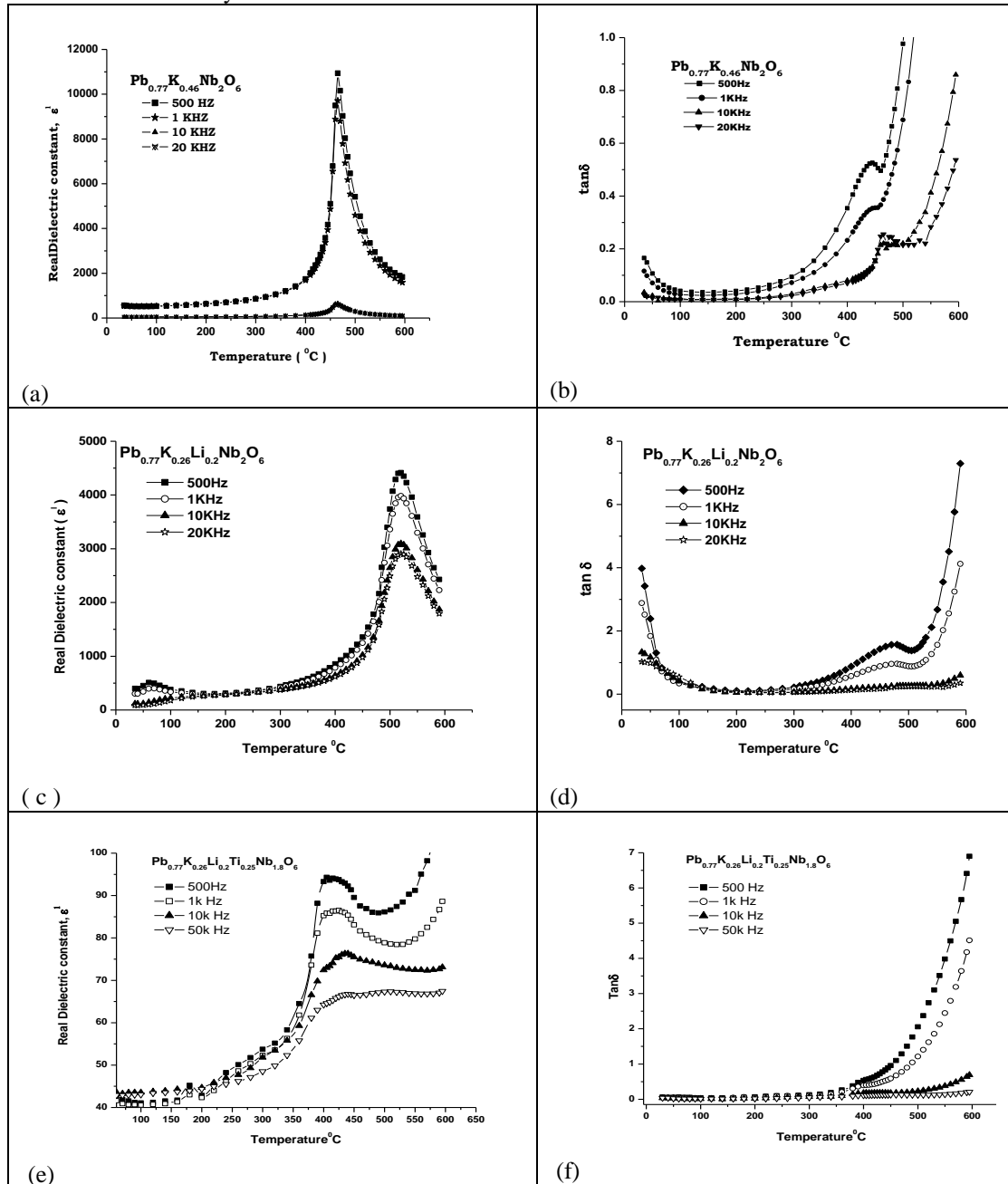


Fig.2 : Variation of temperature dependence of real part of dielectrics constant, $\tan \delta$ in 0.23-PKN, 0.23Li-PKN, and 0.23LiTi-PKN.

