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Fabrication of Calcium Doped PLSZT Ceramics using High Planetary Mill Method

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Abstract. Ca-doped modified Lead Lanthanum Strontium Zirconium Titanate (PLSZT) ceramic, was synthesized with different concentrations of dopant in order to enhance the properties of PZT. Calcium carbonate, CaCO₃ have been used as a source of Ca dopant in the preparation of PCLSZT using high planetary ball mill, palletized and sintered at 1200 °C for 3 hours. The uses of high planetary milling benefit in shorten the time for powder preparation where the calcination was not required. The concentration of CaCO₃ was varied from 0.01, 0.03, 0.05 and 0.10 mol% and their effects on phase formation, surface morphology, density and porosity have been studied using X-ray diffraction (XRD) and Scanning electron microscopy (SEM). XRD results showed that all Ca-doped PLSZT samples present a tetragonal phase. Whereas SEM results showed that the grain size of the samples was increased with increasing calcium concentration. In addition, the density was observed to be decreased with increasing amount of Ca concentrations.

1. Introduction

Lead Zirconate Titanate (PZT) is one of piezoelectric material that is well-known in the field of electroceramics which extensively used in the wide range of electronic applications, such as in actuators, sensors and transducers [1]. The PZT materials having perovskite structure, finding great attention in the field of research compared to other electroceramic materials. PZT is most sensitive material to the doping because its properties can be manipulated by additional of foreign ions. In the last few decades, numerous dopants have been added on the PZT systems to modify due to its interesting in dielectric, pyroelectric, piezoelectric and superconducting properties [2].

The substitutions by many oxides in perovskite structure influenced the microstructure, density, piezoelectric and dielectric properties depending on the different synthesis process. By substituting Pb sites with several acceptor or donor cations improved the electrical properties of the electroceramic systems[3]. Among the dopants, the combination of La³⁺ and Sr²⁺ shows good electrical properties for



electronic applications [4-6]. However, Devi et al. [5] claimed that the dielectric permittivity was decreased with additions of Sr^{2+} . Therefore, a further study is needed to improve the dielectric properties of PLSZT system.

Kour et al. [7] had been study on the Ca^{2+} doped PZT and profound the dielectric constant increases with an addition of calcium concentration due to the increase in electronic polarization. Thus, an effort has been made through this research focusing on the isovalent dopant (Ca^{2+}) in PLSZT system for piezofan application. Pb^{2+} site was substituted with Ca^{2+} while maintaining the perovskite structure responsible for the strong ferroelectric behavior. Synthesis of Ca^{2+} doped PLSZT was performed by high planetary milling due to it tendency to synthesize compound at room temperature with small size. Besides, the PbO was easy to evaporate and cause a loss during calcination and sintering process. So, this milling process will control the loss of PbO by passes the calcination process.

2. Experimental study

The starting raw materials include 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 weighted based on the stoichiometric of $\text{Pb}_{0.93-x}\text{Ca}_x\text{La}_{0.02}\text{Sr}_{0.05}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ with $x = 0.00, 0.01, 0.03, 0.05$ and 0.10 . The raw materials were then dry-mixed in a planetary mill for 40 hours followed by pressing into pellets with 13 mm diameter at 200 MPa. Pallet samples were sintered at 1200°C for 3 hours. The pellet samples then were characterized by X-ray Diffraction (XRD, Bruker AXS D8 Advance Diffractometer) and Scanning Electron Microscopy (SEM, Zeiss SUPRA 35VP) for phase formation and surface morphology analysis, respectively. Meanwhile, the bulk density and porosity of sintered pellets was calculated using Archimedes' Principle and the dielectric properties were measured using LCR meter (RF Impedance Analyzer 4291B Hewlett Packard).

3. Result and Discussion

3.1 Phase formation

The X-ray diffraction patterns of undoped and Ca-doped PLSZT (PCLSZT) samples (different Ca doping mol%) were shown in Figure 1. The XRD patterns indicate that the peaks of all samples were matched with pure perovskite structure. Diffraction pattern of the samples can be assigned to tetragonal related structure accordance with ICSD card No. 98-007-6141. There is no evidence of impurity peak shown in the diffraction patterns.

