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Synthesis and characterization of alkali doped Lead Zirconate Titanate

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Abstract:
In this study, alkali doped ferroelectric lead zirconate titanate (PZT) pellets have been synthesized by solid state reaction method at 1100^{o}C. The crystalline nature of the synthesized PZT pellets has been studied using X-ray diffraction (XRD). Microstructural characterization of the synthesized materials has been performed using scanning electron microscopy (SEM). X-ray diffraction studies have shown that PZT pellets have a rhombohedral structure. The SEM results suggest that the sintered pellets were reasonably dense due to liquid phase sintering. Dielectric constant and dielectric loss measurement of the synthesized materials has also been measured. It has been found that the dielectric loss is very small and is decreasing with frequency above 300°C. The increase of dielectric constant observed at high temperatures and low frequencies in the paraelectric state is explained.

Keywords: *PZT, Ferroelectric, mixed oxide method, XRD, SEM, Dielectric properties.*

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I. Introduction:

Lead zirconate titanate ($PbZr_{1-x}T_{ix})O_3$ or PZT) is a ferroelectric perovskite that shows a strong piezoelectric property in polycrystalline form [1-2]. PZT is one of the most efficient materials [3-4] that is widely used in many applications such as transducers, ferroelectric field effect transistors, sensor, actuator and non-volatile random-access memories [5-7]. The PZT system is well described by a morphotropic phase boundary (MPB) that corresponds to the transition from a tetragonal to a rhombohedral structure. At room temperature, PZT shows a tetragonal and a rhombohedral ferroelectric phase where titanium and zirconium are enriched in tetragonal and rhombohedral phases respectively. Structures near the MPB region show increased efficiency of polarization and electromechanical responses in general, making them particularly suitable for non-volatile memory and piezoelectric actuators. It is observed that PZT perovskite structure deforms below 350^0C [8]. The rhombohedral and the tetragonal phases of $PbZrO_3$ and $PbTiO_3$ appear when Zr^{4+} and Ti^{4+} resides at the center of the unit cell in the PZT structure [9].

A review of the literature suggests that PZT can be synthesized and characterized in a variety of ways, showing that different morphologies. Oliveira *et al.* [10] have synthesized PZT at the ratio of Zr/Ti = 52/48 using the polymeric precursor method (PPM) and the microwave-assisted hydrothermal method. Their results showed that PZT powders are composed of tetragonal and rhombohedral phases. PZT have been prepared by high energy solid-state reaction method and analyzed by XRD, SEM and dielectric properties [11]. Mirzaei *et al*. have synthesized PZT (0.523/0.477) nanocrystalline powders by an alkoxide based sol-gel method [12]. The synthesized powders have been characterized by XRD, SEM and TEM (transmission electron microscopy) studies. Unruan *et al.* [13] have investigated the dielectric and ferroelectric properties of complex perovskite lead zirconate titanate-lead nickel niobate ceramic system under the influence of compressive stress. They found that the dielectric properties and ferroelectric characteristics changed significantly with increasing compressive stress. Dense single phase PZT (with a compositional range of $0.1 > x > 0.9$) has been synthesized by a high-throughput molecular-beam epitaxy technique [14]. Chaisan *et al.* [15] have developed a modified two-stage mixed oxide synthetic route for the synthesis of PZT powder. They found that the perovskite $PbZrO_3$ and $PbTiO_3$ phases together with PZT to form tetragonal and rhombohedral phases. Tang et al. [16] have prepared PZT powder by wet-dry method, where Glycol and zirconium oxychloride have been used as the solvent and the zirconium source respectively. They obtained a single-phase perovskite structure of PZT after sintering at 730 °C for 2 h, where the average size of PZT powder was about 113 nm. Xia [17] has synthesized PZT single crystals with compositions across the morphotropic phase boundary (MPB) by top-seeded solution growth (TSSG) technique, where the growth conditions have been optimized by chemical, thermodynamic and kinetic parameters. He observed that the growth temperature is the key factor for controlling the composition of the

crystals. Huang *et al*. [18] have synthesized PZT nano-particles with the chemical composition $Pb(Zr_{0.52}Ti_{0.48})O_3$ by hydrothermal process using controlled ramping and cooling rates. PZT nano-particles of such composition are finding use in many applications such as such as PZT ink for 3-D printing or seeds for PZT thick films.

In the present study, alkali (Na, K and Li) doped sintered PZT powders at the ratio of Zr/Ti = 70/30 composition have been synthesized by the conventional solid state reaction method. The polycrystalline materials synthesized in the present investigation is $Pb_{1-x}(La_{1-z}D_z)_x(Zr_y Ti_{1-y})_{1-x/4} O_3$.The prepared materials have been characterized by their XRD, SEM and dielectric properties.

