

Modulus spectroscopy study on Ferroelectric Lithium and Titanium modified Lead Potassium Neobate Ceramics

P. Easwaraji¹, Dr.M.P.Srinivasarao², M. Srikanth³

(Physics Department, G.M.R.I.T,Rajam, Srikakulam District, Andhrapradesh, India)

Abstract: Ferroelectric lithium and titanium modified Lead Potassium Neobate Ceramics were prepared by solid state reaction method. The modulus represents the real dielectric relaxation process. The usefulness of the modulus representation in the analysis of relaxation properties was demonstrated both for ionic conductors and polycrystalline ceramics. The complex electrical modulus is a parameter that can be expressed as Fourier transform function $\Phi(t)$ gives the time evolution of electric field with in the dielectric. Variation of real part (M') of electrical modulus with frequency and temperatures was measured on the prepared modified and unmodified materials. The high frequency side of M'' peak represents the range of frequency in which the ions are strictly confined to their potential well and ions can make only localized motions with in the wells. The activation energy of D.C conduction can be obtained from Arrhenius plot of M'' peak frequencies.

Keywords: Ferroelectrics, electrical modulus, D.C.conduction, Arrhenius plot

I. Introduction

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 [1-12]. From the physical point of view, the electrical modulus corresponds to the relaxation of the electric field in the material when the electric displacement remains constant. Therefore, the modulus represents the real dielectric relaxation process [13]. The usefulness of the modulus representation in the analysis of relaxation properties was demonstrated both for ionic conductors [14] and polycrystalline ceramics [15]. In practice, regions of low capacitance, such as grain interiors, are characterized using M'' data, whereas more resistive regions, such as grain boundaries and pellet surface layers, which often have higher associated capacitances, are characterized using M'' spectra [16].

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, K_2CO_3 , Li_2CO_3 , Nb_2O_5 and TiO_2 have been taken to prepare the compositions like (i). $Pb_{0.77}K_{0.46}Nb_2O_6:0.23:PKN$, (ii). $Pb_{0.77}K_{0.26}Li_{0.20}Nb_2O_6 : 0.23Li:PKN$ (iii). $Pb_{0.77}K_{0.26}Li_{0.20}Ti_{0.25}Nb_{1.8}O_6 : 0.23LiTi:PKN$. 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 $900^{\circ}C$ 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 modulus spectroscopy properties.

III. Experimental

The real and imaginary part of electrical modulus at various temperatures and frequencies have been calculated using series resistance R_s and dielectric loss D values obtained from HIOKI 3532-50 LCR HiTESTER.

IV. Results And Discussions

The complex electrical modulus is a parameter that can be expressed as Fourier transform function $\Phi(t)$ gives the time evolution of electric field with in the dielectric,

$$\epsilon^* = \epsilon' - i\epsilon''$$

$$M^*(\omega) = 1/\epsilon^* = M'(\omega) + iM''(\omega)$$

$$= M_\infty [1 - \int \exp(-i\omega t) \{d\Phi(t)/dt\}]$$

$$= (\epsilon' + i\epsilon'') / [(\epsilon')^2 + (\epsilon'')^2]$$

Variation of real part (M') of electrical modulus with frequency (45Hz – 5MHz) at various temperatures (30 – 595°C) has been shown in fig.1 (a,b,c). At a constant temperature, M' increases with increase in frequency and takes nearly a constant value. At low frequency and high temperature region, M' approaches zero conforming an appreciable electrode and/or ionic polarization [17].

