

Effects of compaction pressure on lead zirconate titanate piezoelectric and dielectric properties prepared via high planetary mill

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Lead Zirconate Titanate (PZT) had previously been used as actuators and sensors in electronic application due to its remarkable piezoelectric properties. The main obstacle in the PZT syntheses through solid state sintering is the lost of substantial amount of PbO due to vaporation that accompanied high firing temperature. Elimination of the calcination step and alternative method of treatment could be of a great help. Thus, an investigation of the lead (Pb) Zirconate Titanate PZT properties (piezoelectric and dielectric) synthesized via solid-state reaction by varying compaction pressure (100-300 MPa) was conducted. Compaction pressure that was beneficial to the physical properties of PZT-based ceramic and also effectively improved the dielectric and piezoelectric properties of the PZT ceramics. Optimum average grain size was found to be a very important factor in determining the alignment of the d_{33} particle size value influence and the dielectric constant of PZT. Therefore, the optimum compaction pressure (200 MPa) played an important role in optimizing the sintering temperature. This also enhanced/improved the piezoelectric and dielectric properties of PZT.

Key words: Lead Zirconate Titanate, Compaction pressure, Dielectric, Piezoelectric.

Introduction

Lead zirconate titanate (PZT) is considered as one of the worlds most widely used piezoelectric ceramic materials for various applications such as sensor, transducers and actuators [1]. $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ($x = 0.52$) belongs to the ferroelectric family of ABO_3 perovskite structure [2-3], and it compositional modification is the most widespread piezoelectric ceramic research activities due to its excellent electrical properties such as high electron mechanical coupling coefficient, dielectric constant and high resistance to depolarization [4]. The highest piezoelectric coefficient of PZT is found for composition near the morphotropic phase boundary (MPB) between the tetragonal and rhombohedral regions of the compositions-temperature phase diagram [5-6]. It is well known that PZT materials performance is closely related to the ways they are processed.

To produce the most reliable PZT materials, the synthesis has to be carefully carried out by following the specific procedure. The main problem in PZT

synthesis through solid state is the loss of a substantial amount of PbO during firing. The solid state sintering normally required high sintering temperature which are 1200 °C and above. Besides, the methods involve long times due to slow diffusion rates in the solid state during formation of PZT sample [7]. The sintering temperature that is too high is undesirable because of the volatility of substantial amount of PbO with the consequent change in stoichiometric and deterioration of piezoelectric properties [8-9].

Therefore, it is very essential to avoid the calcinations by substituting it with non firing step such as higher applied compaction pressure during pressing process of the sample. It is reported [10] that there is possible effect of compaction pressure on piezoelectric properties of PZT. The reason is that at higher pressure, the contacts between the particles will be increased thereby enhancing the transport of reaction particles which favours the formation of PZT [11]. However, the pressure used in that study ranged from 210 to 315 MPa but no details study on the effect of compaction pressure on PZT properties was reported. For these reasons, the study focusses on the effect of compaction pressure on the properties of PZT so as to determine the influence of different pressures within the range of 100-300 MPa on the piezoelectric and dielectric properties of PZT.

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Experimental

Lead oxide, PbO (Sigma-Aldrich (M), < 10 μm , 99.9%), zirconium oxide, ZrO₂ (12.78 μm Sigma-Aldrich, 99%), and titanium oxide, TiO₂ (0.48 μm Merck, 99%) are used in this research as the starting raw materials to synthesize pure PZT. The weight of each powder was calculated according to the stoichiometric ratio to produce the compound of Pb(Zr_{0.52}Ti_{0.48})O₃. The samples were mixed in planetary mill up to 40 hours in air at room temperature with the balls to powder weight ratio of 10 : 1. After mixing, the PZT powders were ground using agate mortar for 30 minutes and then pressed into pellets with two different diameters of 6 and 13 mm with five different compaction pressures (100-300 MPa). They were then sintered at 1100 °C for 1 hour while the density was measured by using Archimedes principles. X-ray diffractometer (Bruker D8 Advance) was used to identify the phase formation and crystallite sizes. Field Emission Scanning Electron Microscopy (Carl Zeiss 35V) was used to observe the morphology of the sintered pellets. Prior to FESEM examination, the pellets were polished and thermally etched at temperature 950 °C for 1 hour. To characterize the dielectric and piezoelectric properties, the pellets were coated with silver paint on the upper and bottom surfaces and heated at temperature 160 °C for 1 hour. Poling was accomplished at 120 °C in silicon oil under voltage 3.0 kV mm⁻¹ for 20 minutes. Measurements of the piezoelectric and dielectric properties were taken after 24 h. The d₃₃ value was measured by APC 90-2030 and the dielectric constant and dielectric loss were measured by using an Impedance Analyzer (RF Impedance Analyzer 4291B Hewlett Packard).