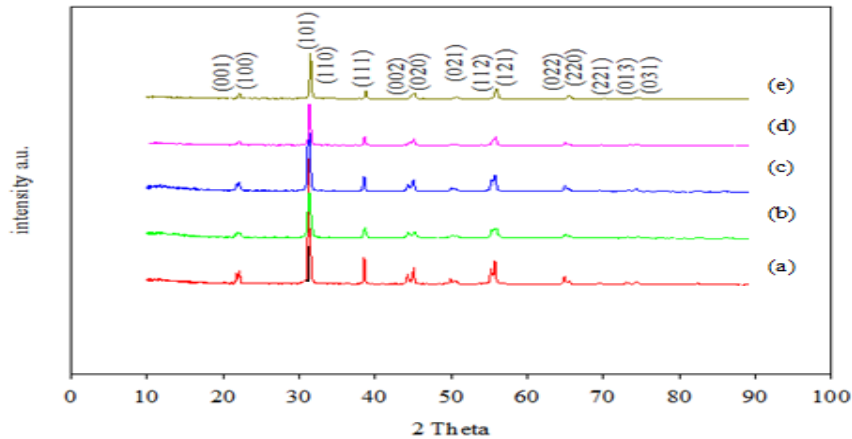


Figure 1. XRD pattern with different Ca doping concentrations (a) undoped PLSZT, (b) 0.01 mol%, (c) 0.03 mol%, (d) 0.05 mol% and (e) 0.10 mol%.

However, the peaks show the changes in intensity with increasing of Ca concentration where the peaks position was shifted to the right as the calcium concentration increases. The shifted of the peaks was due to the existence of lattice strain in the samples which mainly due to the different in ionic size of Ca^{2+} ion is lighter than Pb^{2+} ion [8]. Furthermore, due to slight variation of atomic radius, strain will be generated in the matrix and cause the reduction in crystallite size in PLSZT.

3.2 Microstructure Analysis

Figure 2 shows the SEM micrograph of PLSZT samples. Results show that the average grain size of the sample was slightly decreases from 1.134 μm to 1.056 μm as calcium concentration increases up to 0.03 mol%. The decrease in grain size as calcium concentration increases corresponds to the diffusion of calcium in PLSZT system. According to Kour et al., when the calcium 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 and reduces the average grain size of the samples [7].

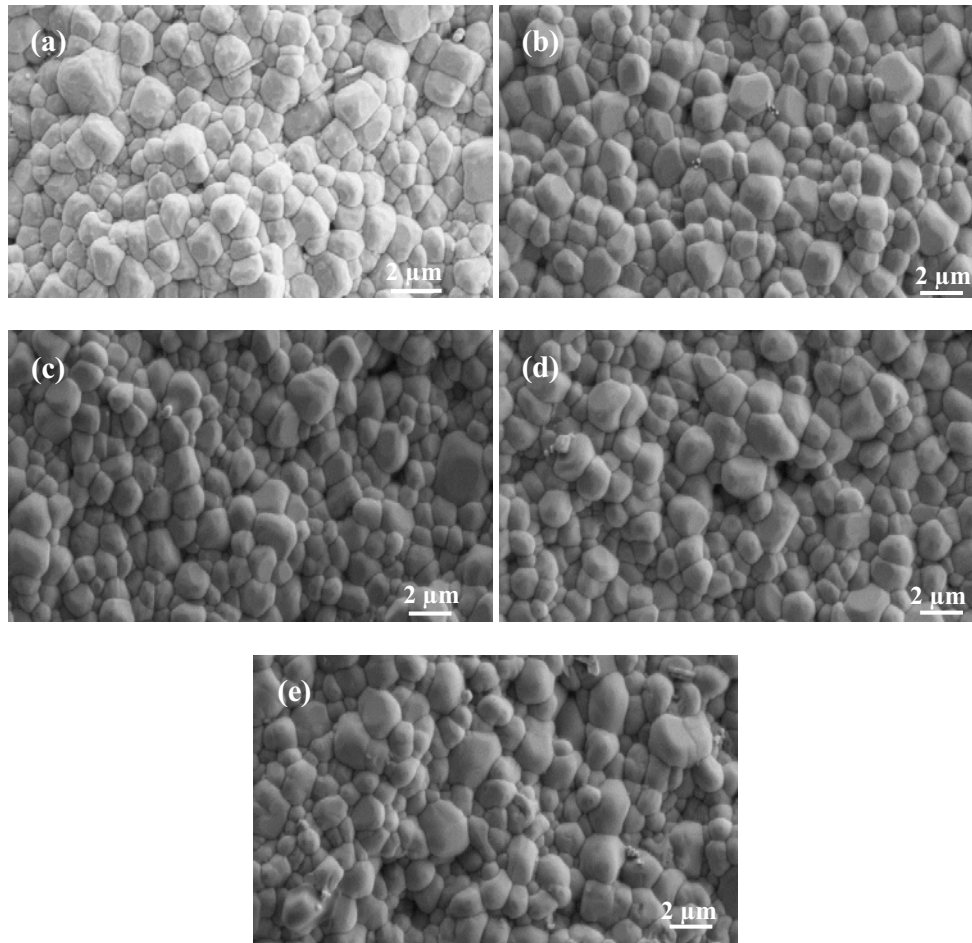


Figure 2. Surface morphology of PCLSZT at different concentrations (a) undoped PLSZT, (b) 0.01 mol%, (c) 0.03 mol%, (d) 0.05 mol% and (e) 0.10 mol%

However, the average grain size were slightly increase at higher concentration of Ca (0.05 and 0.10 mol%). High calcium content seems to promote the grain size enlargement. It is believed the enlargement of grain size was due to the increasing in mass transport at grain boundary and calcium dopant seems to induce that effect. Silva et al. [8] also stated that their study on PZT ceramics doped with calcium shows that the grain size was enhanced with higher amount of calcium doped in PZT.

