STUDY OF STRUCTURAL PROPERTIES OF CALCIUM DOPED PLZT CERAMICS

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ABSTRACT

The present study aims to investigate effect of Ca^{+2} *ions on structural properties properties of PLZT. Calcium doped PLZT with general formulae* $Pb_{0.9}(La_{1-z}Ca_z)_{0.1}(Zr_{0.65}Ti_{0.35})_{0.975}O_3$ *where z=0, 0.02, 0.04, 0.06 were synthesized by solid state reaction method. X-ray diffraction analysis indicates the formation of single phase rhombohedral structure. Crystallite size, as calculated from Scherrer's equation, was found to be 25 nm.*

Key words: *Phase transition, PLZT, SEM, XRD, Microstructure*

INTRODUCTION

Although the application aspects of the research in ferroelectric ceramics are endless, however the biggest use have been in the areas such as dielectric ceramics for capacitor applications, ferroelectric thin films for non volatile memories, piezoelectric materials for medical ultrasound imaging and actuators, and electro-optic materials for data storage and displays. The collective worldwide excitations with deep attention in the research on ferroelectric materials have started in the 1950's, with widespread use of barium titanate (BaTiO3) based ceramics in capacitor applications and piezoelectric transducer devices. Followed by the same, several outstanding efforts have been made and 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. Amongst these some lead based compounds having ABO_3 type pervoskite ferroelectric structure were found to exhibit several interesting properties. Lead zirconate titanate (PZT), a solid solution of $PbTiO_3$ (T_c=490^{0}C) and $PbZrO_3$ (T_c=230^{0}C) crystallizes in ABO_3 type pervoskite structure where Pb^{+2} occupies the A sites and Zr^{+4} and Ti^{+4} ions are accommodated at the B sites. It occupies an important place in the field of ferroelectricity as its properties can be easily modified with addition of appropriate substituents for specific applications. The most common substituent is La^{+3} on Pb^{+2} site, leading to well known high performance PLZT having lower curie temperature, high dielectric constant and high optical transparency as compared to PZT. The physical properties of materials are greatly influenced by particle size. Substitution of some ions at different atomic sites plays a significant role in reduction of particle size. Due to these reasons double doped PZT has become a most attractive topic nowadays. The double doped PZT with common formulae of $Pb_{0.9}$ $(La_{1-z}R_z)_{0.1}$ $(Zr_{0.65}Ti_{0.35})_{0.975}O_3$, where R = Bi, Cs, Fe, Na were investigated for their dielectric, structural, optical, ferroelectric and piezoelectric properties. The purpose of investigation reported here was to partially substitute Pb^{+2} by Ca^{+2} and La^{+3}. The investigation reported here was aimed at developing a system with enhanced ferroelectric properties and studying the effect of calcium doping on the behaviour of PLZT ceramics.

EXPERIMENTAL PROCEDURE

The objective of the present work is to investigate the effect of Ca^{+2} ions on dielectric properties of PLZT. The compounds used in the investigation were synthesized by using conventional solid state reaction method. The polycrystalline sample with formulae $Pb_{0.9}$ $(La_{1-z}Ca_z)_{0.1}(Zr_{0.65}Ti_{0.35})_{0.975}O_3$ where z=0.00, 0.04, 0.06, 0.20 were prepared using required amount of analytical grade reagents PbO, ZrO_2, La_2O_3, $CaCO_3$, TiO_2 as starting materials. The weighed reagents were thoroughly mixed in acetone media. The well mixed powders were the dried and calcined at 1000^0C for 3 hours. The process of grinding and calcination was repeated till homogenous powders of PLCZT were obtained. The homogenous fine powders of PLCZT were then used to make cylindrical pellets of thickness 1-2 mm and diameter about 8 mm under isostatic pressure of 31.2 x 10^6 Pascal, using a uniaxial hydraulic press. These pellets were then sintered at 1200^0C for 2 hours. To prevent the PbO loss, lead zirconate (PZ) powder was used as a setter during sintering. The quality and formation of desired compounds were checked by XRD diffractometer (Brueker D8 advance) using CuK_α radiation (λ=1.5418 A^0) taken on calcined powder at room temperature. Using Scherer's equation: $P_{hkl}=(0.89\ \lambda)/(\beta_{1/2}\mathrm{Cos}\theta)$ the calculation of average crystallite size (P) was done from the broadening of XRD peaks, here $\beta_{1/2}$ represents the half peak width and θ is bragg angle. The distribution of grains on the surface of ceramic was analyzed by scanning electron microscope (SEM). The sintered pellets were cleaned and then gold deposited to analyse the microstructure. Grain sizes were calculated using linear intercept technique from the micrographs of SEM. The pellet surfaces were painted with high purity silver paste and cured at 600 ^{0}C for 1h to form perfect electrodes on the sample surface.

