# CHAPTER 4

# CONCLUSIONS

## 4.1. CONCLUSIONS

PZT and PLZT powders were synthesized by two different routes as nitrate and hydrothermal. In the first route, PZT and PLZT powders were synthesized by nitrate salts of lead, zirconium and titanium. The PZT precursor solution was divided into two parts. The first one was for freeze drying route and the second one was for coprecipitation route. The thermal decomposition and its conversion to PZT were studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The results confirmed that both PZT and PLZT powders completed their thermal decomposition at the temperature above 600 °C.

The freeze drying process produced perovskite pure phase of PZT powders with a uniform morphology at a calcination temperature of 600 °C. At this temperature, PZT powders had a rhombohedral structure. The mean particle sizes were found to be 0.17 μm to 0.25 μm at calcination temperature of 600 °C and 0.33 μm to 0.66 μm at high calcination temperature of 800 °C.

Coprecipitation process produced fine rhombohedral PZT powders at a calcination temperature above 650 °C. At 600 °C, the mean particle sizes were 0.17 μm to 0.25 μm and at 800 °C, their sizes were 0.5 μm to 0.75 μm. Compare to the solid state reaction process[42], the particle size after calcined at 725 °C for 4 hours was found to be 3.8 μm and reduced to 1.1 μm after milling step.

PLZT powders were synthesized from coprecipitation process. At calcination temperature of 650 °C and higher, the powders were cubic. The mean sizes of PLZT powders ranged from 0.30 μm to 0.35 μm at calcination temperature of 600 °C to about 0.50 μm to 0.75 μm at calcination temperature of 800 °C.

In the second route, the PZT and PLZT powders were synthesized hydrothermally from lead acetate trihydrate, zirconium n-propoxide and titanium isopropoxide. Lanthanum acetate used for preparing PLZT at 8, 9 10, and 12 % lanthanum. The important parameters in hydrothermal synthesis are the mineralizer type and concentration, pH value of the condition, synthesis temperature and time. The base mineralizer type and its concentration play an important role in promoting the solubility and rearrangement of the titania and zirconia gels. The smaller the base cation radius, the more efficient it is to diffuse into the gel network. The mineralizer should be above its critical level for providing both soluble Pb species and base ions to cause disruption of the titania and zirconia gels network.

The mineralizer concentration can be used in the higher synthesis temperature or synthesis time. The particle size, morphology and perovskite phase of the PZT powders from the hydrothermal synthesis can be controlled by choosing carefully the mineralizer type and concentration to be used at a moderate synthesis temperature and time in each concentration. Increasing mineralizer concentration will lead to polynuclear growth due to the agglomeration of the cubic PZT particles and increases in the solubility of $Zr^{4+}$, $Ti^{4+}$ and $Pb^{2+}$, which can accelerated the recrystallization process. This process may lead to the larger particle size.

The pH value is one of the important factors, critical pH value for this present work is 13. The synthesis temperature and time are another two important factors. At low synthesis temperature without a very high mineralizer concentration, perovskite PZT cannot form even in a long synthesis time. Increasing synthesis temperature can reduce the minimum concentration required for PZT formation, reducing the agglomerate particle size. Increasing synthesis time can lead to a narrow size distribution but increasing in the particle size of PZT powders. These hydrothermal parameters do not work alone, they have to work together such as at low synthesis temperature, PZT powders can occur at high mineralizer concentration together with long synthesis time. In the case of low mineralizer concentration, PZT powders are produced at high synthesis temperature together with long synthesis time, so, for each mineralizer concentration, they can work only with their moderate synthesis temperature and time.

The thermal decomposition and its conversion to PZT were studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA), the results confirmed that both PZT and PLZT powders from hydrothermal process lost its weight at about 100 °C from the evaporation of water or hydroxyl group, and the second weight loss occurred at about 900 °C due to the evaporation of lead oxide.

The moderate conditions for synthesized rhombohedral PZT are 4.0 M KOH (or 4.0 M NaOH) at synthesis temperature of 200 °C for 6 hours under autogeneous pressure results in PZT powders with the mean particle sizes of 0.3 μm to 0.5 μm.

For tetragonal PZT, the moderate conditions are 4.0 M KOH (or 4.0 M NaOH) at synthesis temperature of 100 °C for 48 hours and at 150 °C for 6 hours or at 2.0 M KOH (or 2.0 M NAOH) at 200 °C for 6 hours which produce PZT powders at the mean sizes ranging from 0.2 μm to 0.4 μm and has a narrow particle size distribution.

