

# Studies on the Structural and Electrical Properties of ZnO added $\text{Na}_{0.47}\text{K}_{0.47}\text{Li}_{0.06}\text{NbO}_3$ Piezoceramics Prepared by Solid State Conventional Method using High Energy Ball Milling

Huidrom Surjalata Devi<sup>1</sup> and Mamata Maisnam<sup>2</sup>

<sup>1,2</sup>Department of Physics National Institute of Technology Manipur-795004, India  
E-mail: <sup>1</sup>[surjalata003@gmail.com](mailto:surjalata003@gmail.com), <sup>2</sup>[mmainsnam.nitm@gmail.com](mailto:mmainsnam.nitm@gmail.com)

**Abstract**—The Lead free KNN (sodium potassium niobates) based piezoceramics are one of the leading candidates for replacing the lead based PZT (lead zirconium titanates). However KNN based piezoceramics find difficulty to sinter to high density. Therefore, various additives may be added to KNN based ceramics to improve density, microstructure, desired stoichiometry, etc. in order to improve the useful piezoelectric properties. ZnO is one of the additives that can be used for this purpose. KNN piezoceramics having compositional formula  $\text{Na}_{0.47}\text{K}_{0.47}\text{Li}_{0.06}\text{NbO}_3$  were prepared adding different amount of ZnO (0 wt. %, 1 wt. %, 2 wt. %, 3 wt. %) by conventional solid state method and using high energy ball milling. The samples were sintered at 1050 °C for 2h. X-ray diffraction (XRD) technique studied the structure of the prepared samples and tetragonal phase has been observed in the samples for ZnO addition upto 1wt% above which the sample showed orthorhombic phase. The electrical properties such as dielectric constant, dielectric loss and a.c. conductivity were measured by using an impedance analyzer. The results obtained were analyzed and systematically discussed in the paper.

## 1. INTRODUCTION

These Polycrystalline lead zirconium titanate ( $\text{PbZrTiO}_3$ ) commonly known as PZT are a type of piezoceramics having a variety of applications such as ultrasonic transducer, sensor, transformer, atomic force microscopy, energy harvesting etc. because of their high piezoelectric properties[1-3]. However, lead oxide which is the main component of PZT is very toxic and hazardous to the environment. Therefore, the development of high potential lead free piezoceramics is the topic of current research. [4-6]. Among the lead free piezoceramics, potassium sodium niobate (KNN) based piezoceramics are considered to be one of the most important piezoceramics due to their high curie temperature (420 °C) and comparable piezoelectric properties to PZT[7-8]. This belief has been reinforced since Saito et.al reported a high piezoelectric coefficient  $d_{33}$  of 416 pC/N on modified KNN with Li, Ta and Sb[9]. However, densification is the main issue for KNN based piezoceramics due to high volatility of alkali element components viz. Na, K. To overcome this problem many methods such as adopting

different processing technique, using additives, controlling processing parameter i.e changing composition are among many methods adopted by many researchers [9-17]. Among them ZnO is an efficient additives which acts as sintering aid thus reducing sintering temperature while improving density and microstructure. In this study, ZnO added  $\text{Na}_{0.47}\text{K}_{0.47}\text{Li}_{0.06}\text{NbO}_3$  piezoceramics were prepared by conventional solid state method using high energy ball milling. The phase structured and electrical properties of the prepared ceramics are studied in this paper.

## 2. EXPERIMENTAL SECTION

The  $\text{Na}_{0.47}\text{K}_{0.47}\text{Li}_{0.06}\text{NbO}_3$  composition ceramics were prepared by solid state conventional method using high energy ball milling. For this  $\text{Na}_2\text{CO}_3$  (99.5%),  $\text{Li}_2\text{CO}_3$  (99.5%),  $\text{K}_2\text{CO}_3$  (98%) and  $\text{Nb}_2\text{O}_5$  (99.9%) powders were used as starting raw materials and weighed according to the stoichiometry. The powders were milled in a high energy ball mill (Insmart make ball mill) with zirconia balls, for 12h at 200 RPM. Afterwards, the resulting powders were calcined at 850 °C for 3h. Then calcined powders were mixed with ZnO (99.5%) using different amount of ZnO (0 wt.%, 1 wt.%, 2 wt.%, 3 wt.%) and remilled for 2h. The resulting powders were pressed into pellets after adding 3wt.% of polyvinyl alcohol (PVA) as binder. The pellets were sintered at 1050 °C for 2h in a conventional furnace using 5 °C/min. Phase structured was studied by using X-ray diffractometer (D8 Advance Eco Bruker) with  $\text{Cu } k_\alpha$  of wavelength 1.5405Å. For the electrical measurements, the sintered pellets were painted with silver paste on both faces of the pelleted samples. The electrical properties such as dielectric constant, dielectric loss and a.c. conductivity were measured by using an impedance analyzer (Keysight E4990A) in the frequency range of 20 Hz to 2 MHz.