II. Experimental Section:

Solid-state synthesis describes interactions where neither a solvent medium nor controlled vapor-phase interactions are used. These reactions occur under extreme conditions of high temperature or high pressure. Solid-state synthesis is used to create the unique compositions and morphologies necessary to generate the desired characteristics in scintillation crystals, piezoelectric and other advanced materials. PZT have been synthesized by solid-state reaction method, which employ a series of mixing, grinding and annealing times with varying temperature and heating schedule time. High purity raw materials (Aldrich) have been used to prepare the ferroelectric PZT ceramics. The raw materials i. e. metals oxides and metal carbonates were weighted according to the stoichiometric formula $Pb_{1-x}(La_{1-z}D_z)_x(Zr_y Ti_{1-y})_{1-x/4} O_3$, where x = 0.10, y = 0.70, z = 0.0, 0.1, 0.2, and 0.3, D = Na, K and Li. Zirconium and titanium citrates with known concentrations has been used to prepare PZT powders in the ratio Zr/Ti of 70/30. The particle size of the powder must be in the sub-micron range for the solid phase reaction to occur by atomic diffusion. The raw materials are mixed in acetone medium for 50 to 60 minutes with the help of agate mortar and pestle for homogeneous mixing of the mixture. Since calcination is necessary for the completion of solid-state reaction, therefore, the composite material has been calcined at 1000°C for 2 hours. The pellets were formed by the powder with the help of uniaxial hydraulic press and die punch. To make the pellets more compact with reduce porosity, the pellets were sintered at 1100°C for 6 hours.

Furthermore, the XRD spectra of sintered pellets have been characterized by an X-ray diffractometer ((Brucker D8 Advance) using monochromatic CuK_α (λ = 0.15418nm) radiation over a wide range of Bragg angles ($20^o \leq 2\theta \leq 60^o$) at room temperature. The surface morphological properties of the PZT particles have been obtained by scanning electron microscope (SEM, Leo 435VP). The dielectric study (dielectric constant and dielectric loss measurement) of sintered pellets has been performed by LCR controller (Hioki 3522-50).

III. Results and Discussion

Structural analysis:

Figures (1-3) show XRD patterns of powders $Pb_{1-x}(La_{1-z}D_z)_x(Zr_y Ti_{1-y})_{1-x/4} O_3$ for Na, K and Li compounds, respectively, where x = 0.10, y = 0.70, z = 0.0, 0.1, 0.2, and 0.3. It is clear that the diffraction peaks are very sharp in the XRD patterns, which indicates that the pellets have better homogeneity and crystallinity. It has been observed that the splitting of triplets takes place into compositional fluctuations in their reflections leads to the coexistence of tetragonal and rhombohedral phases. Absence of the triplets in the XRD patterns of Figures1 to 3 indicates that there is no coexistence of ferroelectric phases in the entire range of modified compositions. The peaks of the XRD pattern have been indexed by a standard computer program [19]. The preliminary XRD measurements reveal that PZT composition has a rhombohedral structure. By increasing the concentration from x = 0.1 to x = 0.3, a very small difference in the d-value is observed, however, a systematic change in intensity of some reflections is observed when the final structure invariant. This change in intensity may be due to the variation of particle size and the presence of different number of dopants.

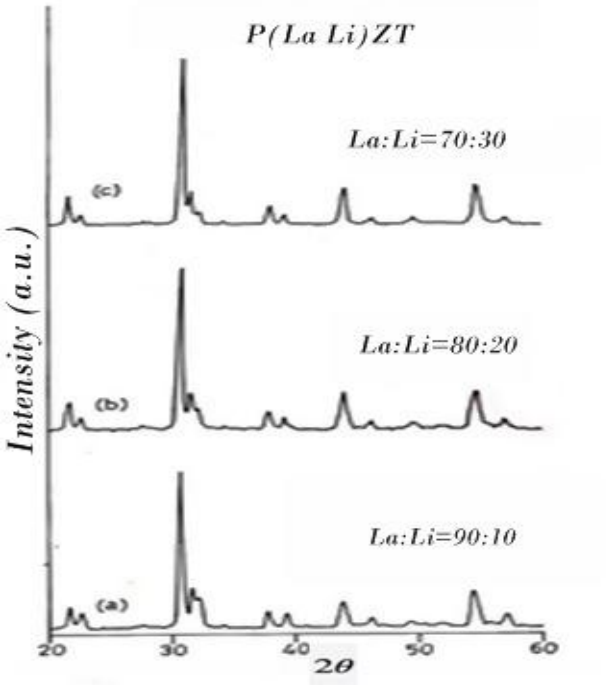


Figure 1. X-ray diffraction pattern of $Pb_{0.9}(La_{1-x}Li_x)(Zr_{0.7}Ti_{0.3})O_3$ sintered at 1100^0C, 6 hours in presence of PbZrO3 in which (a) x =0.1, (b) x = 0.2 and (c) x =

