



Characterization of Hydrothermally Synthesized PLZT for Pyroelectric Applications

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Abstract. PLZT fine powders have been synthesized by a hydrothermal process using lead acetate, lanthanum acetate, zirconium *n*-propoxide and titanium isopropoxide as starting materials. The synthesis was performed at 200°C for 8, 12 and 24 h. 4 M KOH was used as a mineralizer to adjust the pH to an optimum value for the mixed precursor solution. After hydrothermal treatment the solid portion was separated out, washed and dried at 100°C for 12 h, where PLZT fine powders were obtained. PLZT powders were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The PLZT powders were pressed and sintered to obtain high density ceramics, which then were investigated by XRD and SEM. The dielectric properties of the ceramics were investigated by measurements of dielectric constant and dielectric loss as a function of temperature at a fixed frequency.

Keywords: PLZT, hydrothermal, pyroelectric

1. Introduction

Lead lanthanum zirconate titanate, PLZT is a ferroelectric material formed as a solid solution of lead zirconate and lead titanate, where some lead atoms are replaced by lanthanum atoms. Some PLZT compositions can be used as pyroelectric detector such as PLZT 12/40/60 which contains lanthanum La³⁺ 12 at.% and a zirconium to titanium (Zr/Ti) ratio of 40/60. The tetragonal PLZT 12/40/60 bulk material has a relatively high sensitivity, low electrical loss, large pyroelectric coefficient and moderate permittivity [1–6].

Conventionally, PLZT has been synthesized by solid state reaction [7]. During the reaction precise control of the stoichiometry and powder characteristics is difficult to maintain because of lack of consistency in raw material sources and local inhomogeneities arising from incomplete mixing and reaction of the constituents. To overcome these deficiencies, alternative

methods of powder synthesis have been developed and described by many authors such as co-precipitation of nitrates [8, 9], oxalates [10], citrates [11, 12], sol-gel [13], hydrothermal [14, 15] and others [16–21]. In this study, PLZT 12/40/60 powders were synthesized by a hydrothermal process previously developed in our group. It is able to produce fine particles with high homogeneity and high purity in one step without any high temperature calcination. The obtained PLZT powders and ceramics have been investigated by XRD and SEM.

2. Experimental Details

The PLZT 12/40/60 powders were synthesized using the following precursors: lead acetate trihydrate Pb(CH₃COO)₂·3H₂O (Fluka), lanthanum acetate hydrate La(CH₃COO)₃·H₂O (Aldrich), zirconium *n*-propoxide Zr(C₃H₇O)₄ (Aldrich) 70 wt.% solution in isopropanol, and titanium (IV) isopropoxide Ti[(CH₃)₂CHO]₄ (97% Aldrich) in the desired stoichiometry. Clear solutions of zirconium *n*-propoxide and titanium isopropoxide in isopropanol were mixed

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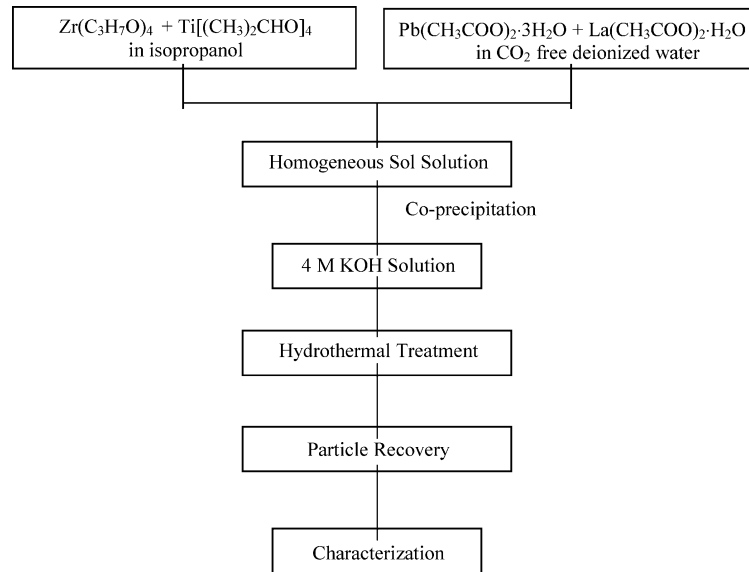


