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Electrical Properties of A-site Substituted Lead - free Potassium Sodium Niobate Ceramics

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Abstract: ***The effect of A-site (Li) substitution on electrical properties of lead free $(K_{0.5}Na_{0.5})_{1-x}$ Li_x NbO_3 with x = 0.00 and 0.02 has been investigated. Samples were prepared using conventional solid state reaction method with sintering at 1050^0C temperature. X-ray diffraction (XRD) analysis confirmed single phase perovskite structure of both samples. Dielectric constant and Dielectric loss were studied as a function of frequency ranging from 100Hz to 1MHz at room temperature. The comparison of ferroelectric behavior (P-E hysteresis loop) for both samples revealed that substituted sample obtained better saturation at same applied electric fields at room temperature. It is also found that Li substituted sample showed higher resistivity and capacitance. The variation in electrical properties indicates strong dependency of KNN ceramic on Lithium substitution.***

Keywords: **Dielectric properties, Lead free Ceramics, X – ray diffraction.**

I. INTRODUCTION

Lead based compounds, like lead zirconate titanate (PZT), are widely used in many applications like actuators, sensors etc [1]. However, PZT–based ceramics contain more than 60 % lead by weight which is highly hazardous for environment due to its evaporation during sintering process [2-6]. Therefore, the development of lead free ceramics has been the most important issue to current researchers.

Among the studied lead free ceramics, potassium sodium niobate (KNN), alkali niobate based ceramic has been found to be the most promising candidate because of its good electrical properties. However, Due to hygroscopic and volatile nature of alkaline elements, there is some problem in preparation of hard KNN ceramics [7]. There are some different techniques like spark plasma sintering (SPS), microwave sintering etc. which are very useful in achieving high densities [8-9]. But such processing techniques are not appropriate for industrial applications.

Another method for getting good properties is substitution of a suitable element in place of K and Na which can enhance density and sinterability of KNN ceramics. In this paper, we present the effect of minimal Li substitution ($(K_{0.5}Na_{0.5})_{(1-x)}$ Li_xNbO_3, KLNN) on electrical properties of KNN with x = 0.02 in detail. The results reveal that Li substitution can enhance the electrical properties of KNN which is good for device applications.

II. EXPERIMENTAL DETAILS

The carbonates (with assay 99.9%) of corresponding metals i.e. Na_2CO_3, K_2CO_3, Nb_2O_5, Li_2CO_3 were used as precursor for synthesis of KNN and KLNN ceramics via solid state route. The mixing and grinding process of weighed powders according to composition requirement was carried out in a high energy planetary ball mill using ethanol as wetting agent. Zirconia balls with 10 mm diameter were used as grinding media and samples were dried at 200^0C. The calcination of samples was carried out at 850^0C. The small amount of diluted polyvinyl alcohol was used as a binder and powders were pressed into circular discs using uniaxial hydraulic press. The green discs were sintered at 1050^0C for 3 hrs in conventional furnace. The experimental density of sintered pellets was determined using Archimedes principle.

The crystal structure was determined using X-ray diffraction (XRD) analysis with Cu-K_α radiations (λ = 1.5406 A^o) using X'Pert PRO – model. To measure the dielectric and ferroelectric properties, silver paste was fired on the both sides of discs to form the electrodes. The dielectric properties as a function of frequency at room temperature were measured using

Hioki 3532-50 LCR meter. P-E hysteresis loops were recorded at room temperature with different applied electric field using an automated P-E loop tracer based on Sawyer-Tower circuit.

III. RESULTS AND DISCUSSION

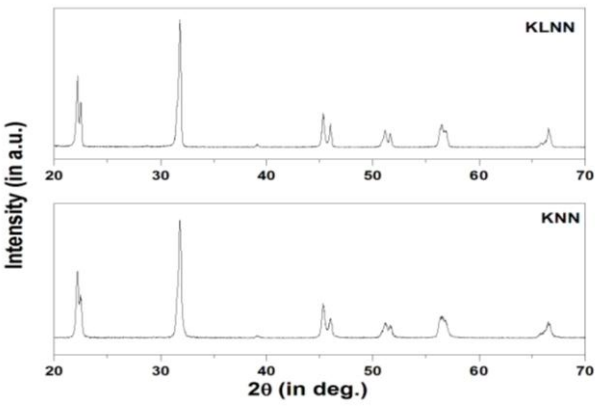

Fig 1. X-ray Diffraction patterns of calcined KNN and KLNN samples.