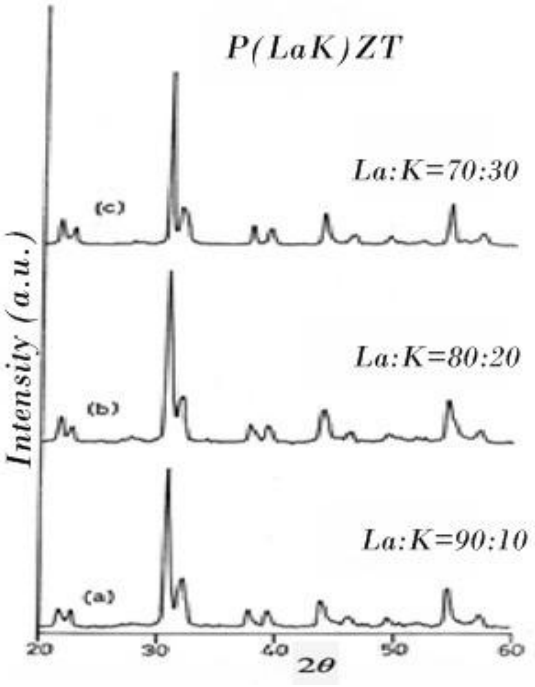


Fig. 2. X-ray diffraction pattern of $Pb_{0.9}(La_{1-x}K_x)(Zr_{0.7}Ti_{0.3})O_3$ sintered at 1100°C, 6 hours in presence of $PbZrO_3$ in which (a) x = 0.1, (b) x = 0.2 and (c) x = 0.3.

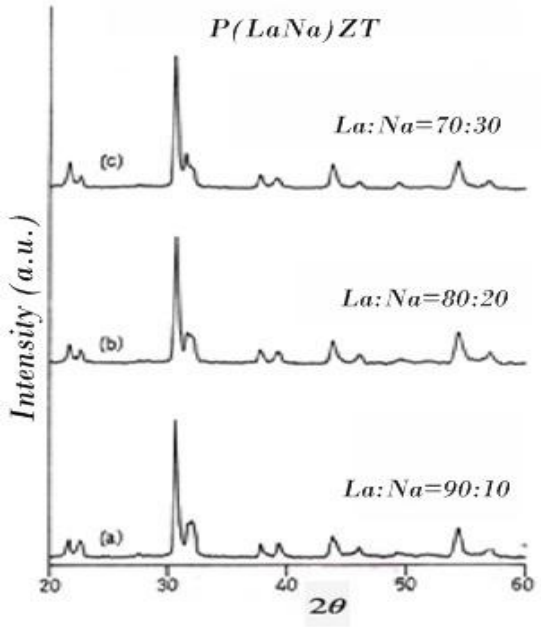


Fig. 3. X-ray diffraction pattern of $Pb_{0.9}(La_{1-x}Na_x)(Zr_{0.7}Ti_{0.3})O_3$ sintered at 1100°C, 6 hours in presence of $PbZrO_3$ in which (a) x = 0.1, (b) x = 0.2 and (c) x = 0.

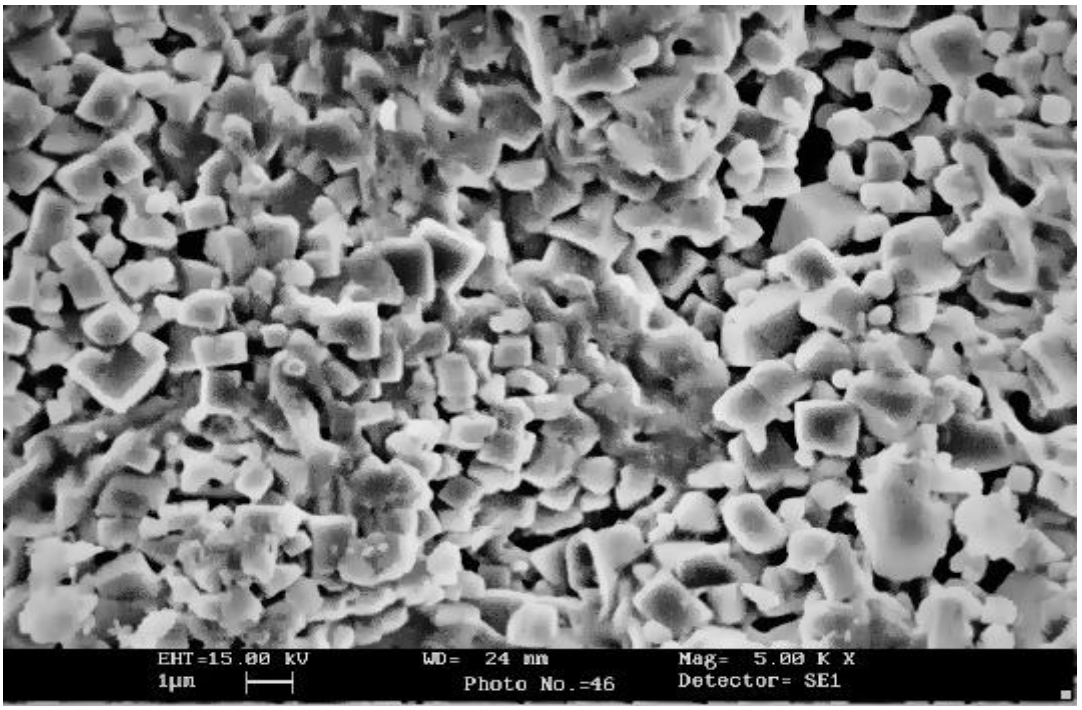
Microstructure analysis:

The surface morphology of PZT pellets with the composition $Pb_{0.9}(La_{0.9}Na_{0.1})_{0.1}(Zr_{0.7}Ti_{0.3})O_3$ has been studied by scanning electron microscope (SEM). The samples were broken up, coated with gold and placed in vacuum (10^{-5}Torr) electron microscope chamber. Figure 4 shows SEM images of PZT sintered pellets at 1100^0C. The microstructures of the sintered pellets show almost spherical shaped grains, which are uniformly and homogeneously distributed. It is also clear from Figure 4 that the sintered pellets are reasonably dense due

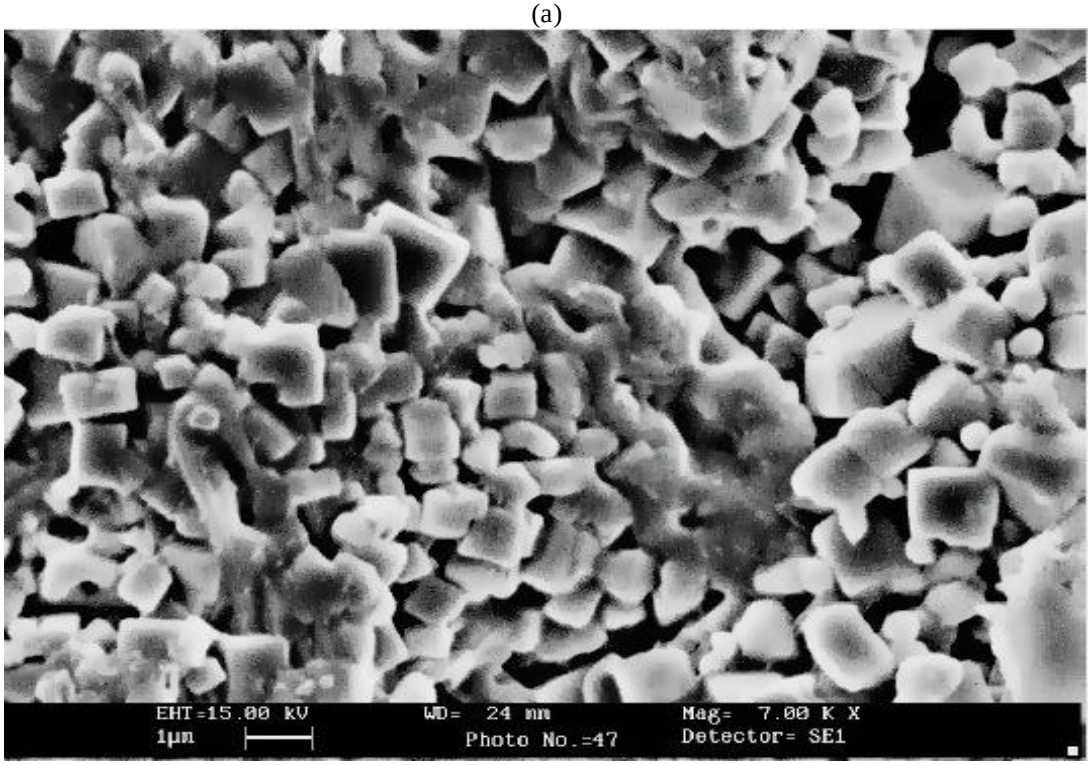
to liquid phase sintering. Other compositions and dopants (such as Li and K) also show nearly identical results. The average grain size (determined by linear interception method) has been found to be in the 10 – 20 μm range. The SEM study shows that the grain size decreases from Li to K.

Dielectric properties:

The dielectric constant (ε) and dielectric loss (tanδ) of all samples with the frequency have been measured in the frequency range of 10^2 Hz to 10^5 Hz at room temperature. The results shows that dielectric constant and dielectric loss decrease with increase of frequency. Figures 5 to 7 show the variation of dielectric constant and dielectric loss as a function of temperature (40-400^{0}C) and frequency (100Hz-100Kz) for the composition of $Pb_{0.9}(La_{1-x}Li_x)_{0.1}(Zr_{0.7}Ti_{0.3})O_3$, where x = 0.1, 0.2 and 0.3. Generally, both these parameters decrease with increase in frequency and show a distinctive feature.