### 3. RESULTS AND DISCUSSION

#### 3.1 Structural Analysis

Fig.1 shows the XRD patterns corresponding to  $\text{Na}_{0.47}\text{K}_{0.47}\text{Li}_{0.06}\text{NbO}_3$  added with ZnO (0 wt.%, 1 wt.%, 2 wt.%, 3 wt.%) ceramics sintered at 1050 °C for 2h. All compositions formed a single perovskite phase. A tetragonal phase is observed in  $\text{Na}_{0.47}\text{K}_{0.47}\text{Li}_{0.06}\text{NbO}_3$  with ZnO addition of 0 wt.% and 1 wt.% and a phase transition from tetragonal to orthorhombic phase occurs at 2 wt.% ZnO addition and higher. This is indicated by the abrupt change in intensity on the diffraction of (002) at  $2\theta \sim 45^\circ$  and the diffraction peak (101) shifts into lower angle. The ionic radius of  $\text{Zn}^{2+}$  (0.74 Å) is less than those of A-site ions ( $\text{K}^+$ :1.33 Å,  $\text{Na}^+$ :0.97 Å,  $\text{Li}^+$ :0.76 Å) and larger than that of B-site ( $\text{Nb}^{5+}$ :0.69 Å). Therefore  $\text{Zn}^{2+}$  could inter A-site or B-site.

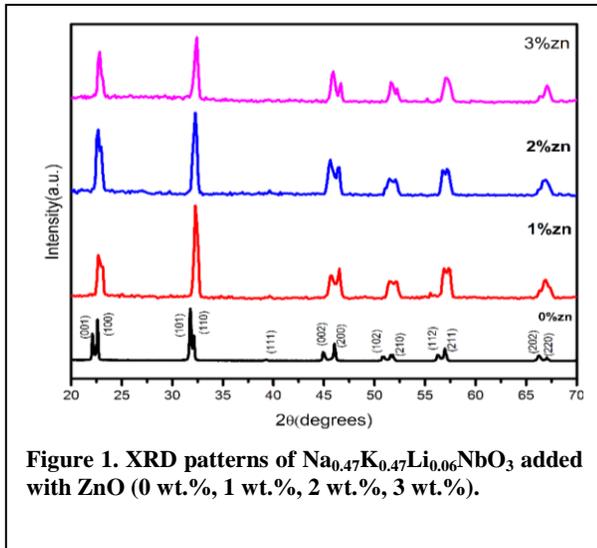


Figure 1. XRD patterns of  $\text{Na}_{0.47}\text{K}_{0.47}\text{Li}_{0.06}\text{NbO}_3$  added with ZnO (0 wt.%, 1 wt.%, 2 wt.%, 3 wt.%).

#### 3.2 Electrical Measurements

The plot for  $d_{101}$  all the samples is shown in fig.2. The variation of  $d_{101}$  may be understood from the partial substitution of the elements in A-site or B-site by  $\text{Zn}^{2+}$  ions. As reported by other researchers [18]  $\text{Zn}^{2+}$  ions having ionic radius 0.74 Å have higher tendency to incorporate into A-site of the perovskite substituting A-site ions of larger ionic radius such as ( $\text{K}^+$ :1.33 Å,  $\text{Na}^+$ :0.97 Å,  $\text{Li}^+$ :0.76 Å). Therefore for lesser ZnO addition upto ~1wt%, it is likely that the  $\text{Zn}^{2+}$  ions have substituted A-site ions hence decrease in  $d_{101}$  is expected. Further, for ZnO addition ~2wt% and above it is likely that some of  $\text{Zn}^{2+}$  ions is likely to migrate to B-site and substituting comparatively smaller  $\text{Nb}^{5+}$  ions leading to an overall increase in the  $d_{101}$  as shown in fig.2. Thus simultaneous incorporation of  $\text{Zn}^{2+}$  ions in both A-site and B-site for higher concentration of ZnO addition may have resulted in the phase transition from tetragonal to orthorhombic phase. The lattice parameters

are calculated by using program Unit cell –method from the XRD data. The corresponding values are given in the table