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Fig. 1 shows the XRD pattern of calcined powder of KNN and KLNN ceramics synthesized at 850^0C. Both samples exhibit single phase perovskite structure and have orthorhombic symmetry at room temperature. With substitution of Li, there is little shifting in diffraction peaks towards higher angle. Therefore, there is decrease in cell parameters with Li substitution. The volume decreases and density increases for substituted sample. The cell parameters are calculated from the XRD pattern by using Bragg's equation $2d\sin\theta = n\lambda$ for n=1 given in Table 1.This may be due to small ionic radii of Li^+ ion in comparison to Na^+ or K^+ ions with the same co-ordination number. However, increase in c/a ratio suggests that there is an increase in tetragonality for KLNN. The experimental density for both samples is calculated by Archimedes Principle. Higher value is obtained in Li substituted sample which given in Table1.

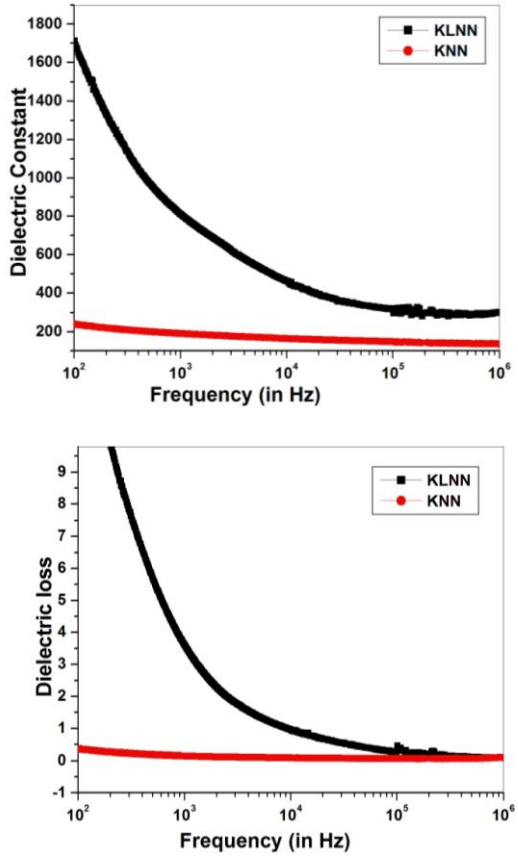

Fig 2. Variation in dielectric constant and dielectric loss with frequency at room temperature for KNN and KLNN.

Fig. 2 shows the variation of dielectric constant and dielectric loss with frequency at room temperature (~ 25^0C). The high value of dielectric constant is observed at lower frequencies and this may be due to space charge polarization. The decrease in dielectric constant with frequency is rapid because as the frequency increases, ionic and orientation polarization decreases [10]. A similar behavior is observed in case of the loss tangent with frequency. The value of dielectric constant is higher and loss is minimum for Li substituted KNN at higher frequencies.

Table 1. Values of experimental density, cell parameters (c & a), ε_{RT} (room temperature dielectric constant) for KNN and KLNN both samples

Sample	Exp. Density	c(A^0)	a(A^0)	ε_{RT}
KNN	4.09	3.959	3.907	280
KLNN	4.23	3.956	3.894	1700