Results and Discussion

Phase composition

Fig. 1 shows the XRD patterns for all samples sintered at 1100 °C for 1 hour. All samples have a

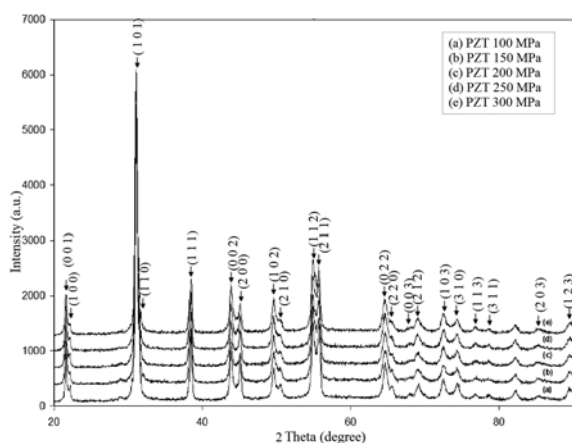


Fig. 1. XRD patterns of pure PZT samples that being pressed at (a) 100, (b) 150, (c) 200, (d) 250 and (e) 300 MPa.

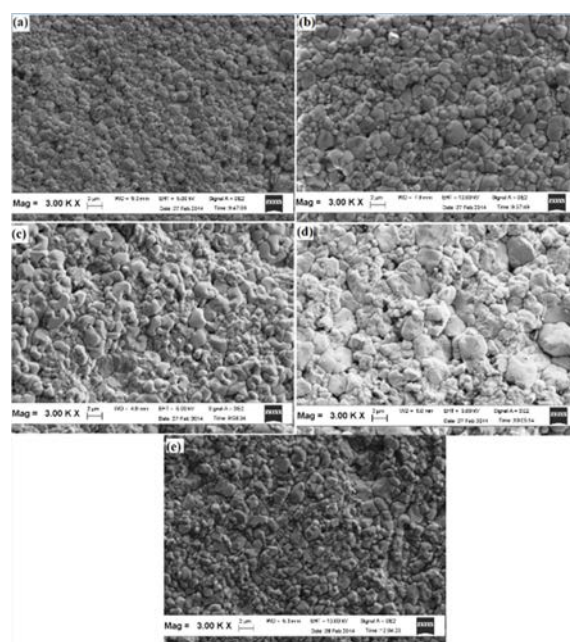


Fig. 2. FESEM micrograph of the PZT surface after thermally etched that being pressed at (a) 100, (b) 150, (c) 200, (d) 250 and (e) 300 MPa.