3. RESULTS AND DISCUSSION

The XRD pattern of PLCZT (z=0, 0.02, 0.04, 0.06) after sintering are presented in Fig. 1. The single and sharp regularly distributed peaks indicate the formation of single phase compounds having rhombohedral structure. The diffraction peaks were indexed and lattice parameters were calculated which were found to be in good agreement with reported values. Compared to pure PLZT, no shift in major peak position was observed. From this, we conclude that the basic crystal structure of pure PLZT has not been affected by the incorporation of the Ca ions. However, little shifts are observed in the peak positions indicating a small change in the lattice parameters.

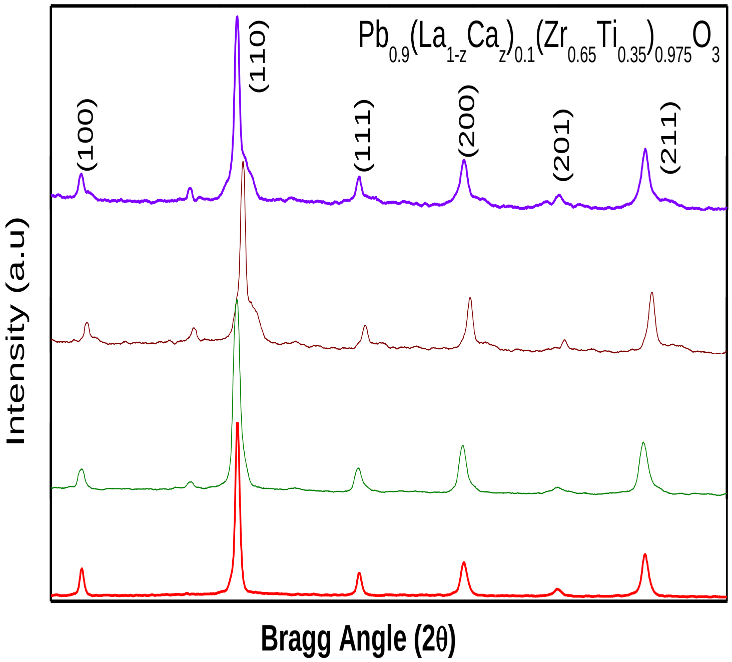
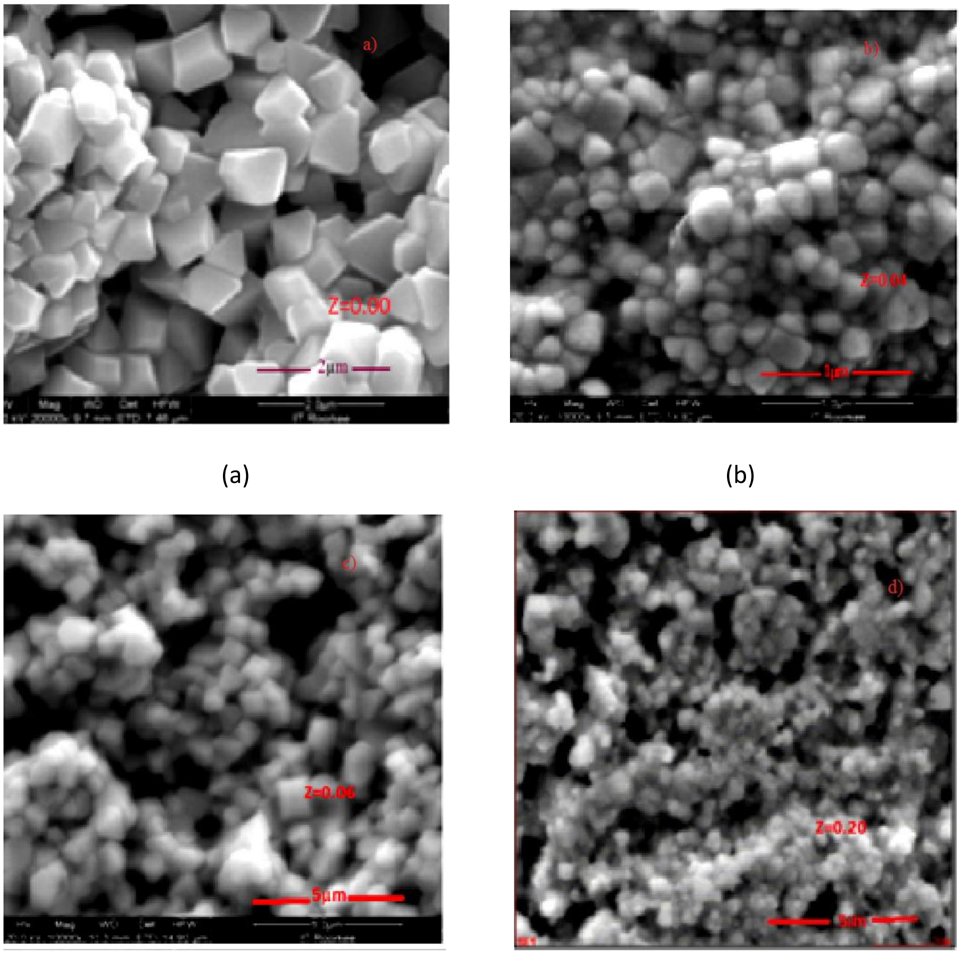