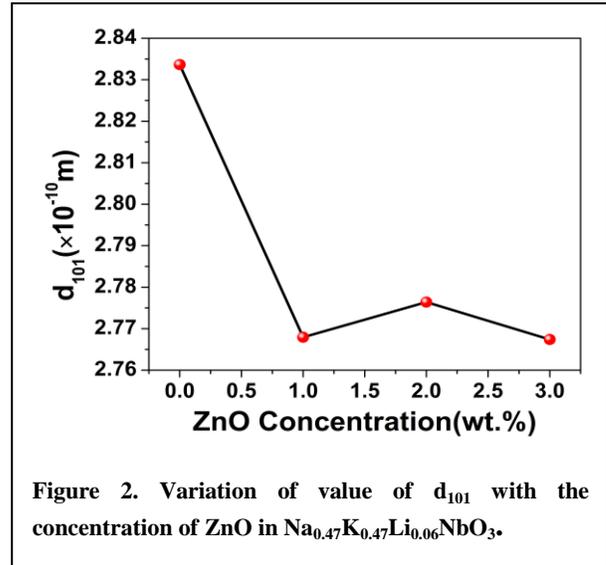


Figure 2. Variation of value of  $d_{101}$  with the concentration of ZnO in  $\text{Na}_{0.47}\text{K}_{0.47}\text{Li}_{0.06}\text{NbO}_3$ .

1. Table1 further showed that crystallite size calculated from XRD data decreased with the increase of ZnO addition upto 2wt% as shown in table1. Correspondingly the density increased for ZnO addition upto 2wt% and then decreased. It is found that ZnO act as sintering aid as reported by the others [19, 20] leading to refinement in crystallites and increasing of density  $\leq 2\text{wt}\%$ .

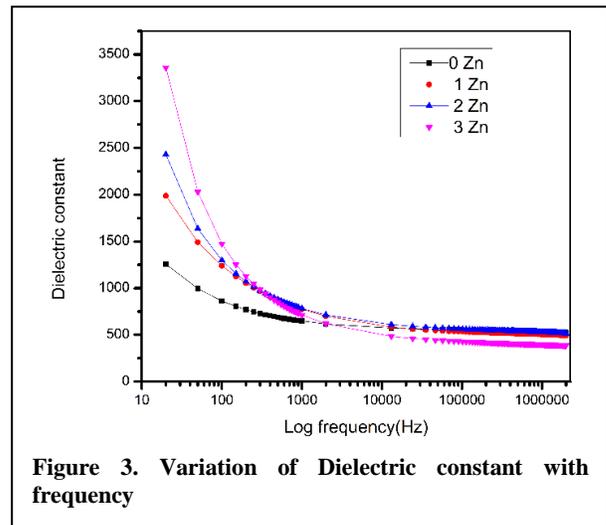
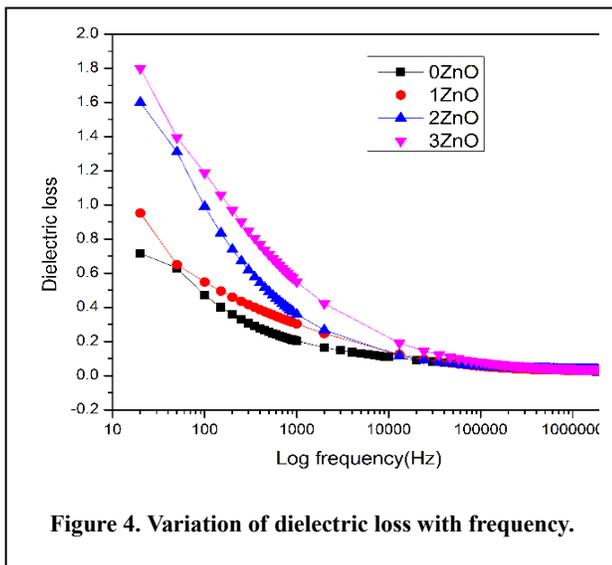