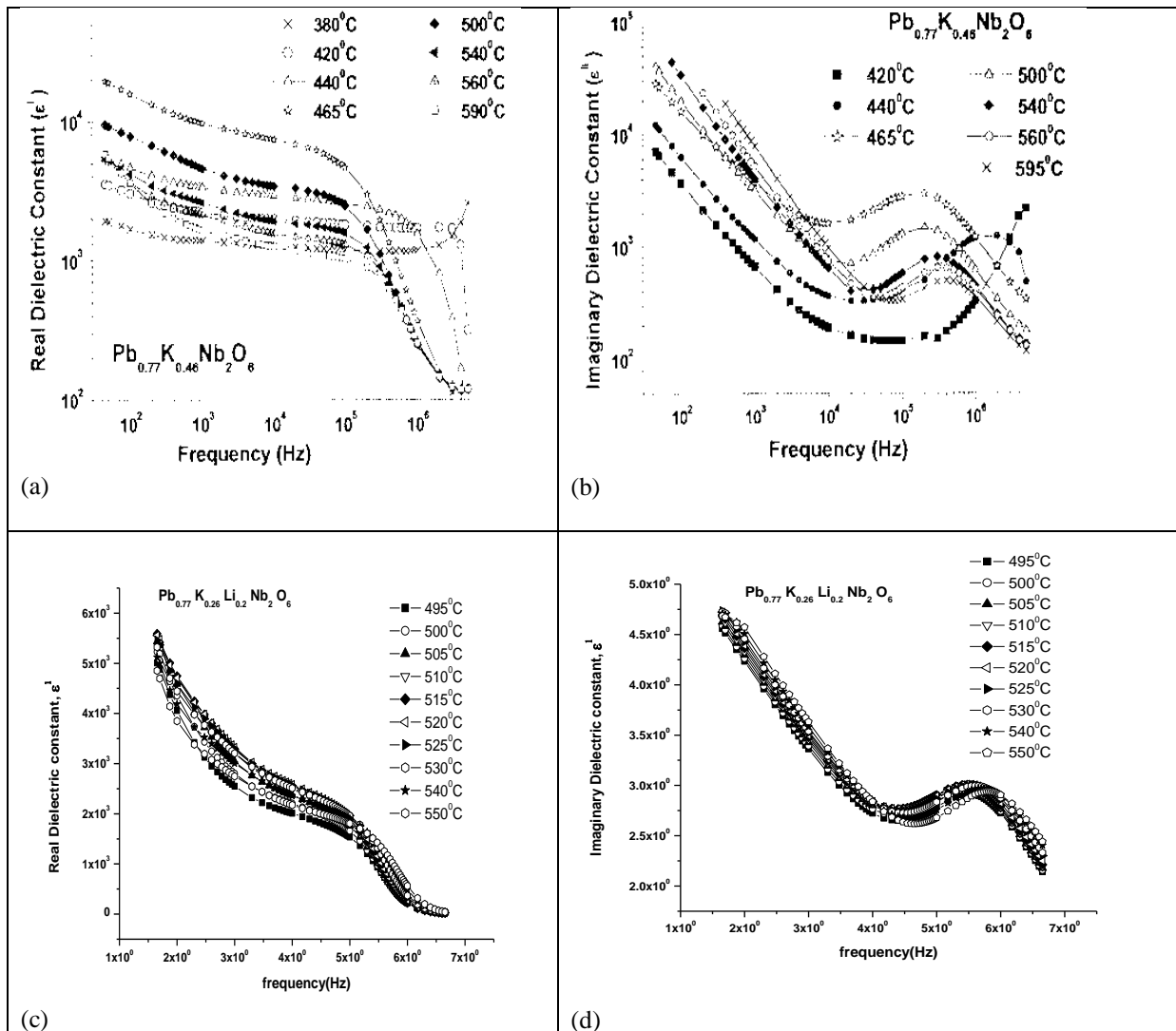
The values of ϵ' and $\tan \delta$ increases with decrease in frequency, which is the characteristic feature of the polar dielectric materials. At low frequencies high value of dielectric constant may be due to the presence of different types of polarizations (i.e., dipolar, ionic and electronic polarization) and at higher frequencies the main contribution comes from atomic and electronic polarization. The curie constant (k) has been calculated

from curie-weiss law and found to be the order of 10^5 revealing the materials belongs to oxygen octahedra[29-32] for example: Lead Barium Niobate (PBN)[29,30]etc.,The values of dielectric constant at room temperature ϵ_{RT} , Dielectric constant at transition temperature ϵ_{Tc} , curie constant (k) and dielectric loss at room temperature ($\tan \delta$) are given in Table.II.