(a)



(b

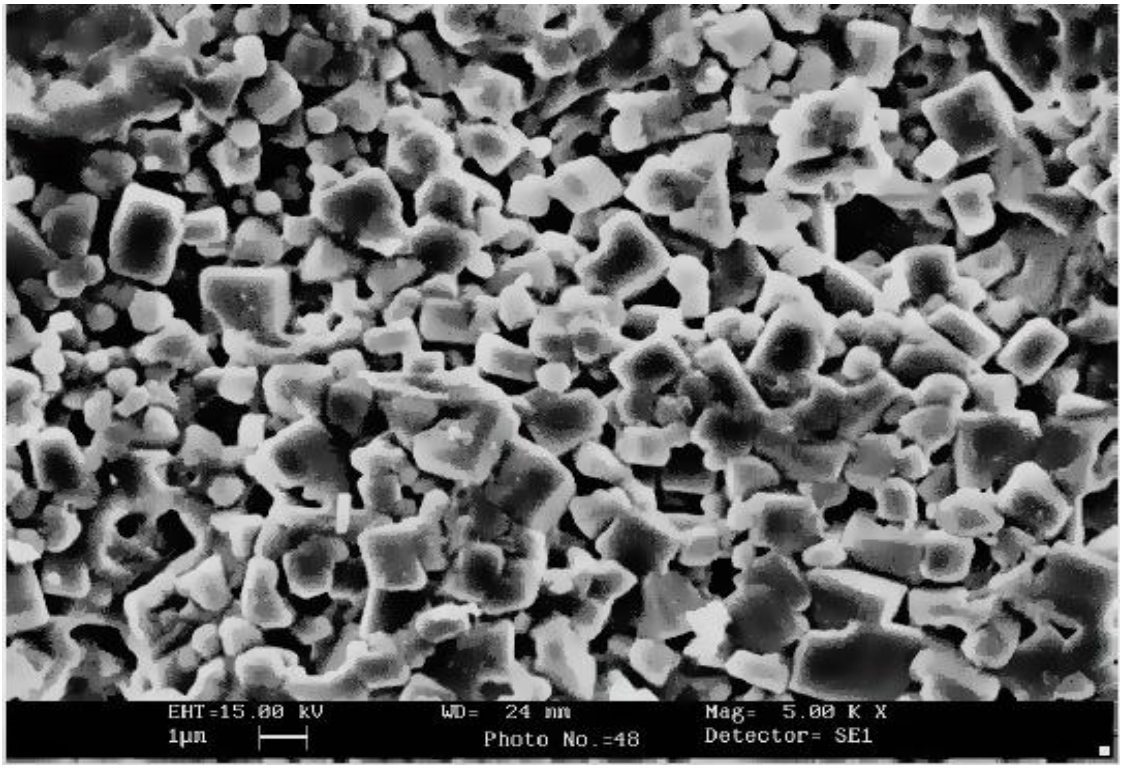
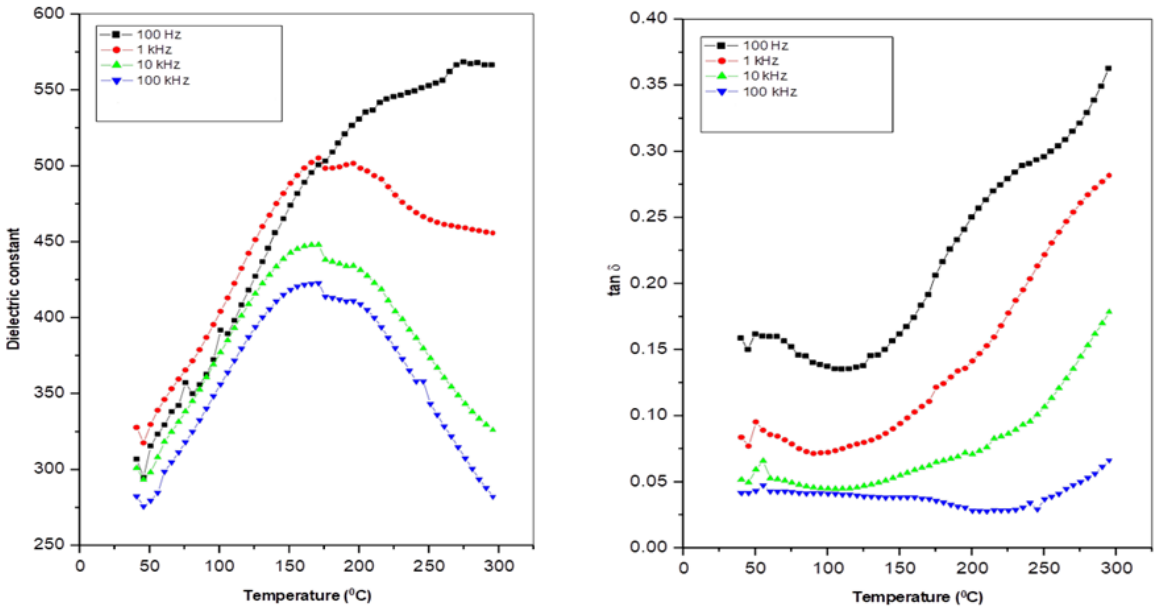