Figure 3. Variation of Dielectric constant with frequency

**Table 1: Lattice parameters, crystallite size and density.**

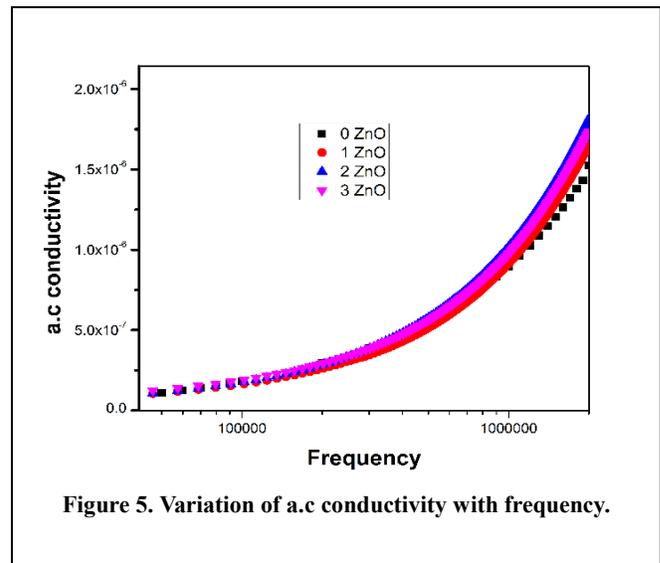
Name	a (Å)	b (Å)	c (Å)	volume (Å) <sup>3</sup>	Crystallite size (Å)	Density (gm/cc)
0 wt% ZnO	3.94257		4.03180	62.6696	306.70	4.50
1wt% ZnO	3.92091		3.97369	61.0898	142.15	4.64
2 wt% ZnO	3.93099	3.87280	3.98177	60.6180	132.92	4.70
3 wt% ZnO	3.91279	3.92983	4.00538	61.5891	140.23	4.65

Fig. 3. shows the variation of dielectric constant with frequency at room temperature where the dielectric constant is high at lower frequencies which is the indicative of space charge polarization, a characteristic of polycrystalline material and the dielectric constant decreased gradually as the frequency increased upto a certain frequency above which the value maintain an almost constant value. This is the general frequency dispersion behavior of dielectric constant. At higher frequency, the dipole which produced polarization could not follow the oscillating applied field hence, the dielectric constant maintain an almost constant value at higher frequencies. The variation of dielectric loss (loss tangent) with frequency corresponding to  $\text{Na}_{0.47}\text{K}_{0.47}\text{Li}_{0.06}\text{NbO}_3$  added with different amounts of ZnO (0 wt.%, 1 wt.%,

**Figure 4. Variation of dielectric loss with frequency.**

2 wt.%, 3 wt.%) which has the similar behavior as in the variation of dielectric constant as shown in fig.4. The a.c conductivity of the samples were calculated with the dielectric data using the relation:  $\sigma_{a.c} = 2\pi f \tan \delta \epsilon_0 \epsilon_r$  Where, f is the frequency of applied field,  $\tan \delta$  is the loss tangent available

from dielectric measurement,  $\epsilon_r$  is the relative permittivity of the sample and  $\epsilon_0$  is the permittivity of free space ( $8.854 \times 10^{-12} \text{F/m}$ ). The plot of fig.5 shows that a.c conductivity increased slowly with the increase of frequency upto a certain frequency above which the value increased rapidly. At higher frequencies the conducting grains become more active leading to enhanced exchange charges and hence an increased in a.c conductivity.