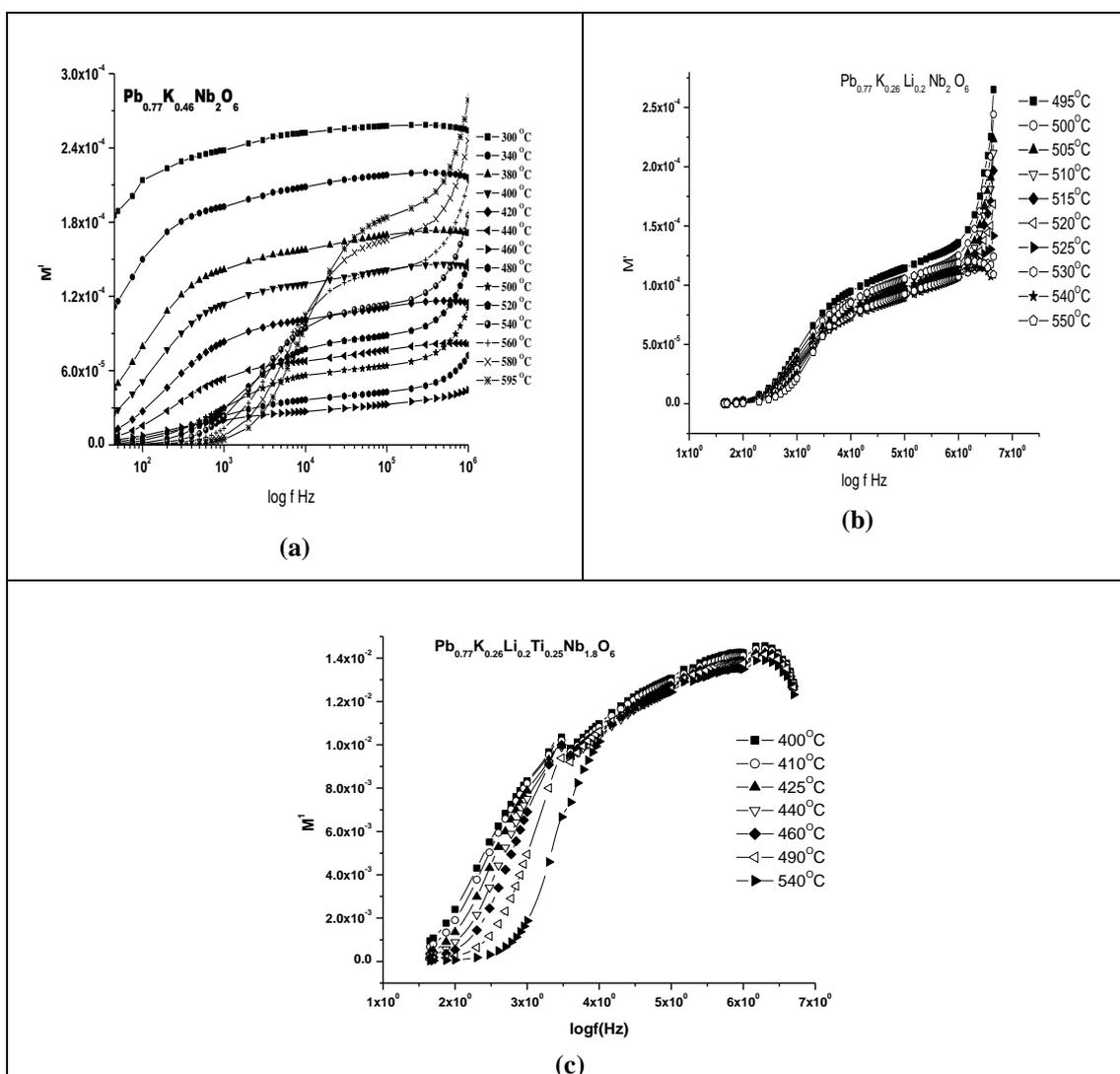


Fig.1: Variation of real part of electrical modulus with frequency at different temperatures

Variation of imaginary part of modulus M'' with frequency at various temperatures (300-595°C) has been shown in fig.2(a,b,c). As the temperature increases peak frequency of M'' shifts to higher frequency side. The low frequency side of peak represents the range of frequency in which the ions can move over long distances, i.e., ions can perform successful hopping from one site to the neighboring site. The high frequency side of M'' peak represents the range of frequency in which the ions are strictly confined to their potential well and ions can make only localized motions with in the wells[18-21].