3.3 Density and Porosity

Figure 3 shows the density and porosity for undoped PLSZT and PCLSZT samples. The density of Ca-doped PLSZT samples was lower than undoped PLSZT sample. This is due to the light weight of Ca^{2+} ion doped into Pb^{2+} site. The formation of cation vacancies resulted the increasing of crystal volume thus decreased in density. This phenomenon was in agreement with Chu et al. [9] who claimed the density of ceramic is reduced as the amount of Ca dopants increased.

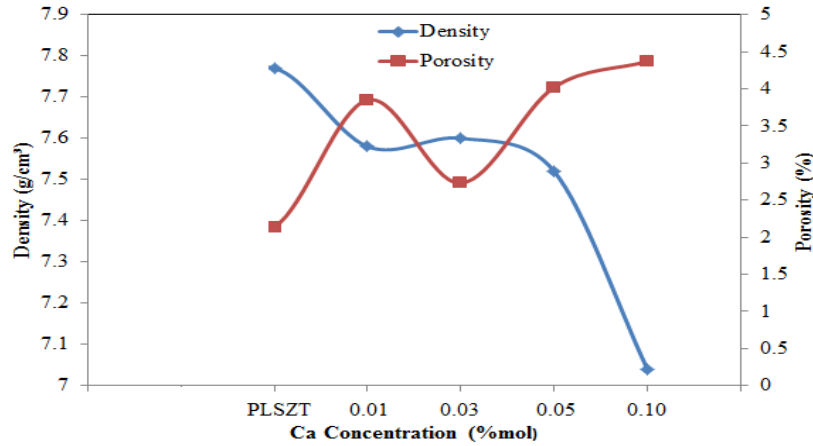


Figure 3. The bulk density and porosity for undoped PLSZT and Ca doped PLSZTs.

3.4 Dielectric properties

The dielectric properties of undoped PLSZT and Ca-doped PLSZT (PCLSZT) were measured at 1 MHz at room temperature and the results obtained was shown in Figure 4.

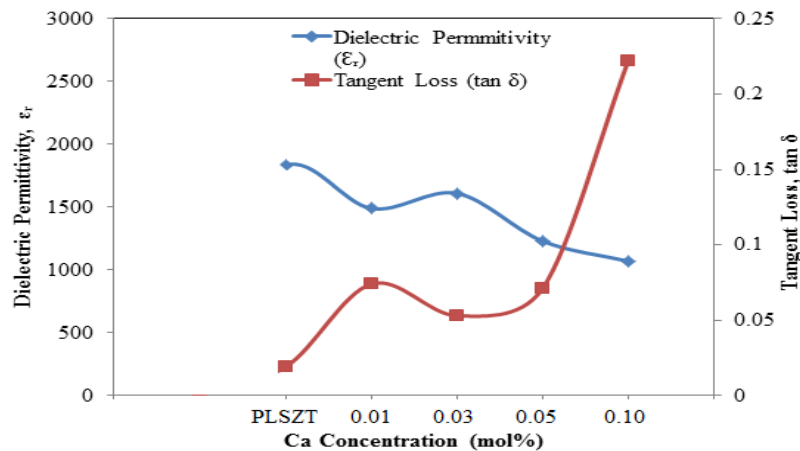


Figure 4. Dielectric permittivity and tangent loss of PZT, PLSZT and PCLSZTs at 1 MHz

Results show that the dielectric permittivity (ϵ_r) was decreased with increasing of the Ca concentration and vice versa for dielectric loss ($\tan \delta$). The decreasing of ϵ_r was related to the density and porosity present as mentioned by Adel et al. (2013), where the ϵ_r start to decrease as the density of the sample decrease [10]. Sample doped with 0.10 mol% Ca shows the lowest ϵ_r due to the lowest density and highest porosity compared to other samples. According to previous research, high porosity in the sample will block the mobility of domain in enhancing the ϵ_r . Meanwhile, $\tan \delta$ was increased as increasing of Ca concentration was due to the defect created in Pb site which increases anisotropy in the material. Hence the internal stress was not strong enough to switch the polarization back after the electric field was removed [7].

4. Conclusion

The Ca addition shows promising effects toward microstructure, density led to the improvement of dielectric properties of PLSZT material. XRD results confirmed the formation of perovskite structure. Whereas, the grain size decreases with addition of calcium concentration from 1.134 μm to 1.056 μm but begins to enlarge again at 0.05 mol% calcium added. In addition, the density of the sample decreases with increasing calcium concentration and dielectric permittivity was decreased as increasing in calcium concentration.

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