The conditions for synthesized PLZT powders are 4.0 M KOH (or 4.0 M NaOH) at 200 °C for 6 hours. At this condition, PLZT has a cubic shape and its mean sizes range from 0.33 μm to 1.0 μm.

Trace impurities in PZT powders were analyzed by atomic absorption spectrophotometry. The average impurities in PZT were found to be 0.035±0.007 ppm consisting of Na and Mg ions. The source of impurities may be from lead acetate. The amounts of lead to zirconium to titanium were determined using gravimetric and photometric methods. The average mole ratio of Pb:Zr:Ti in PZT powders was 1:0.525:0.487±0.006:0.001. These results confirmed that the impurities contents in the powders were minimize and the lead to zirconium to titanium ratio is close to the desired composition of the starting materials.

The sintering temperature for nitrated-PZT is about 100 °C lower than that of hydrothermally synthesized PZT powders due to the finer particle size and narrower size distribution. The sintering condition of nitrated-PZT is 1150 °C for 5 hours, and has 94.32 % theoretical density with 13.5 % linear shrinkage and the grain sizes are between 2.0 μm to 5.0 μm. While for hydrothermally synthesized PZT, the sintering temperature is 1250 °C for 5 hours with 94.71 % theoretical density, 13.5 % linear shrinkage and the grain sizes are between 3.0 μm to 5.0 μm. Kim *et. al*[42], reported that grain size of PZT ceramics obtained from solid state reaction sintered at 1200°C were found to be 2-3 μm and had 98.2 % theoretical density with dielectric constant of about 700 at frequency of 1 kHz.

Ceramics PZT from nitrate route has a rhombohedral structure while hydrothermally synthesized PZT ceramics have coexist phases between rhombohedral and tetragonal, (when these two ceramics are chosen from the rhombohedral structure powders). This is because lead losses during sintering process due to the precipitation of $ZrO_2$ in hydrothermally synthesized PZT is much more than in nitrated-PZT. It can be concluded that, the nitrated-PZT is much more stable to sintering process than hydrothermally synthesized PZT.

PLZT powders after hot pressing process at the temperature of 1250 °C for 4 hours at 30 MPa under argon atmosphere were investigated using scanning electron microscope. The micrograph shows no transparent PLZT, only the porous structure has occurred. This is because of the deficient of soaking time, or the contamination from carbon mold.

The dielectric constant of PZT and PLZT from both nitrate solution and hydrothermal process were measured at room temperature. The dielectric constant of PZT from both processes is found to be about 350 at frequencies of 1 kHz to 1 MHz while the dielectric constant of hydrothermally synthesized PZT is slightly higher than that of nitrated-PZT. But still lower than the dielectric constant of solid state reaction process[42]. This is because of the higher porosity and bigger grain growth of PZT ceramics produced by nitrate solutions and hydrothermal processes.

For PLZT ceramics contained 10% La , the dielectric constants are found to be 610 at frequncies of 1 kHz to 1 MHz for hydrothermally synthesized PLZT and 580 at the same frequencies for nitrated-PLZT. PLZT ceramics has higher dielectric constant than undoped PZT due to rapid transfer of Pb vacancies in their atoms.

Both nitrate solutions and hydrothermal processes can produce high purity and homogeneity of fine PZT powders. For nitrate route, the composition control, morphology, homogeneity and purity of the resulting PZT are managable. However, several parameters such as pH, concentration, temperature and mixing rate have to be carefully controlled. While during calcination step, the agglomerate particles are generally formed. For hydrothermal route, morphology, phase and particle size of the PZT particles can be controlled by choosing the moderate conditions. Calcination steps are not necessary which can avoid the particle agglomeration that the solid state reaction usually causes at high temperature. However, hydrothermal route needs high pressure processing and the apparatus has high cost.

## 4.2. SUGGESTIONS FOR FUTURE WORK

1. For future work, the exact phase transformation between tetragonal and rhombohedral by varied molar concentration of NaOH or KOH mineralizer between 3.0 M and 4.0 M should be performed.
2. Attempt to determine the exact minimum mineralizer concentration between 1.0 M and 2.0 M for synthesizing perovskite PZT powders.
3. Attempt to determine the more efficient mineralizer which can decrease the critical mineralizer concentration required for perovskite PZT formation. The mineralizer with a smaller radius of cation or anion such as lithium or fluorine is expected to improve the efficiency. However, it would cause impurities in PZT because they can increase the level of retention of the associated alkaline or halide[75].