Table II: Dielectric data at 1 KHz.

Composition	ϵ_{RT}	ϵ_{Tc}	T_c °C	$K^\circ Cx 10^5$	Tan δ
0.23PKN	539	10932	465	2.5	.389
0.23Li:PKN	303	3950	505	1.28	.980
0.23LiTi:PKN	64	123	425	1.25	.423

The broadness in the dielectric constant versus temperature may be attributed to the compositional fluctuations caused by the substitution of oxide materials and analogues to certain compounds with Pervoskite structure [31]



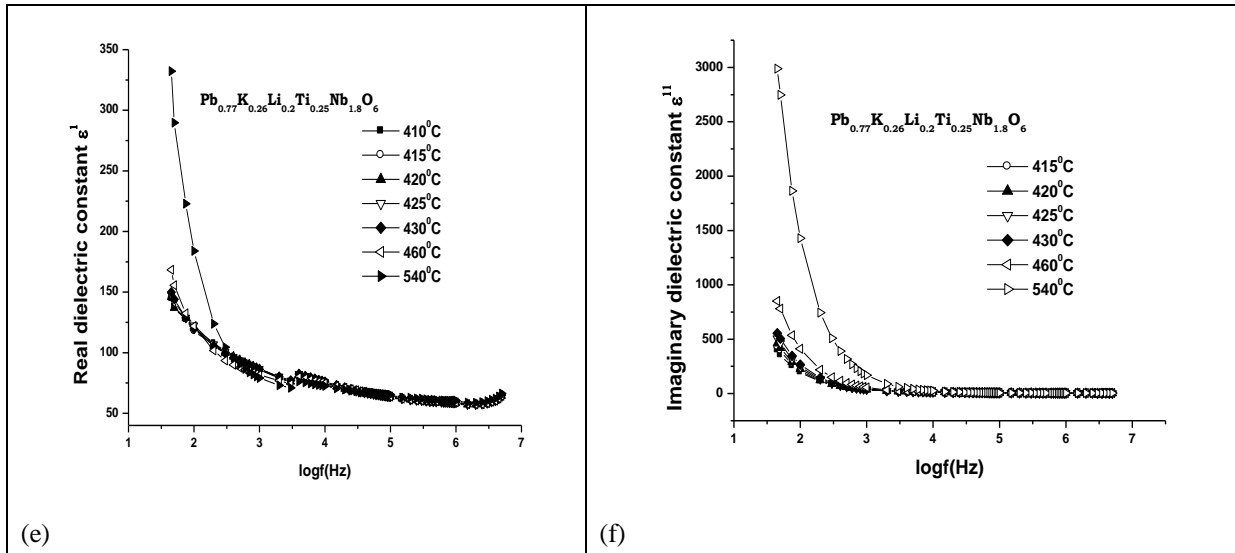


Fig.3: Variation of real part of dielectric constant (ϵ'), imaginary part of dielectric constant (ϵ'') with $\log f$ at different temperatures on 0.23-PKN, 0.23Li-PKN, 0.23LiTi-PKN.

Fig.3(a,c,e; b,d,f) shows the variation of real and imaginary part of dielectric constant (ϵ' and ϵ'') exhibited dispersions at low frequency region. In conducting dielectric materials, high ϵ' values may be related to accumulation of charges at the interface between sample and electrode i.e., space charge polarization. Correspondingly ϵ'' of the low frequency becomes very high due to free charge motion within the materials and arc connected to ac conductivity relaxation.