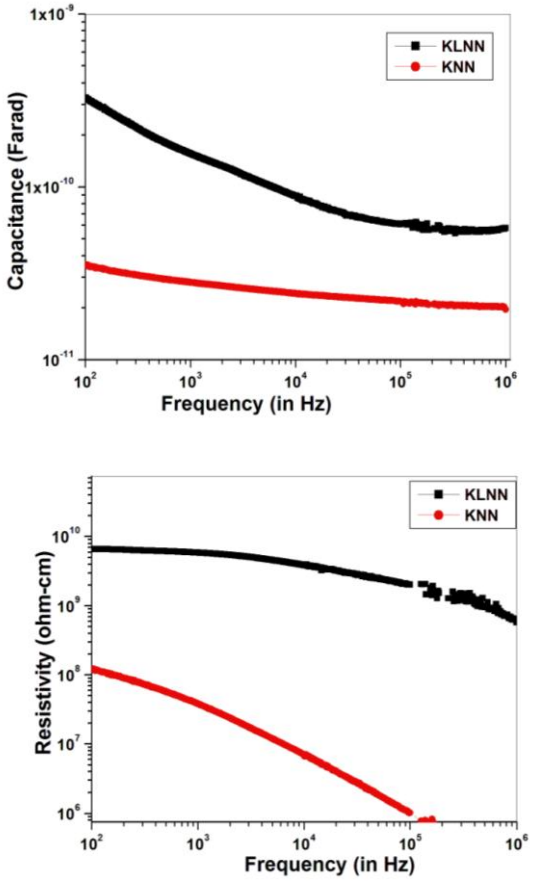

Fig 3. Variation in capacitance and resistivity with frequencies up to 1 MHz at room temperature for KNN and KLNN samples.

The frequency dependency of capacitance and resistivity is also studied. The decrease in the electrical resistivity or intern increase in electrical conductivity with increase in frequency of applied field is shown in fig. 3. The electrical conductivity of KNN material decrase with Li substitution. This may be due to decrease in leakage current. The dispersion of resitivity with frquency can be explained by Koop's Theory [11]. The increase in capacitance with substitution can be explained by space charge polarization. The capacitance also decreases with increase in frequency but the variation in resitivity with frequency is larger than capacitance.

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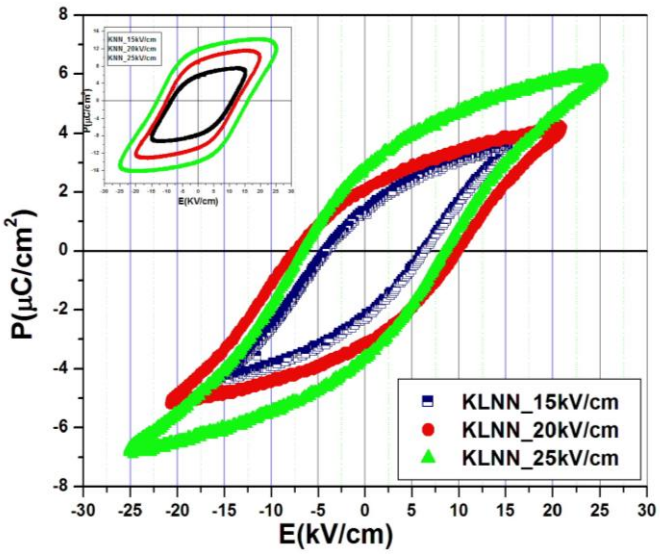

Fig 4. Ferroelectric behavior of KNN and KLNN at different applied electric fields.

Fig. 4. shows room temperature P-E hysteresis loops for both samples. A comparison of P-E loops reveals that both remenant polarization (P_r) and saturation polarization (P_s) increase with increase in applied electric field in both cases. There is not much effect of substitution on the coercivity. However, the Li substituted sample shows better saturation in comparison to pure sample which is a characteristic of good ferroelectric material [12]. Hence, Li substitution improves the electrical properties of pure lead free KNN ceramics which is very useful for device applications.

IV. CONCLUSION

The materials were prepared by conventional solid state reaction route. X-ray diffraction analysis shows that all the samples were well crystallized into pervoskite structure. The lattice parameters are less in case of substituted sample due to lower ionic radii of Li.The better dielectric properties were obtained on substitution of Li with high dielectric constant and minimum loss at higher frequencies.The KNN with Li shows higher resitivity as well as capacitance and also shows higher saturation of P-E loop.

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