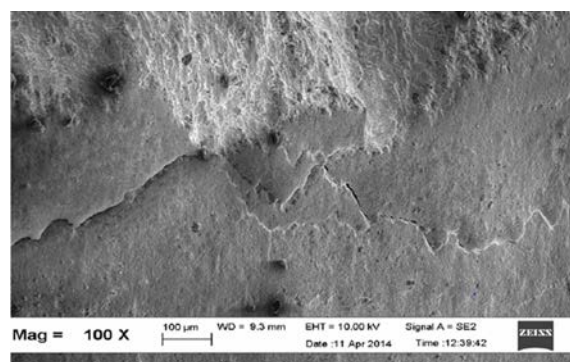


Fig. 3. FESEM micrographs of the fragmentation on PZT for the sample surface pressed at 300 MPa.

single phase perovskite structure and the diffraction peaks was indexed according to the similar diffraction data of the tetragonal structure for PZT with ICDD No. 00-033-0784. There were changes in the intensity of peaks especially at (1 0 0) and (2 0 0), which started to reduce with the increasing of the powder compaction pressure. These results have shown the similar trend as observed by Vaidhyathan *et al.* [10] and Shaoxin *et al.* [12].

Microstructure

Fig. 2 shows the FESEM micrographs for the thermally etched polished surface of PZT samples. The effect of compaction pressure on the average grain sizes is very clear. The smallest size was 1.25 μm from 100 MPa compaction pressure and the largest one was 3.95 μm from 250 MPa. The previous researcher asserted that with increasing the compaction pressure,

better particle-particle contact which enabling facile material transport and diffusion reaction to occur [10]. However, when the optimum compaction pressure was exceeded, the average grain size started to reduce. This was due to the effect of very high compressive strength, which induced massive deformation to the microstructure. The relief of the pressure resulted in relaxation of the material with a release of the stored elastic energy noted by dimensional springback. The relaxation is shown by the compact's failure to fit back into die cavity after ejection and fragmentation of the sample. For these reasons, the grain growth during sintering was not completely grown due to the energy released through the fragmentation [13] as shown in Fig. 3.

Density and porosity

The densities of the ceramics were measured using the Archimedes' principle [14]. As shown in Fig. 4, all PZT samples show relatively high density and low porosity. This indicates that with increasing the compaction pressure, the density of the sample also increased. German *et al.* [13] claimed that at higher compaction pressure, density was increased due to better packing and led to the decreasing in porosity with formation of new particle contacts. Besides, the density was enhanced by contact enlargement through plastic deformation. The porosity had decreased up to 200 MPa stress application and then later increased as the stress reached 250 MPa [10, 15]. The results were similar to that observed by Loncar *et al.* [15] where it was reported that if the average grain size $< 2.4 \mu\text{m}$, the porosity was lower but otherwise as the grain size exceeded $2.4 \mu\text{m}$. This was due to the reduction in the uniformity of the grain structure and wider grain size distributions [15].

Piezoelectric and dielectric properties

Effect of powder compaction pressure on the piezoelectric properties of the samples is shown in Fig. 5. The values of d_{33} were steadily increasing with the compaction pressure up to 200 MPa before it's went

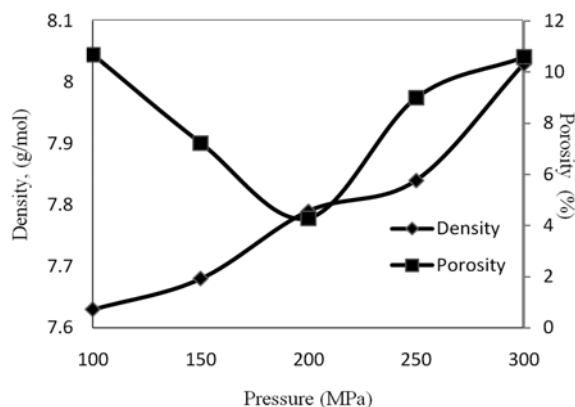


Fig. 4. Density and porosity of PZT sintered pellets that being pressed at five different compaction pressure.

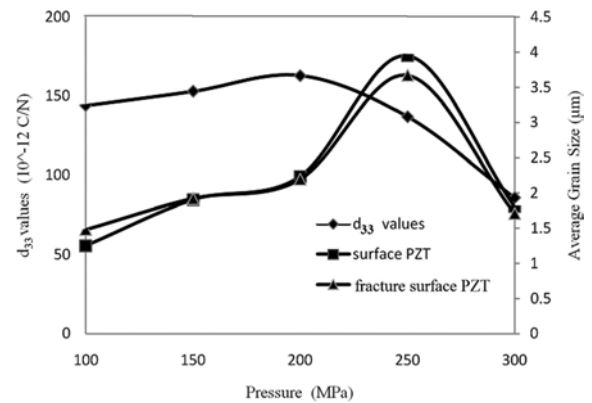


Fig. 5. Variations in d_{33} value and grain size at different compaction pressure.