In 0.23 PKN and its Li and LiTi substituted materials a decrease in ϵ' has been observed in high frequency side of para region with a corresponding relaxation peak maxima in the ϵ'' curves as shown in Fig.3(b,d,f). The origin [32] of such relaxation was ascribed to the crystalline network owing to the motion of active Nb^{5+} ions. Since at low frequency dispersion is a characteristic feature of the TB type materials we feel that coupling between the dielectric dispersion mode (dielectric relaxation mode) and the soft mode is a factor contributing to the enhancement of dielectric constant in PKN materials. The geometrical rotation of a group of eight oxygen octahedral linked to the Pb ion, on a certain number of localized sites, appear to the likely mechanism of dielectric dispersion. The strong dispersion of complex dielectric constant in the PKN materials is common feature in ferroelectrics associated with non-negligible ionic conductivity and is referred to as the low frequency dielectric dispersion (LFOD) [33,34]. Detailed studies of this phenomenon were carried by Joncher et al [35]. The complex dielectric constant can be resolved into real ϵ' and imaginary ϵ'' parts as a function of the frequency ω by means of Kramer – Kronig relations as follows.

$$\epsilon' = \epsilon_{\infty} + \sin(n(T)\pi/2)(A(T)\epsilon_0)(\omega^{n(T)-1}) \quad (1)$$

$$\epsilon'' = \sigma / \epsilon_0 \omega + \cos(n(T)\pi/2)(A(T) / \epsilon_0)(\omega_0^{n(T)-1}) \quad (2)$$

Where ϵ_{∞} is the high frequency value of the dielectric constant, where exponent $n(0 < n < 1)$, pre factor A are thermally activated quantities and is formed to vary with angular frequency. The detailed analysis has been given in conductivity response. The first term in equation (1) and (2) determine the lattice response and dc conduction part respectively, while 2nd term in the both equations reflects the charge carrier contribution to the dielectric constant. The temperature and frequency dependencies of ϵ' yield a straight line for a constant (n) with a slope equal to (n-1) in double logarithmic plot. A unit of value of n implies a Debye case, and it is attainable [36] at low temperatures. However as the temperature increase, the interaction between the charge carriers participating in the polarization process increases, leading to decrease in n. The value n calculated from the high frequency region decreases as the temperature increases and attains a minimum near T_C and subsequently it increases with further increase in temperature. The observed minimum at T_C implies the strong interaction between the charge carriers and the lattice. At high frequencies the charge carriers fail to respond to the external field, therefore the measured dielectric constant is due to the contribution from lattice polarization. This accounts for linear decrease in the low frequency region and a frequency – independent plateau region at high frequencies. The temperature dependence $n(T)$ is shown in Fig.4(a,d,e).

