

INVESTIGATION ON LATTICE PARAMETERS AND DIELECTRIC PROPERTIES OF Li-Ti MODIFIED PbKNb CERAMIC MATERIAL

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Abstract— Ferroelectric Lithium and Titanium modified Lead Potassium Niobate ceramic material is prepared by using solid-state reaction method. The lattice parameters and dielectric behavior were investigated in a range of frequencies (500Hz-20 KHz) and temperatures (425^oC-505^oC). The phase transition temperatures (T_c) have been observed from real and imaginary parts of the dielectric constant versus temperatures at 1 KHz in the composition. High ϵ' and ϵ'' in low frequency region related to space charge polarization. The interaction between charge carriers exponent $n(T)$ and strength of polarizability $A(T)$ are observed to be minimum and maximum at T_c respectively.

Keywords— 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 ($BaTiO_3$) [1-6] based ceramics in capacitor applications and piezoelectric transducer devices. Since then, many other Ferroelectric ceramics including Lead Titanate ($PbTiO_3$), 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 ($CaTiO_3$) having a structure of the type ABO_3 . Many piezoelectric (including ferroelectric) ceramics such as Barium Titanate ($BaTiO_3$), Lead Titanate ($PbTiO_3$), Lead Zirconate Titanate (PZT), Lead Lanthanum Zirconate Titanate (PLZT), etc., have a perovskite type structure.

II. PREPARATION

In the present work the ceramic composition of modified Lead Potassium Niobate, have been

prepared by using a high temperature sintering technique. Analar grade chemicals of PbO , K_2CO_3 , Li_2CO_3 , Nb_2O_5 and TiO_2 have been taken to prepare the compositions like

$Pb_{0.77}K_{0.26}Li_{0.20}Ti_{0.25}Nb_{1.8}O_6:0.23LiTi:PKN$.

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 pellet is polished to make the two surfaces parallel and dried over a hot plate. The sample which was electroded having dimensions around 10 mm diameter and 2.3 mm thickness has been used to study the lattice parameters and 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 $Cu K\alpha$ with 1.54056 ^oA has been used. The lattice parameters and dielectric properties for orthorhombic structure of present PKN modified compositions have been calculated.

III. EXPERIMENTAL

The X – Ray diffractogram patterns obtained at room temperature on modified PKN composition have been shown in the Fig.1 XRD has been studied for $2\theta = 10$ to 80^o. 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 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 the material is in limit of solubility. The values of **lattice parameters** obtained, a, b and c axial ratio ($\sqrt{10} c/a$),

unit cell volume ($V^{\circ}A$), experimental density (d_{exptl}), X-ray density (d_{cal}) and percentage of density on the sample have been given in table I.

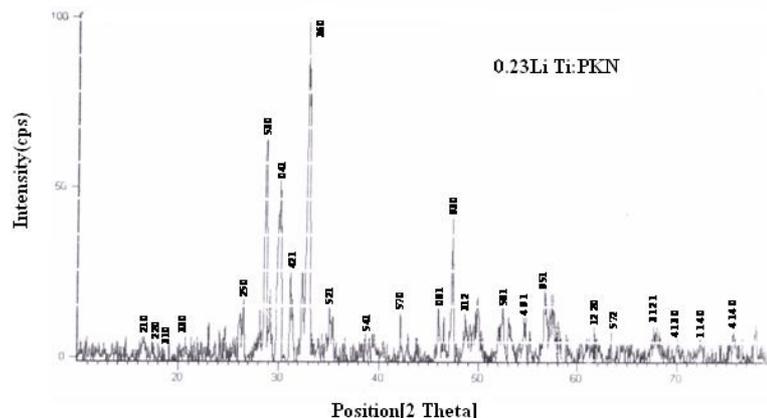


Fig. 1: XRD for 0.23LiTi:PKN

Table I: Lattice Parameters

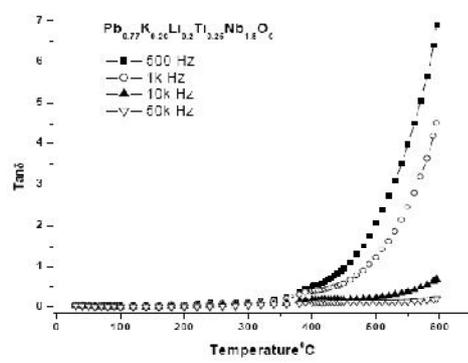
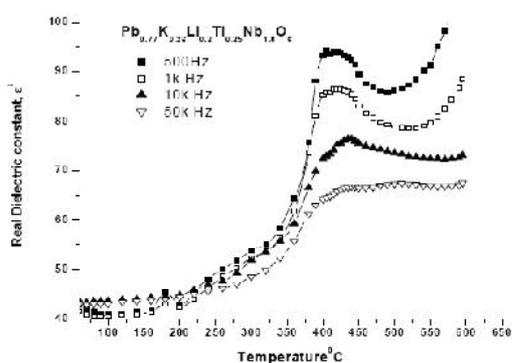
Composition	$\sqrt{10} c/a$	Lattice parameters			Cell Volume		Density (gm/cm^3)	
		aA°	bA°	cA°	$V A^{\circ}$	d_{exp}	d_{cal}	%
0.23:Li Ti: PKN	0.674	18.245	18.297	3.894	1299.92	5.65	5.70	95.4

The dielectric permittivity and variation of dielectric permittivity against temperature and frequency on prepared material was obtained from the capacitance value measured using computer interfaced HIOKI 3532 – 50 LCR Hi TESTER.