Fig. 1. Processing stages for synthesis of PLZT 12/40/60 by a hydrothermal method.

in a PTFE cup. An aqueous solution of lead acetate was added to the mixed solution and 4 M KOH was then introduced as a mineralizer to adjust the pH of the final solution to 13. Hydrothermal synthesis of the PLZT powders was performed under autogeneous pressure in a 500 ml autoclave lined with a PTFE cup. The synthesis temperature was 200°C for holding periods of 8, 12 and 24 hours. After cooling, the solid portion was separated from the suspension by filtration. The product was washed successively with deionized water until neutrality. The wet powders were dried in an oven at 100°C for 12 hours. Figure 1 summarizes the processing procedure for the synthesis of PLZT 12/40/60 by hydrothermal process. The as dried powders were examined by X-ray diffractometer (SIEMENS, D500 using $\text{Cu K}\alpha$ radiation) at room temperature. All prepared PLZT powders at different holding periods were pressed into pellets and sintered at 1300°C for 3 hours. The microstructure and grain size of PLZT powders and sintered ceramics were investigated using a Scanning Electron Microscope (JEOL JSM-6335F with 15 kV energy). The dielectric properties were measured by LCR meter (HP 4284A) at an excitation frequency of 1 kHz.

3. Results and Discussion

PLZT 12/40/60 fine powders have been synthesized by hydrothermal processing using lead acetate, lan-

thanum acetate, zirconium *n*-propoxide and titanium isopropoxide as starting materials at 200°C for 8, 12 and 24 hours. Figure 2 shows X-ray diffractograms of the dried PLZT powders synthesized with different holding periods. All XRD patterns showed the presence of the tetragonal polymorph, which could be matched with JCPDS file number 46-504. As the used reaction times step up gradually with holding periods of 8, 12 and 24 hours the resulted particle size ranges from 0.2–0.3 μm , 0.2–0.3 and 0.3–1.0 μm , respectively as shown in Fig. 3. PLZT powders obtained with holding periods of 8 and 12 h were agglomerated and basically irregular in shape, while the powders obtained with a holding period of 24 h showed a cubic-like morphology with a crystallographic structure corresponding to the tetragonal polymorph phase as was confirmed by XRD. The particle sizes are much smaller than PLZT powders synthesized by other wet chemical processes [8–14].

The as dried PLZT powders were pressed into pellets and sintered at 1300°C for 3 hours. Figure 4 shows the XRD patterns for ceramics prepared from powders with different reaction time holding. A tetragonal perovskite-type structure was identified for ceramics prepared from powders with a holding period of 24 hours, also a small amounts of PbO was detected (peak at $2\theta = 28.7^\circ$). Ceramics prepared from PLZT powdered with holding periods of 8 and 12 h contain some PbO, PbLaTiO_3 and ZrO_2

