Effect of Calcium Concentration on the Microstructure and Electrical Properties of Ca-Doped PLSZT (Pb-La-Sr-Zr-Ti) System

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Abstract. Lanthanum and strontium modified Lead Zirconate Titanate (PLSZT) was doped with Ca\textsuperscript{2+} to improve the dielectric properties. Ca-doped PLSZT was prepared using high planetary ball mill, palletized and sintered at 1200 °C for 3 hours with heating rate 5 °C per minute. XRD results showed that all Ca-doped PLSZT samples consist of tetragonal and rhombohedral phase whereas SEM results showed that the grain size of the samples was decreased with an increase in calcium concentration but began to decrease at 8 mol% of calcium. The density was observed to decrease and the dielectric constant increased with the increase in concentration of calcium.

1. Introduction
The development of PZT materials is well established in electronic applications where numerous dopants have been added on the PZT systems to optimize their piezoelectric properties. In the last few decades, the synthesis of PZT modified with various dopants including soft isovalent doping had been extensively investigated for various applications [1, 2]. Lead modified by isovalent cations such as Ba\textsuperscript{2+}, Sr\textsuperscript{2+} and Ca\textsuperscript{2+} shows undisturbed crystal symmetry which is responsible for the strong ferroelectric behavior of the samples [3].

Kalem et al. [4] have reported that the addition of Sr and La as co-dopants into PZT ceramics is able to stabilize the tetragonal phase. The incorporation of Sr\textsuperscript{2+} and La\textsuperscript{3+} into the PZT lattice has intense implications on the dielectric and piezoelectric properties of PZT ceramics. Bahanurddin et al. have doped PZT with Sr\textsuperscript{2+} and La\textsuperscript{3+} via high energy planetary ball mill process [5, 6]. They found that the evaporation of PbO during calcination and sintering processes can be avoided by virtue of its ability to skip the calcinations step. However, the piezoelectric properties were not mentioned by them. Meanwhile, Kour et al. [7] had studied the Ca\textsuperscript{2+} doped PZT and claimed that the dielectric constant increases with the increase in calcium concentration due to the increase in electronic polarization.

Therefore, calcium substituted PLSZT (Pb-La-Sr-Zr-Ti) for various dielectric applications have been studied. In this research, calcium was doped to “A” site of Pb\textsubscript{0.93}La\textsubscript{0.02}Sr\textsubscript{0.05}(Zr\textsubscript{0.52}Ti\textsubscript{0.48})O\textsubscript{3} (PLSZT) to enhance its electrical properties. The influence of calcium concentration on the microstructure and dielectric properties of Ca-doped PLSZT were also studied.
2. Materials and Method
The Ca-doped PLSZT (PCLSZT) ceramic was fabricated in accordance with the molecular formula Pb_{0.93-x}Ca_xLa_{0.02}Sr_{0.05}(Zr_{0.52}Ti_{0.48})O_3, with x = 0.00, 0.02, 0.04, 0.06, 0.08 and 0.10. The starting raw materials included lead (II) oxide (PbO), zirconium oxide (ZrO_2), titanium oxide (TiO_2), strontium carbonate (SrCO_3), lanthanum oxide (La_2O_3), and calcium carbonate (CaCO_3) were weighed with excess 10 wt.% PbO to present the loss of lead oxide. The PCLSZT powder was synthesized by high planetary ball mill method [5]. After milling process, the mixed powder was ground using agate mortar and pressed into pellet at 200 MPa. The green pellets were then sintered at 1200 °C for 3 hours with 5 °C/min heating rate. Phase analysis, surface morphology analysis of pellet samples were carried out by X-Ray Diffraction (XRD) (Bruker AXS D8 Advance) and Scanning Electron Microscopy (SEM) (Zeiss Supra 35VP), respectively. The bulk density of sintered pellets was calculated using Archimedes’ Principle. The samples were painted with silver layer to make a conductive layer prior to measure the dielectric properties using LCR meter (RF Impedance/Material Analyzer 4291B Hewlett Packard).

3. Results and Discussion
3.1 X-Ray Diffraction (XRD) analysis
The X-ray diffraction pattern of undoped and Ca-doped PLSZT samples (PLSZT, PCLSZT2, PCLSZT4, PCLSZT6, PCLSZT8 and PCLSZT10) has been illustrated in Figure 1. XRD patterns indicated that the diffraction peaks of all samples were matched with pure perovskite structure. Diffraction pattern of the samples can be assigned to tetragonal related structure (ICDD card No. 98-007-6141) and rhombohedral (ICDD card No. 98-000-8531). There is no evidence of impurity peak as shown in the diffractograms.