Fig. 4. SEM of $Pb_{0.9}$ ($La_{0.9}$ $Na_{0.1}$)$_{0.1}$($Zr_{0.7}$ $Ti_{0.3}$) O_3 sintered at 1100^0C, 6 hours at different locations (a), (b) and (c).

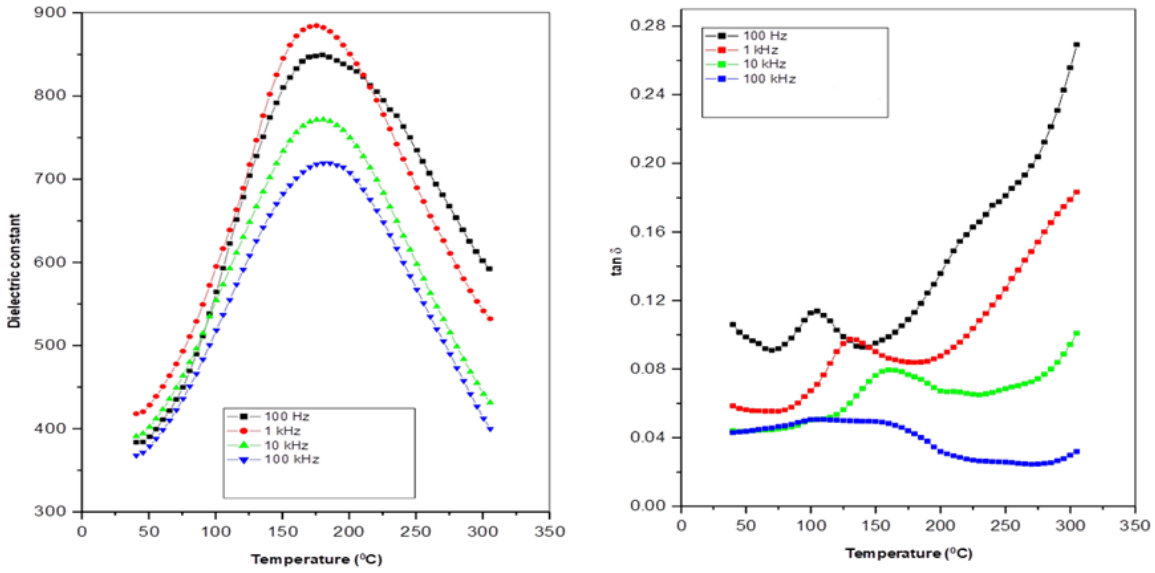
The magnitude of the dielectric constant depends on the doping and the frequency measured. The frequency dependence of the dielectric constant shows strong dispersion over the low frequency range. This phenomenon has been attributed to the low frequency space charge accumulation effect. Strong dispersion in the dielectric constant is a common feature of ferroelectrics associated with non-negligible ionic conductivity and is called low frequency dielectric dispersion [20]. The region around the dielectric peak appears to be broad due to compositional fluctuations, which is one of the most important features of a disordered perovskite structure with diffuse phase transition [21]. In ABO_3 type compounds, compositional fluctuations can develop at the A site occupied by Pb^{2+}, alkali elements (Li^+, Na^+, K^+) or La^{3+} or at the B site occupied by Ti^{4+}, Zr^{4+} or La^{3+}.

From Figures 5-7, it is clear that the dielectric constant of all compositions increases with increasing temperature, and reaches a peak at a particular temperature called transition temperature and then decreases. The dielectric constant of all compositions decreases with increasing frequency. It is also seen that dielectric constant gets modified significantly for different values of x. The dielectric loss is found to be very small which is decreasing with frequency, however, a sharp increase in tanδ is found above 300^0C. This growth in tanδ is due to an increase in the conduction of the residual current and the conduction of the absorption current. Almost identical results have been obtained for the Na and K compositions of PZT.