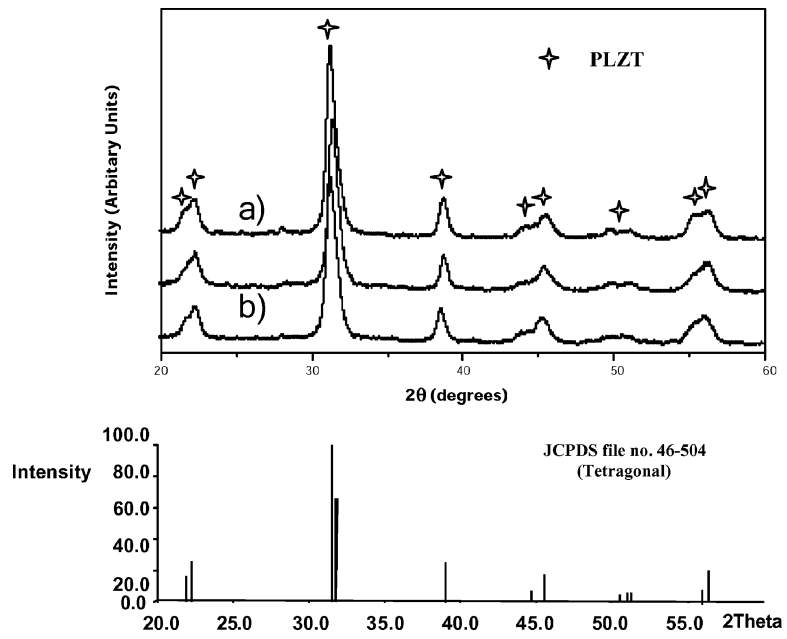


Fig. 2. XRD patterns of PLZT powders synthesized by hydrothermal process at 200°C with different holding periods of (a) 8 h, (b) 12 h, and (c) 24 h.

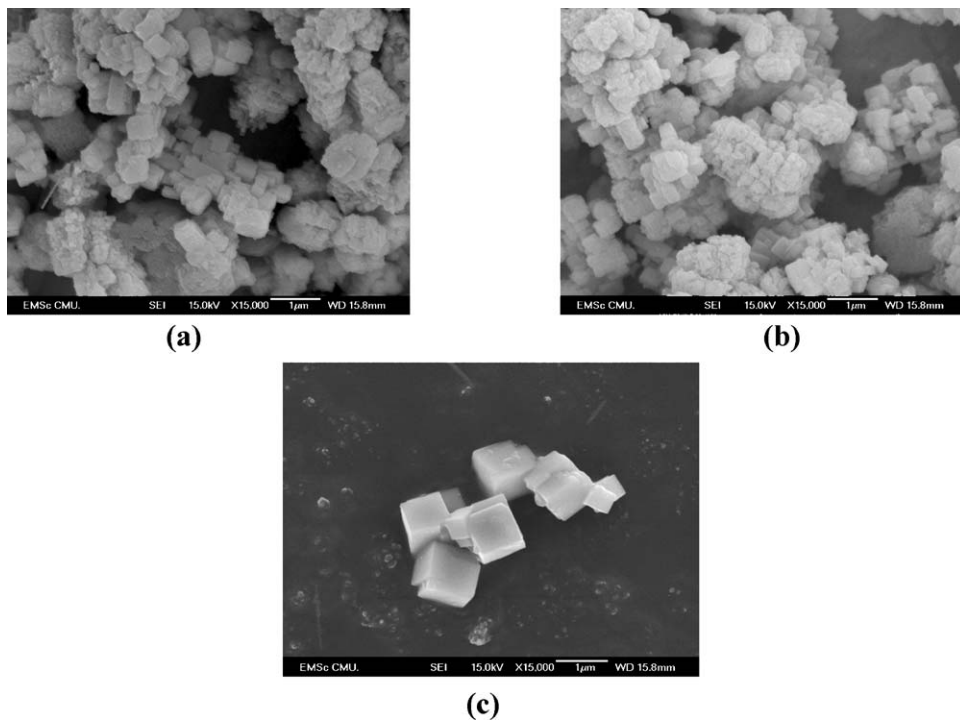


Fig. 3. SEM micrographs of the hydrothermally synthesized PLZT powders with different holding periods of (a) 8 h, (b) 12 h, and (c) 24 h.