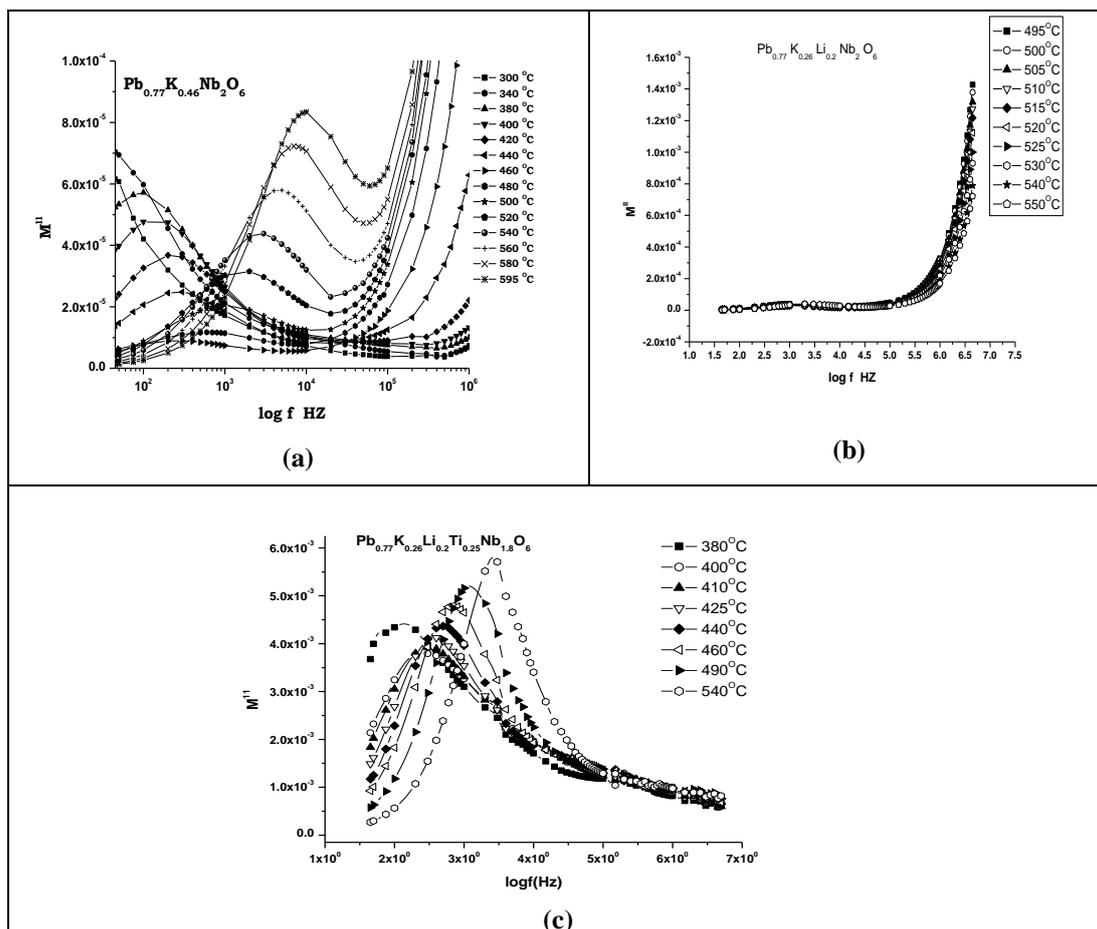


Fig.2: Variation of Imaginary part of electrical modulus a with frequency

The shift in the frequency of M'' peak corresponds to the so called conductivity relation. Since the change in the dielectric constant of the grain boundary phase is relatively small (almost constant) with temperature, the change in the value of M'' indicates the grain contribution. The activation energy of D.C conduction can be obtained from Arrhenius plot of M'' peak frequencies. The reciprocal of frequency of M'' peak represent the time τ_p .