Fig. 1 : XRD patterns for PLCZT compositions with various Ca content

Pyrochlore phase in minute quantity is observed in all compounds except PLZT where the relative amount of that phase was observed using following ratio:

$$\% \text{ Pyrochlore} = \frac{\text{Apyrichlore}}{\text{Apyro+A(110)}}$$

where $A_{pyrochlore}$ and A_{110} represent the area under 100% pyrochlore peak (100) and pervoskite peak (110) respectively. Except PLZT the relative amount of pyrochlore phase is estimated to be in the range of 2% - 4% in the samples. The amount of pyrochlore phase is negligibly small and therefore the materials can still be considered as single phase. From the SEM micrographs [Fig. 2] the surface microstructure of sintered samples is observed. It can be seen that well developed and single shaped grains are observed in all compositions, which confirms the formation of a single phase in all the samples. The grain size was calculated using linear interception method and the grain size data is reported along with crystallite size as a function of Ca doping. Less compactness and porosity is observed in all samples. Microstructure controls the properties of the ceramic materials being this a consequence of the processing route. The strong extrinsic mechanisms help to tailor the specific properties of the ferroelectric ceramic materials. Several investigations have demonstrated that A-site and B-site cation substitutions have significant influence on domains and properties of given materials. As the concentration of Ca^{+2} is increased, the average grain size is found to increase up to 6 mol % and to decrease beyond it.



(a) (b)

(c) (d)

Fig. 2. SEM micrographs of Calcium doped PLZT a) z=0.00, b) z=0.02, c)z=0.04 and d)z=0.06

The increase in grain size is due to smaller grains nucleation as evidenced by the SEM pictures and this considerable grain growth would release the internal stress field from grain boundaries resulting in high domain wall movement which leads to enhancement of grains bonding. At higher concentration of calcium (20 mol %) the grain size is found to decrease as there is possibility of partial substitution at B site which will decrease the grain size. Moreover the grain boundaries become nonuniform at higher concentration.

The densities of sample were measured from mass and dimensions of sintered sample and are found to be in range 65%-85%. The density is calculated using following relation:

$$\rho = \frac{\frac{\sum A}{N}}{V}$$

Where ρ represents the density (gm/cm^3), ΣA denotes the sum of atomic weights of all the atoms in unit cell, N denotes the Avogadro's number and V represents the volume of the unit cell(cm^3).

CONCLUSION

I have studied the effect of calcium doping on the properties of PLZT. Calcium doped PLZT with general formulae $Pb_{0.9}(La_{1-z}Ca_z)_{0.1}(Zr_{0.65}Ti_{0.35})_{0.975}O_3$ where z=0, 0.02, 0.04, 0.06 were synthesized by solid state reaction method. X-ray diffraction analysis indicates the formation of single phase rhombohedral structure. Crystallite size, as calculated from Scherrer's equation, was found to be 25 nm.

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