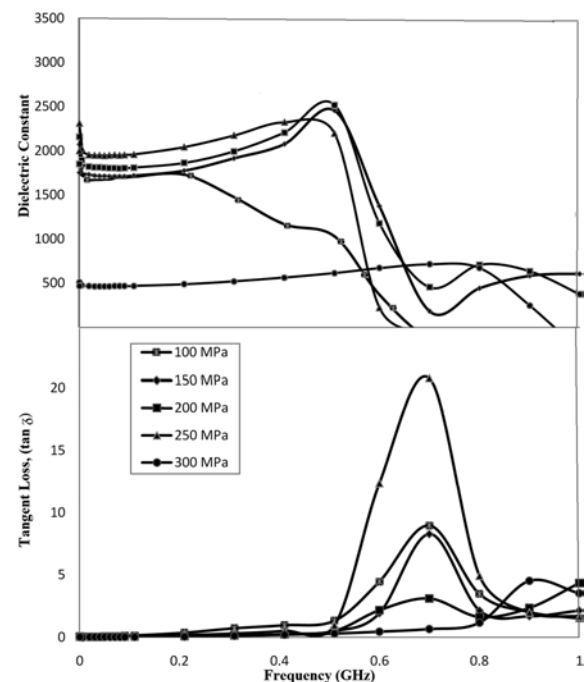


Fig. 6. Variations in dielectric constant and tangent loss with increase the compaction pressure.

down. This phenomena was due to increasing pressure during powder compaction up to 250 MPa, which caused average grain size to become bigger. It also shows that the larger grain size increased the d_{33} value [11, 16]. The other researcher [17] stated that if the average grain size was too big (above $3.0 \mu\text{m}$), the d_{33} values would start reducing. The maximum piezoelectric and dielectric properties can be achieved when the grain size is in the range of $1.0\text{--}3.0 \mu\text{m}$ [17]. When the average grain size was more than $2.4 \mu\text{m}$, the porosity will also start to increase. The presence of porosities reduced the polarization per unit volume which was leading to decrease in d_{33} [15 and 18]. Fig. 5 shows that at smaller grain size, the d_{33} value was lower due to the domain wall orientations that were being hindered during poling of sample [11]. Referring to the sample pressed at 300 MPa, the fragmentation that occurred

on the sample was the reason for the reduction in piezoelectric property (d_{33} value).

Fig. 6 shows the result of dielectric constant and tangent loss for PZT samples. The maximum dielectric was obtained for sample compacted at 200 MPa. Other researchers reported that dielectric constant of the sample would be increased when the grains size and density of the PZT sample was higher. This was due to high density of sample will provide more space for holding larger quantity of charge at longer period of time [11-12, 17-21]. Therefore, sample compacted at 300 MPa that had lower dielectric constant was basically due to higher porosity. The porosity was originated from the fragmentation that caused higher current leakage. It was also observed that the tangent loss trend of the samples opposed that of the dielectric constant.

Conclusions

Compaction pressure is beneficial to the enhancement of physical properties of PZT- based ceramic. It also effectively improved the dielectric and piezoelectric properties of the PZT ceramics due to the effect of average grain size. The average grain sizes were increasing as the compaction pressure increased up to 250 MPa, before it decreased at pressure of 300 MPa. Optimum average grain size is another very important factor to consider in determining the alignment of the domain where influence of the d_{33} value and dielectric constant of PZT are possible. Therefore, the optimum compaction pressure (200 MPa) plays a critical role in optimizing the sintering temperature that favour the improvement of the piezoelectric and dielectric properties of PZT.

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