Fig.3(a,b,c) shows the normalized imaginary part of the electric modulus M''/M''_{max} as a function of logarithmic frequency at several temperatures in corresponding compositions of PBKNN. The M''/M''_{max} parameter exhibits a peak or maximum value with a slightly asymmetric degree at each temperature. The region of the left of the peak is one where the carriers are confined to potential wells being mobile over short distance. The frequency range at around the peak indicates the transition from short range to long range mobility, considering the decrease in frequency. In the peak, the relaxation is defined by the condition $\omega\tau = 1$. Where, τ is the most probable relaxation time. The reciprocal of frequency of M'' peak frequency (f_{max}) represent the time scale of transition from long range mobility and is defined as the characteristic relaxation time, $\tau = (2\pi f)^{-1}$.

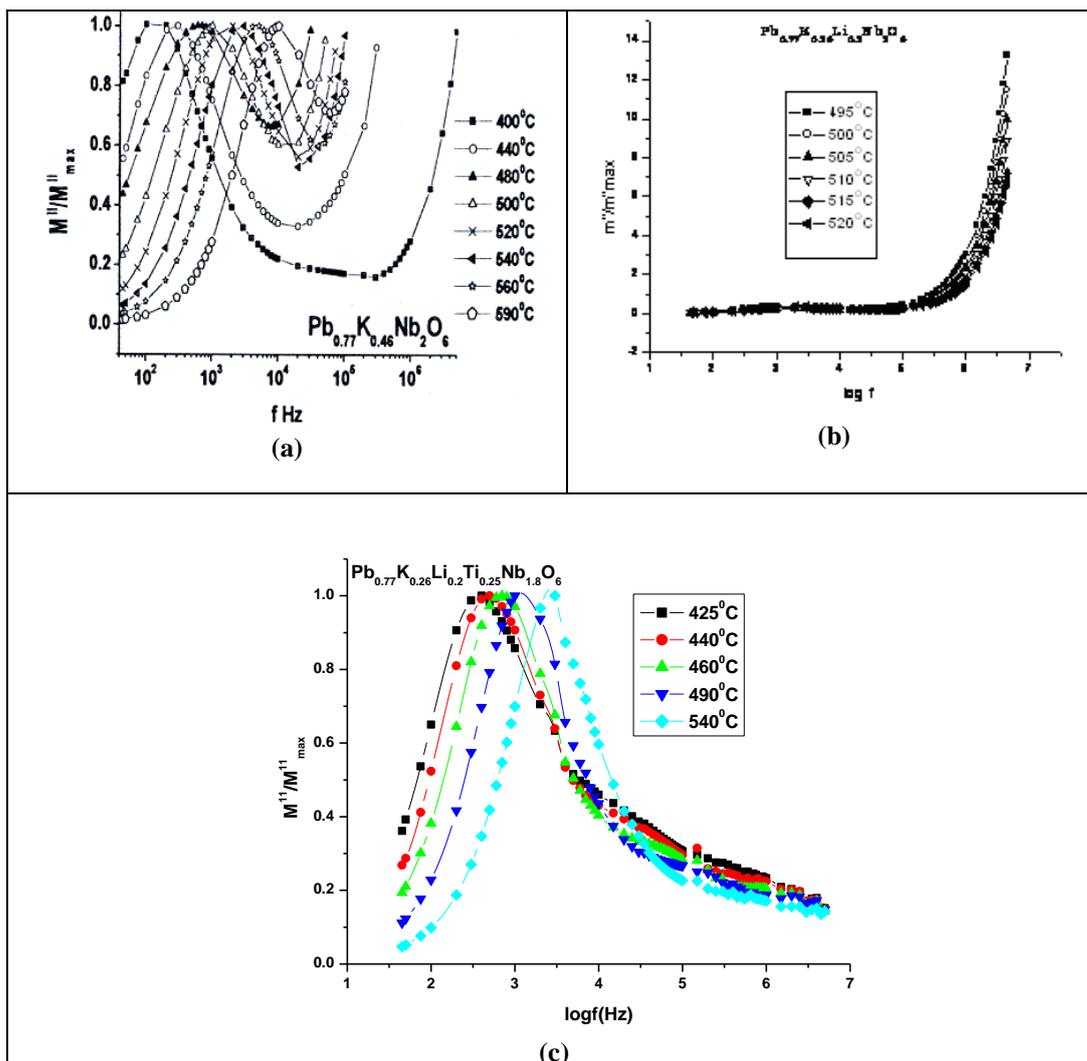


Fig.3: The normalized imaginary part of M''/M''_{max} of impedance as a function of frequency at several temperatures.