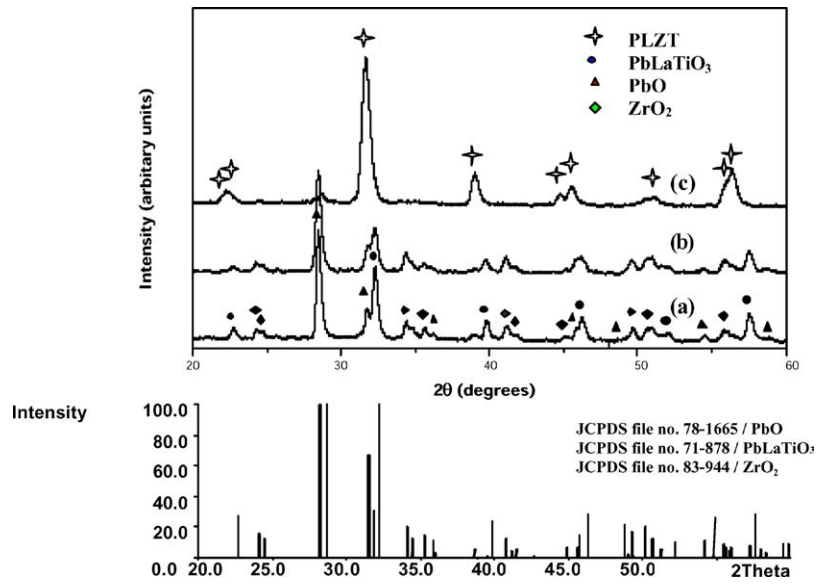


Fig. 4. XRD patterns of PLZT ceramics sintered at 1300°C for 3 h prepared from powders with different holding periods of (a) 8 h, (b) 12 h, and (c) 24 h.

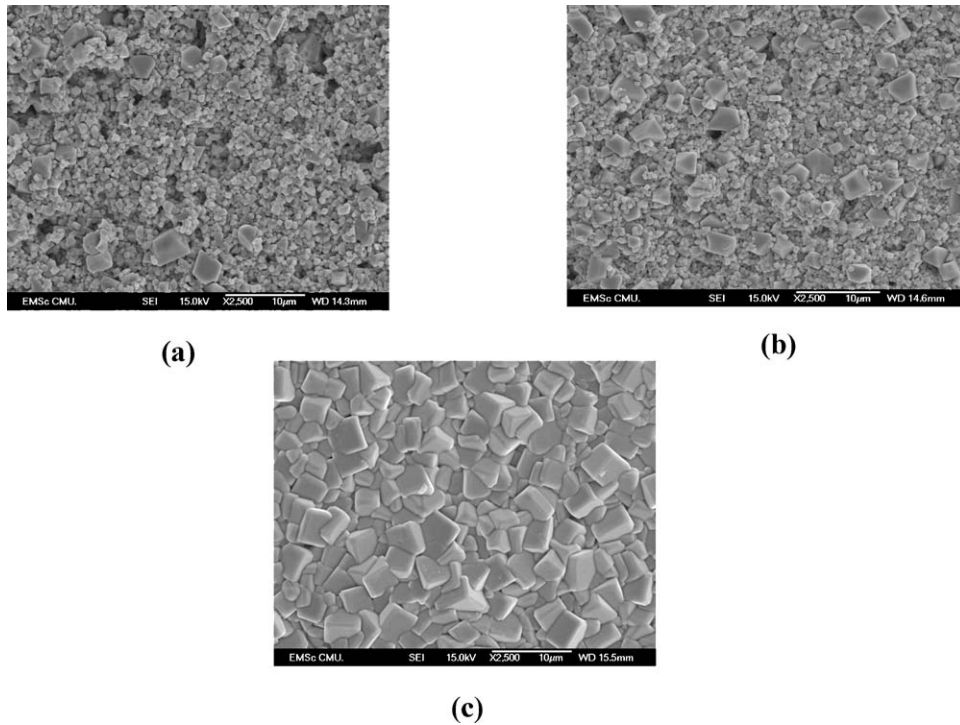


Fig. 5. SEM micrographs of the hydrothermally synthesized PLZT ceramics prepared from powders with different holding periods of (a) 8 h, (b) 12 h, and (c) 24 h.