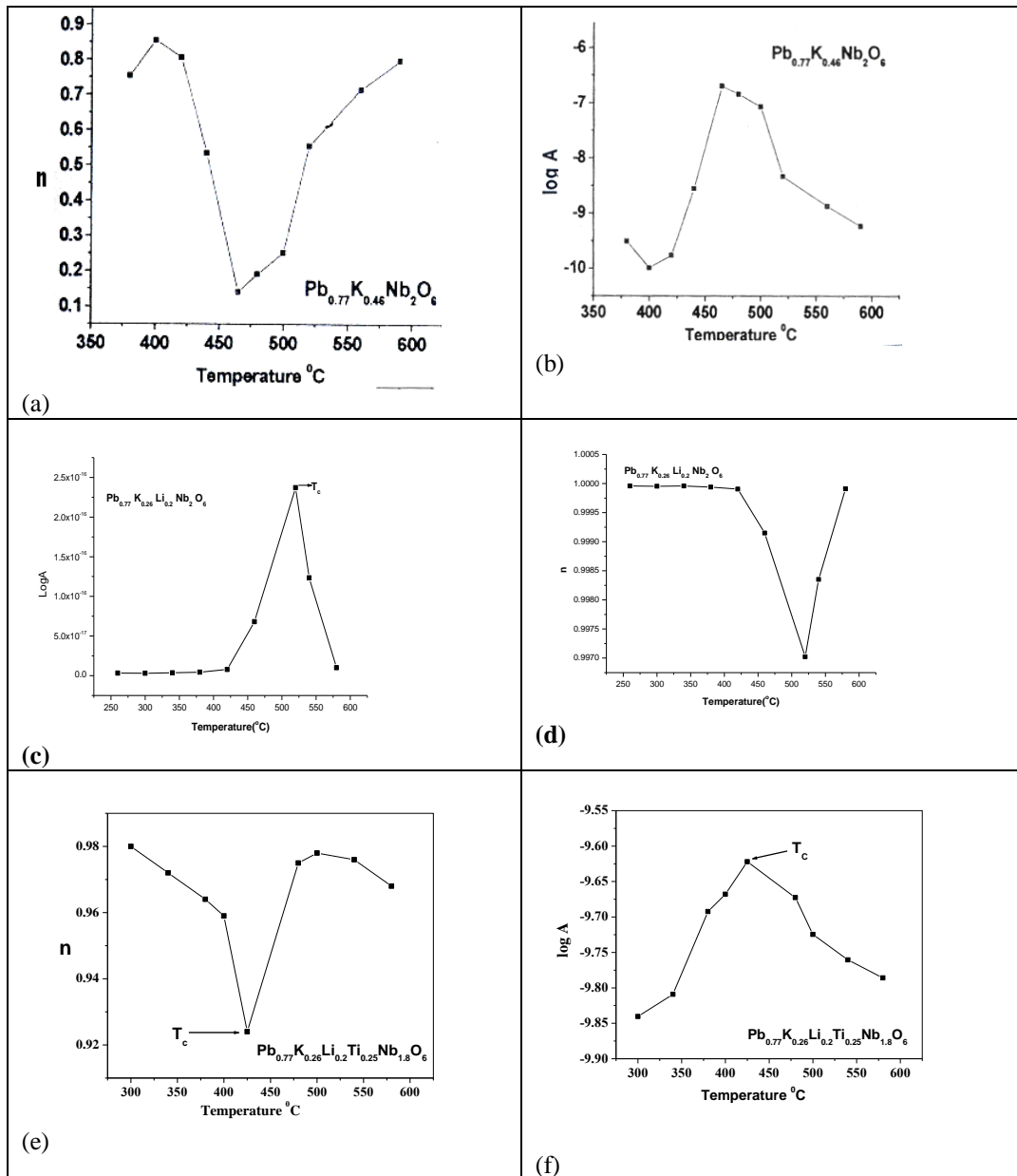


Fig.4: Variation of critical exponent $n(T)$ with temperature showing a minimum T_C on 0.23-PKN, 0.23Li-PKN, 0.23LiTi-PK

The exponent $n(T)$ decrease with increase in temperature and rapidly falls to a minimum at T_C and subsequently increases with further increase in temperature. The possible way of explaining the observed minimum at T_C is to consider the interaction of the charge carriers with the lattice. The pre factor A , shows a sharp peak at T_C . It arising from the diffusive motion of carriers is obtained in phase transition region. The results of Fig.4 (b,c,f) show a strong temperature dependence of pre-factor A [37]. The fitted plots of the experimental dielectric data to the dielectric dispersion relation (equation.2).

V. Conclusions

Modified and unmodified $Pb_{1-x}K_xNb_2O_6$ (PKN) materials have been prepared by the usual double sintering method and achieved density between 91 -95 % to that of theoretical value. From X-ray diffraction studies the compositions under investigation have been characterized to be single phase homogeneous with orthorhombic structure. Substitution of Lithium and Titanium ions does not change the crystal structure, but decreased the lattice parameters and eventually the cell volume. The cell volumes in the Li substituted compositions have been found to be less, when compared with the unsubstituted PKN.

The phase transition temperatures (T_C) have been observed from real and imaginary parts of the dielectric constant versus temperature at 1K Hz in each of the composition. The phase transition temperatures

for 0.23 : PKN, 0.23 : Li-PKN, 0.23 : LiTi-PKN are 465⁰C, 505⁰C, 425⁰C respectively. The values of TC in unmodified PKN compositions are well matched with the reported values. Substitution of Li ion in PKN compositions indicated an increase in T_C and substitution of LiTi in PKN composition indicated a decrease in T_C from unmodified PKN composition. The value of Curie's constant (K) is found to be order of 10⁵⁰C indicates the compositions are of oxygen-octahedra ferroelectrics.

High ϵ' and ϵ'' in low frequency region related to space charge polarization, free-charge motion and ac conductivity relaxation. Using Jonscher's power law at low frequency dielectric dispersion (LFDD) studies have been carried out. The interaction between charge carriers exponentn(T) and strength of polarizability A(T) are observed to be minimum and maximum at T_c respectively.

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