The relaxation time exhibits a thermally activated dependence. The dc conductivity relaxation can be obtained from the peak position, i.e., f_{max} . Fig.4 ($1000/T$ Vs ω_p) shows the Arrhenius plot, relaxation angular frequency, $\omega_p = \omega_0 \exp[-E_\mu / KT]$ as a function of inverse of temperature, where ω_0 is the pre exponential factor of angular frequency, τ_0 be the relaxation time and T is the absolute temperature.

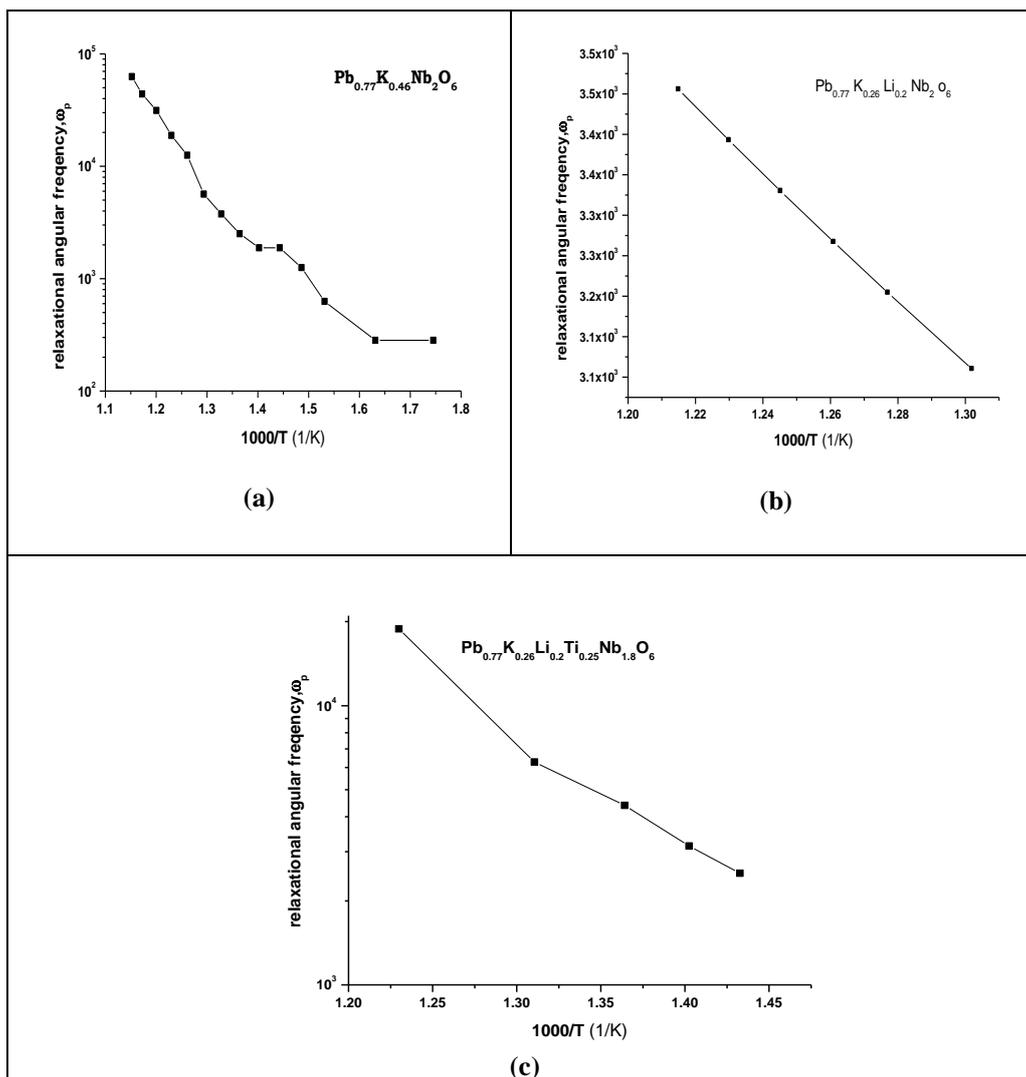


Fig.4: The Arhenius plot of relaxation frequency as a function of 1000/T

The activation energies obtained from fig.4(a,b,c) are tabulated in table I

TableI: Activation energies of relaxation energies frequencies from M'' peaks as a function of 1/T

Composition	Temperature range ($^{\circ}\text{C}$)	Dc conduction activation energy (ev)
0.23PKN	390-520	0.29
0.23Li:PKN	580-520	0.54
0.23LiTi:PKN	530-590	0.49

V. Conclusions

d.c conduction activation energies are calculated using the M'' peak frequencies in all the three compositions. The value lies between 0.29ev – 0.54 ev.

The d.c and a.c conduction activation energies are calculated from Arrhenius plots and the values of activation energies reveals the ionic conduction mechanisms in the compositions under investigation.

References

- [1]. H. D. Megaw, Ferroelectricity in Crystals (Methuen, London, 1957)
- [2]. W. G. Cady, Piezoelectricity (Dover Publications, New York, 1962)
- [3]. M. Deri, Ferroelectric Ceramics (Gordon and Breach, New York, 1969)
- [4]. J. C. Burfoot, Ferroelectrics (Van Nostrand, New York, 1967)
- [5]. B. Jaffe, W. R. Cook Jr., and H. Jaffe, Piezoelectric Ceramics (Academic Press, London, 1971).