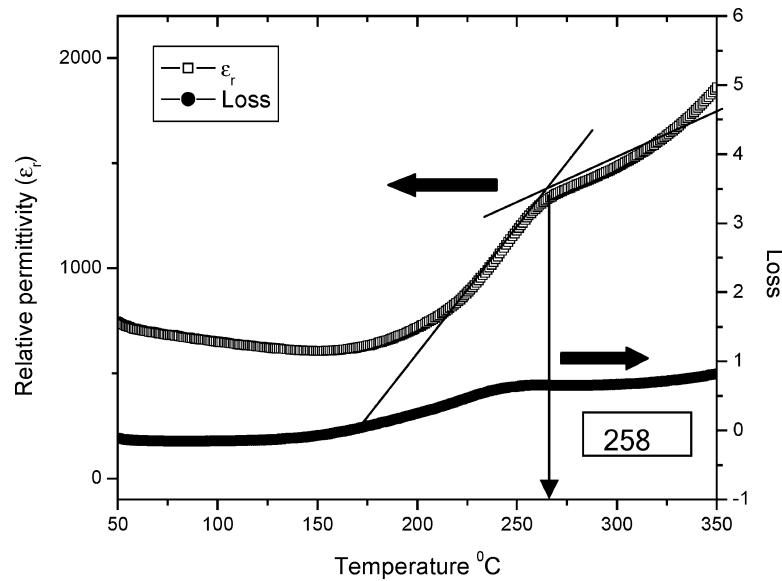


Fig. 6. Temperature dependence of dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) for the hydrothermally synthesized PLZT ceramic sintered at 1300°C for 3 hours.

components as indicated in Fig. 4. It was found that the variation in holding period of the hydrothermally synthesized PLZT powders results in a significant variation in the microstructure of the ceramics as shown in Fig. 5. The grain size of the PLZT ceramics is smaller compared to other reported values [7, 13, 19].

The variation of dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) with temperature at 1 kHz for hydrothermally synthesized PLZT 12/40/60 ceramic prepared from PLZT powders with a holding period of 24 h is shown in Fig. 6. The measured Curie temperature of 258°C at which the phase transition occurs is quite high compared to the other reported values of PLZT 12/40/60 ceramics in the literature [4, 22]. The PLZT 12/40/60 ceramics synthesized by the nitrate process [4] has the Curie temperature of 140°C with dielectric constant of 6,000; while the hot-pressed PLZT 8/40/60 ceramics synthesized by the mixed oxide process [17] has the Curie temperature of 143°C with dielectric constant of 4435 at the same frequency of 1 kHz of excitation. As the increase of lanthanum amount in PLZT composition decrease the Curie temperature, this indicates that the amount of lanthanum in the hydrothermally synthesized PLZT 12/40/60 ceramics is actually less than 8 at.%. The optimum condition to synthesize exactly 12 at.% PLZT should be attempted by adding

more lanthanum salt and adjusting reaction time, temperature and pH in the final solution before hydrothermal treatment. The dielectric constant of the PLZT ceramics from this study is 1450, which is higher than the value (1270) in the PLZT 12/40/60 ceramics synthesized by the mixed oxide process [22]. The dielectric loss of 0.03 is similar as compared to the hot-pressed PLZT 8/40/60 ceramics [17].

4. Conclusion

PLZT 12/40/60 fine powders with high homogeneity, high purity and small particle size have been synthesized by hydrothermal processing in a single reaction step at 200°C with different holding periods: 8, 12 and 24 hours. The synthesized PLZT 12/40/60 powders demonstrated a tetragonal crystallographic phase, which could be matched with XRD JCPDS file number 46-504. PLZT 12/40/60 ceramics of pure perovskite phase with an average grain size of 3.10 μm can be obtained from powders hydrothermally synthesized with a holding period of 24 hours. The high measured Curie temperature of 258°C from the obtained PLZT ceramics indicates the amount of lanthanum is less than 8 at.%. The dielectric constant of PLZT ceramics is 1450 with dielectric loss of 0.03.

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