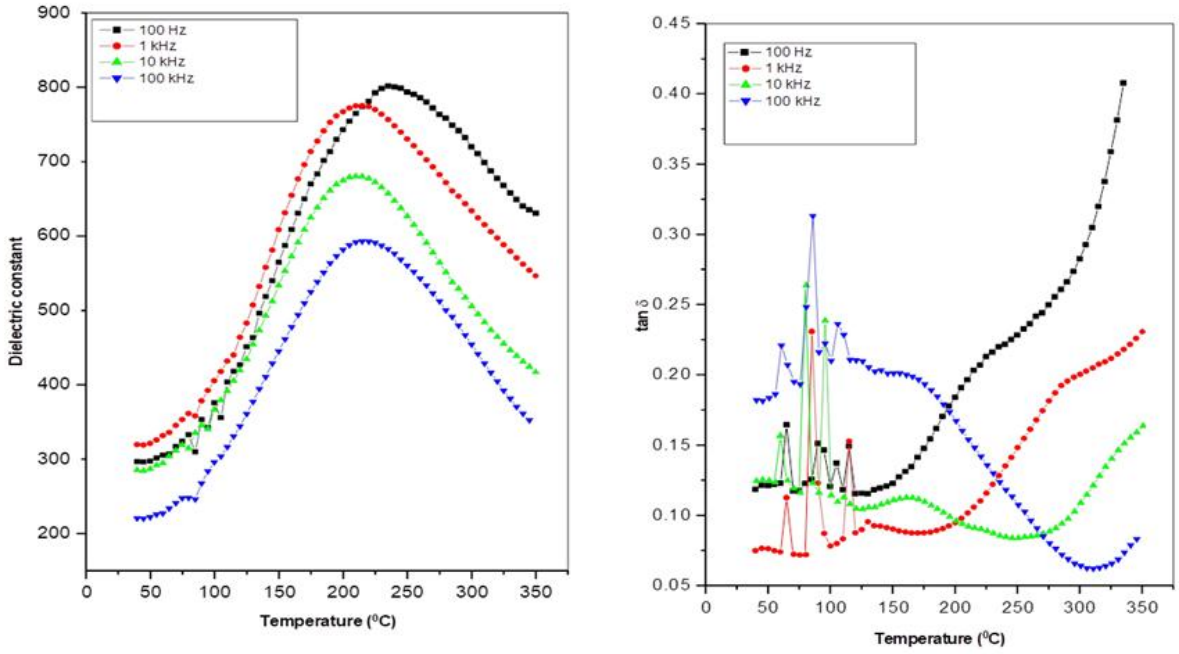
(a) (b)

Fig. 5. Variation of dielectric constant (a) and dielectric loss (b) with temperature at different frequency for $Pb_{0.9}(La_{0.9}Li_{0.1})_{0.1}(Zr_{0.7}Ti_{0.3})\ O_3$ (1100^0C, 6hours).



(a) (b)

Fig. 6. Variation of dielectric constant (a) and dielectric loss (b) with temperature at different frequency for $Pb_{0.9}(La_{0.9}Li_{0.2})_{0.1}(Zr_{0.7}Ti_{0.3})O_3$ (1100^0C, 6hours).



(a) (b)

Figure 7. Variation of dielectric constant (a) and dielectric loss (b) with temperature at different frequency for $Pb_{0.9}(La_{0.9}Li_{0.3})_{0.1}(Zr_{0.7}Ti_{0.3})O_3$ (1100^0C, 6hours).

IV. Conclusions:

This work presents a systematic study of the effect of alkali (La, Li, Na and K) dopants on the structural and dielectric properties of PZTs. In summary, alkali doped lead zirconate titanate (PZT) pellets have been successfully prepared by a solid-state reaction technique. The XRD pattern reveals the rhombohedral structure of the PZT powder. Microstructure studies (SEM) show that the grain size of PZT powders decreases from Li to K. The dielectric analysis indicates that alkali doped PZT ceramics undergo a diffuse type of phase transition. The expansion of the dielectric peak and the decrease in the maximum value of dielectric constant correspond to a decrease in the grain size as the concentration of dopants increases. High dielectric constant and low dielectric loss have been observed for all compositions. This study may be useful for many applications as a piezoelectric-grade as well.

References:

[1]. B. Jaffe, W.R. Cook, B. Jaffe, "Piezoelectric ceramics" Academic Press, New York, USA, 1971.
[2]. S. I. Shkuratov, "Explosive Ferroelectric Generators: From Physical Principles to Engineering" World Scientific, Singapore, 2019, Pages 25-44.
[3]. X.Y. Zhang, X. Zhao, C.W. Lai, J. Wang, X.G. Tang, J.Y. Dai, "Synthesis and piezo response of highly ordered $Pb(Zr_{0.53}Ti_{0.47})O_3$ nanowire arrays"; Applied Physics Letters, Volume 85, Issue 18 (2004) Pages 4190–4192.
[4]. G. Xu, W.J. Weng, H.X. Yao, P.Y. Du, G.R. Han, "Low temperature synthesis of lead zirconate titanate powder by hydroxide co-precipitation"; Microelectronic Engineering, Volume 66, Issue 1-4 (2003) Pages 568–573.
[5]. G. H. Haertling, "Ferroelectric Ceramics: History and Technology"; Journal of the American Ceramic Society, Volume 82, Issue 4 (1999) Pages 797-818.
[6]. W. Wersing, "In Piezoelectric Materials in Devices"; Setter, N.; (Eds.) ISBN 2-9700346- 0-3; Ceramic Laboratory, EPFL Swiss Federal Institute of Technology, Lausanne, Switzerland, (2002) Pages 29-66.
[7]. Xinhua Zhu, "Piezoelectric Ceramic Materials: Processing, Properties, Characterization, and Applications" Nova Science Publishers, 2010, Pages 1-34.
[8]. G. Xu, W. Jiang, M. Qian, X.X. Chen, Z.B. Li, G.R. Han, "Hydrothermal synthesis of lead zirconate titanate nearly free-standing nanoparticles in the size regime of about 4 nm"; Crystal Growth and Design, Volume 9, Issue 1(2009). Pages 13-16.
[9]. M. Klee, R. Eusemann, R. Waser, W. Brand, andH. Vanhal, "Processing and electrical-properties of $Pb(Zr_xTi_{1-X})O_3$ (X = 0.2–0.75) films—comparison of metalloorganic decomposition and sol–gel processes"; Journal of Applied Physics, Volume 72, Issue 4 (1992) Pages 1566–1576.
[10]. C.A. Oliveira , E. Longo, J.A. Varela, M. A. Zaghete, "Synthesis and characterization of lead zirconate titanate (PZT) obtained by two chemical methods";, Ceramics International, Volume 40, Issue 1 (2014) Pages 1717-1722.
[11]. M. Kumari, A. Singh, and J. Mandal, "Structural, Dielectric Properties of PZT Ceramics Prepared by Solid-State Reaction Route"; International Journal of Scientific & Engineering Research, Volume 5, Issue 4 (2014) Pages 404-406.
[12]. A. Mirzaei, M. Bonyani, S. Torkian, "Synthesis and characterization of nanocrystalline PZT powders: From sol to dense ceramics"; Processing and Application of Ceramics, Volume 10, Issue 1 (2016) Pages 9-16.

[13]. M. Unruan, A. Prasartketrakarn, A. Ngamjarurojana, Y. Laosiritaworn, S. Ananta, R. Yimnirun, "Dielectric and ferroelectric properties of lead zirconate titanate-lead nickel niobate ceramics under compressive stress"; Journal of Applied Physics, Volume 105, Issue 8 (2009) Pages 084111.
[14]. P.S. Anderson, S. Guerin, B.E. Hayden, Y. Han, M. Pasha, K.R. Whittle, I.M. Reaney, "Optimization of synthesis of the solid solution, $Pb(Zr_{1-x}Ti_x)O_3$ on a single substrate using a high-throughput modified molecular-beam epitaxy technique"; Journal of Materials Research, Volume 24, Issue 1(2009) Pages 164-172.
[15]. W. Chaisan, O. Khamman, R. Yimnirun, Supon Ananta, "A two-stage solid-state reaction to lead zirconate titanate powders"; Ferroelectrics, Volume 356, Issue 1 (2007) Pages 242-246.
[16]. H. Tang, J. Wang W. Gao, "Synthesis of PZT power by wet-dry method and its structure"; Journal of Central South University of Technology, Volume 15, Issue s2 (2008) Pages 257–260.
[17]. Y. Xie, Ph. D Thesis, "Synthesis and characterization of piezo-/ferroelectric lead zirconate-titanate (PZT) single crystals and related ternary ceramics" Simon Fraser University, Canada, 2013.
[18]. Hsien-Lin Huang, G.Z. Cao, I. Y. Shen, "Hydrothermal synthesis of lead zirconate titanate (PZT or $Pb(Zr_{0.52}Ti_{0.48})O_3$ nano-particles using controlled ramping and cooling rates"; Sensors and Actuators A: Physical, Volume 214, Issue 4 (2014) Pages 111-119.
[19]. POWD – An interactive powder diffraction data interpretation and Indexing program Version 2.1. By E.W.U.L., School of Physical Sciences, Flinders University of South Australia Bedford Park, S.A. 5042, Australia.
[20]. K. Prasad, R. Sati, S. N. Choudhary, R. N. P. Choudhary, K. L. Yadav, "$(Pb,Ca)[(Mn_{0.5}W_{0.5}),Ti]O_3$ ceramics: X-ray and dielectric studies"; Journal of Materials Science Letters, Volume 12, Issue 10 (1993) Pages 758–759.
[21]. Puja Goel, K L Yadav, A R James, "Double doping effect on the structural and dielectric properties of PZT ceramics"; Journal of Physics. D, Applied Physics, Volume 37, Issue 22 (2004) Pages 3174-3170.

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