IV. RESULTS AND DISCUSSION

Variation of dielectric constant (ϵ') with temperature at different frequencies (500Hz, 1 KHz, 10 KHz and 20KHz) on composition have been shown in Fig.2 (a). A phase transition from ferroelectric to paraelectric has been observed at temperature (T_c) 425 $^{\circ}C$ in 0.23 Li Ti PKN. 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 0.23 Li Ti PKN. 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 0.23 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 composition 0.23 Li Ti: PKN have been shown in Fig.2 (b). 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.



(a) (b)

Fig.2: Variation of temperature dependence of real part of dielectrics constant, $\tan \delta$ in 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	$K^o Cx 10^5$	Tan δ
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 Perovskite structure [31]

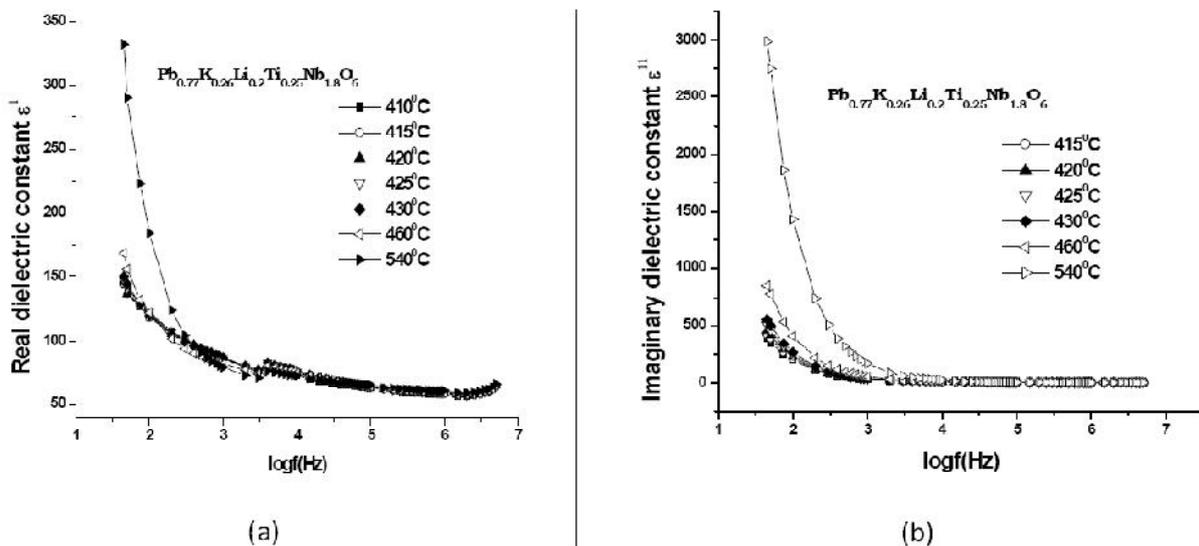


Fig.3: Variation of real part of dielectric constant (ϵ'), imaginary part of dielectric constant(ϵ'') with $\log f$ at different temperatures on 0.23LiTi-PKN.

Fig.3 (a,b) 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). 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.

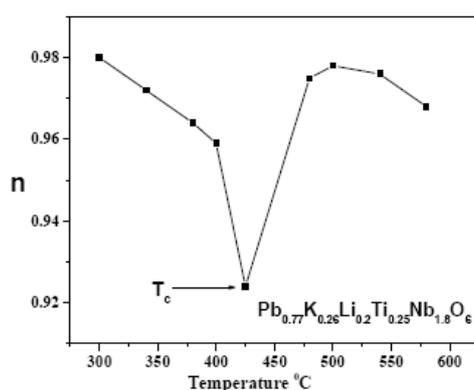
$$\epsilon' = \epsilon_{\infty} + \sin(n(T)\pi / 2)(A(T)\epsilon_0)(\omega^{n(T)-1}) \quad (1)$$

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

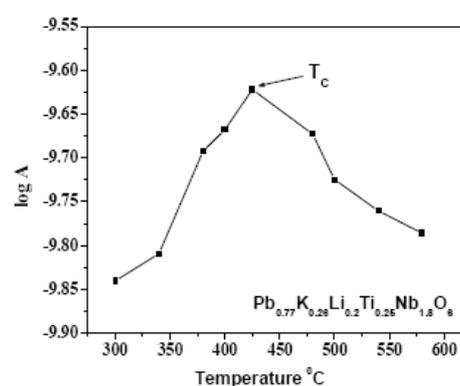
Where ϵ_{∞} is the high frequency value of the dielectric constant, where exponent $n(0 < n < 1)$, pre factor A are thermally activated quantities and is formed to vary with angular frequency. The detailed analysis has been given in conductivity response. The first term in equation (1) and (2) determine the lattice response and dc conduction part respectively, while 2^{nd} term in the both equations reflects the charge carrier contribution to the dielectric constant.

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).



(a)



(b)

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) 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).

CONCLUSIONS

Modified $Pb_{1-x}K_{2x}Nb_2O_6$ (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. 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 temperature 0.23 : LiTi-PKN is $425^{\circ}C$. The value of Curie's constant (K) is found to be order of $10^{50}C$ 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 exponent $n(T)$ and strength of polarizability $A(T)$ are observed to be minimum and maximum at T_C respectively.

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