- [6]. T. Mitsui, I. Tatsuzaki, and E. Nakamura, An Introduction to the Physics of Ferroelectrics (Gordon and Breach, London, 1976)
- [7]. M. E. Lines and A. M. Glass, Principles and Applications of Ferroelectric Related Materials (Clarendon Press, Oxford, 1977)
- [8]. J. M. Herbert, Ferroelectric Transducers and Sensors (Gordon and Breach, London, 1982)
- [9]. R. C. Buchanan, ed., Ceramic Materials for Electronics - Processing, Properties Applications (Marcel Dekker, New York, 1986)
- [10]. L. M. Levinson, ed., Electronic Ceramics - Properties, Devices and Applications (Marcel Dekker, New York, 1987)

- [11]. A. J. Moulson and J. M. Herbert, *Electroceramics, Materials, Properties, and Applications* (Chapman and Hall, London, 1990)
- [12]. Y. Xu, *Ferroelectric Materials and their Applications* (North Holland, Amsterdam, 1991)
- [13]. H.Wagner and R.Richer, *Polymer* 38, 5801 (1997).
- [14]. P.B.MacdoC.T.Moynihan and R.Bose, *phys.Chem. Glsses* 13, 171 (1972).
- [15]. J.liu, Ch-g Dun , W..G.Yin, Q, NMeiR.W.Smith and J.R. Hardy *J.Chem.Phys.* 119, 2812 (2003).
- [16]. N. Horse, and A.R.West, *J. Am.Ceram.Soc.Japan* 79, 1633 (1996).
- [17]. JinSoo Kim and Tae Kwon Song, *J.Phy.Soc. Japan* 70, (3419 (2001).
- [18]. R.L. Nagai and C.Leon: *Solid State Ionics* 125, 81 (1999).
- [19]. P.Pissis and A. Kyritsis: *Solid State Ionics* 97, 105 (1997).
- [20]. V.V.Shilov, V.V.Shevchenko, P.Pissis, A.Kyritsis, G.Georgoussis, Yu.P.gommza, S.DNesin and N.S.Klimeko: *J.Non-cryst.Solids*, 275, 116 (2000).
- [21]. D.L. Sidebottom, P.F.Green and R.K.Brow: *J.Non-cryst.Solids*, 183, 151 (1995).