**Figure 5. Variation of a.c conductivity with frequency.**

## REFERENCES

- [1] M. J. Hoffmann and H. Kungl, "High strain lead-based perovskite ferroelectrics," *Curr. Opin. Solid State Mater. Sci.*, vol. 8, no. 1, pp. 51–57, 2004.
- [2] F. Levassort, L. P. Tran-huu-hue, D. Certon, and M. Lethiecq, "Piezoelectric Materials for Ultrasonic Transducers: Review of Recent Developments."
- [3] W. Jo *et al.*, "Wook Jo," vol. 31, pp. 2107–2117, 2011.
- [4] E. Cross, "Lead-free at last," *Nucl. Med. Commun.*, vol. 32, no. 7, pp. 666–668, 2011.
- [5] T. R. Shrout and S. J. Zhang, "Lead-free piezoelectric ceramics: Alternatives for PZT?," *J. Electroceramics*, vol. 19, no. 1, pp. 111–124, 2007.
- [6] P. K. Panda, "Review: Environmental friendly lead-free piezoelectric materials," *J. Mater. Sci.*, vol. 44, no. 19, pp. 5049–5062, 2009.
- [7] R. E. JAEGER and L. EGERTON, "Hot Pressing of Potassium Sodium Niobates," *J. Am. Ceram. Soc.*, vol. 45, no. 5, pp. 209–213, 1962.
- [8] L. EGERTON and D. M. DILLON, "Piezoelectric and Dielectric Properties of Ceramics in the System Potassium???Sodium Niobate," *J. Am. Ceram. Soc.*, vol. 42, no. 9, pp. 438–442, 1959.
- [9] Y. Saito *et al.*, "Lead-free piezoceramics," *Nature*, vol. 432, no. 7013, pp. 84–87, Nov. 2004.
- [10] J. F. Li, K. Wang, B. P. Zhang, and L. M. Zhang, "Ferroelectric and piezoelectric properties of fine-grained  $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$  lead-free piezoelectric ceramics prepared by spark plasma

- sintering,” *J. Am. Ceram. Soc.*, vol. 89, no. 2, pp. 706–709, 2006.
- [11] G. H. HAERTLING, “Properties of Hot-Pressed Ferroelectric Alkali Niobate Ceramics,” *J. Am. Ceram. Soc.*, vol. 50, no. 6, pp. 329–330, 1967.
- [12] E. Hollenstein, M. Davis, D. Damjanovic, and N. Setter, “Piezoelectric properties of Li- and Ta-modified ( $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ ) ceramics,” *Appl. Phys. Lett.*, vol. 87, no. 18, pp. 1–3, 2005.
- [13] D. Lin, K. W. Kwok, and H. L. W. Chan, “Phase structures and electrical properties of  $\text{K}_{0.5}\text{Na}_{0.5}(\text{Nb}_{0.925}\text{Ta}_{0.075})\text{O}_3$ -LiSbO<sub>3</sub> lead-free piezoelectric ceramics,” *J. Phys. D: Appl. Phys.*, vol. 40, no. 19, pp. 6060–6065, 2007.
- [14] E. M. Alkoy and M. Papila, “Microstructural features and electrical properties of copper oxide added potassium sodium niobate ceramics,” *Ceram. Int.*, vol. 36, no. 6, pp. 1921–1927, 2010.
- [15] F. Rubio-Marcos, J. J. Romero, M. G. Navarro-Rojero, and J. F. Fernandez, “Effect of ZnO on the structure, microstructure and electrical properties of KNN-modified piezoceramics,” *J. Eur. Ceram. Soc.*, vol. 29, no. 14, pp. 3045–3052, 2009.
- [16] J. Wu, “High piezoelectricity in low-temperature sintering potassium–sodium niobate- based lead-free ceramics,” *RSC Adv.*, vol. 4, no. 96, pp. 53490–53497, 2014.
- [17] D. Lin, K. W. Kwok, and H. L. W. Chan, “Dielectric and piezoelectric properties of  $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ - $\text{AgSbO}_3$  lead-free ceramics,” *J. Appl. Phys.*, vol. 106, no. 3, p. 34102, 2009.
- [18] H. T. Li, B. P. Zhang, M. Cui, W. G. Yang, N. Ma, and J. F. Li, “Li, H. T., Zhang, B. P., Cui, M., Yang, W. G., Ma, N., & Li, J. F. (2011). Microstructure, crystalline phase, and electrical properties of ZnO-added  $\text{Li}_{0.06}(\text{Na}_{0.535}\text{K}_{0.48})_{0.94}\text{NbO}_3$  ceramics. *Current Applied Physics*, 11(3 SUPPL.), S184–S188. <https://doi.org/>,” *Curr. Appl. Phys.*, vol. 11, no. 3 SUPPL., pp. S184–S188, 2011.
- [19] L. A. Ramajo, J. Taub, and M. S. Castro, “Effect of ZnO Addition on the Structure, Microstructure and Dielectric and Piezoelectric Properties of  $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$  Ceramics,” *Mater. Res.*, vol. 17, no. 3, pp. 728–733, 2014.
- [20] R. Hayati and A. Barzegar, “Microstructure and electrical properties of lead free potassium sodium niobate piezoceramics with nano ZnO additive,” *Mater. Sci. Eng. B-Advanced Funct. Solid-State Mater.*, vol. 172, no. 2, pp. 121–126, 2010.