![Figure 1. XRD pattern of sintered Ca-doped PLSZT pellets](image)

By comparing the maximum intensity peak for all samples, samples with Ca dopants (PCLSZT2, PCLSZT4, PCLSZT6, PCLSZT8 and PCLSZT10) have slightly higher diffraction angle than the sample PLSZT. The peak shift towards the higher angle by increasing calcium concentration was due to the existence of lattice strain in the samples which are mainly due to the difference in ionic size of Ca^{2+} and Pb^{2+}. When Ca^{2+} was added, it occupied and replaced the sites of Pb^{2+}. The difference in ionic size of between Ca^{2+} and Pb^{2+} causes a significant strain to the lattice; hence stress was induced in the samples. Thus, this implies the incorporation of Ca^{2+} as a dopant in the PLSZT lattice [8].
3.2 Scanning Electron Microscopy (SEM) analysis

Figure 2 shows the SEM micrograph of the surface for all samples. Generally, no remarkable pores were observed with uniform grain size distribution. The grain size decreased as calcium concentration of the sample increased up to 6 mol % Ca. However, the grain size increased when 8 mol % Ca (PCLSZT8).

![Figure 2. Surface view of (a) undoped PLSZT, (b) PCLSZT2, (c) PCLSZT4, (d) PCLSZT6, (e) PCLSZT8, and (f) PCLSZT10 samples at 5K magnification](image)

The decrease in grain size as calcium concentration is increased corresponds to the diffusion of calcium due to ionic size mismatch and increase of lattice strain. The similar trend was observed by Kour et al. [7]. When the calcium was doped into PZT it replaced the lead, the decrease in the bond length gives rise to stress in the structure. The stress was increased with the increase in calcium concentration which obstructs the nucleation of the crystallite. As a result, the grain size of the samples was reduced. However, the increase in grain size began after 8 mol% of calcium was doped in PLSZT. The calcium content seems to promote the grain size enlargement. The enlargement of grain size was due to the increasing in mass transport at grain boundary and calcium dopant seems to induce that effect. In the study by Silva et al. [8], PZT ceramics were doped with calcium and the results showed that the grain size was enhanced with higher amount of calcium doped in PZT.

3.3 Density Analysis

Table 1 shows the bulk density for all samples. The density of Ca-doped PLSZT samples was lower than undoped PLSZT sample and the density had decreased slightly with increasing calcium substitution. This was due to the fact Ca$^{2+}$ was doped into Pb$^{2+}$ site of ceramic where Ca was lighter than Pb. Such results were also observed by Chu and Chen [9] in their study in which they showed similar trend where the density of ceramic reduced as the amount of Ca dopants increased.
Table 1. Bulk density for PLSZT doped with various calcium concentration

| Sample  | Bulk density (g/cm³) |
|---------|---------------------|
| PLSZT   | 9.01                |
| PCLSZT2 | 8.84                |
| PCLSZT4 | 8.84                |
| PCLSZT6 | 8.78                |
| PCLSZT8 | 8.82                |
| PCLSZT10| 8.82                |

3.4 Dielectric Properties

The dielectric properties of PLSZT and Ca-doped PLSZT were measured in the frequency range from 1 kHz to 1 MHz at room temperature. Figure 3 shows the variation of dielectric constant, $\varepsilon_r$, of all the samples at different frequencies measured at room temperature. It was observed that dielectric constant increases with calcium concentration. This phenomenon was due to two factors: (i) lattice distortion increased with the increase in calcium concentration due to ionic radius mismatch and (ii) local distortion in Pb site. The electronic polarization was affected leading to increase in the dielectric constant. This has been proved in previous study of effect of calcium modified PZT on electrical properties [7].

The decrease in dielectric constant with increasing frequency was due to the fact that polarization does not occur instantaneously with the application of electric field because of inertia. The delay response towards the alternating electric field leads to a decrease in dielectric constant. At low frequencies, all the polarizations have contributed. However, those with large relaxation times cease to respond and hence causing a decrease in dielectric constant at higher frequencies [10].

![Figure 3. Dielectric constant vs. frequency](image)

Figure 3. The variation of dielectric constant, $\varepsilon_r$ of all the samples at different frequency

Figure 4 shows the variation of dielectric loss, $\tan \delta$ of all the samples at different frequencies measured at room temperature.
These results show that the dielectric loss was enhanced with an increase in calcium concentration. It is due the fact that Ca creates Pb site defect in lattice and increases anisotropy in the material. Besides, size mismatch creates stress in the lattice site leading to anisotropy. Hence, the internal stress was not strong enough to switch the polarization back after the electric field was removed [7]. This phenomenon was in agreement with results found by Siddique et al. [11]

4. Conclusion
The effect of various calcium concentrations on the microstructure and dielectric properties of Ca-doped PLSZT (Pb-La-Sr-Zr-Ti) synthesized via high planetary ball mill reaction method were investigated. XRD results showed that pure PZT perovskite phase with tetragonal and rhombohedral structure were observed in all Ca-doped PLSZT (Pb-La-Sr-Zr-Ti) samples. The grain size decreased with addition of calcium concentration from 1.59 μm to 1.32 μm but began to enlarge again at 8 mol% calcium was added. The density of the sample also decreased with increasing calcium concentration. The dielectric constant and dielectric loss increased with the increase in the frequency as well as by increase in calcium concentration.

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