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Synthesis and characterisation of ferroelectric material PLZT using x-ray diffractometry

Feiyee Yeoh, Radzali Othman and **Azizan Aziz**

School of Materials & Mineral Resources Engineering, University Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia.

ABSTRACT Phase identification and crystallite size calculation of ferroelectric smart material, Lead Lanthanum Zirconate Titanate (PLZT) was performed with X-Ray Diffractometry (XRD). PLZT was synthesized based on a wet chemical process – Coprecipitation. Phase formation and crystallite sizes of precursor material and powder calcined were studied at various temperatures and various soaking periods.

(PLZT, XRD, Crystallite Size)

INTRODUCTION

Ferroelectric materials are technologically important materials in microelectronic industry. Among these materials, Lead-based Titanate compositions have been recognized as prominent candidates for their versatile applications. Doped with Zirconium and rare earth element Lanthanum, Lead Lanthanum Zirconate Titanate (PLZT) has been proven to improve electronic and optical properties of Lead-based Titanate.

PLZT has been a useful material in electronic and optical applications. Its high dielectric constant and improved fatigue characteristic (with the introduction of lanthanum) make it a suitable candidate as insulator and capacitor. Its behaviour in hysteresis loops enables it to be memory material such as DRAM [1]. Moreover transparent PLZT has a great potential to be an optical material by displaying satisfactory optical properties. Combining these excellent properties, PLZT has been chosen to be research target as optoelectronic and photostrictive materials. Synthesize of PLZT have been carried out to study its ferroelectric behaviour. Many synthesis routes have been developed such as sol-gel [2], precipitation [3], conventional mixed-oxide method [4], and jet vapour deposition[5] techniques. Each technique has its own advantages and disadvantages, for example: sol-gel can produce very fine particle but it also requires compromise of many synthesis parameters such as pH, viscosity and so forth, whereas precipitation is relatively simpler with the sacrifice of the particle sizes. On the other hand, conventional mixed-oxide is capable of providing accurate stoichiometric of the product but it will also induce impurities compared to JVD which yields high purity product but cost involved high.

In this work, synthesis of PLZT using wet chemical - coprecipitation route was presented. Phase formation study of PLZT was performed using XRD. Besides the XRD results, the crystallite size of the samples were calculated via Sherrer's Equation and Full Width Half Maximum (FWHM) of the diffractogram.

EXPERIMENTAL PROCEDURES

Lead Lanthanum Zirconate Titanate (PLZT) was synthesized from a coprecipitation method to produce precursor PLZT before it was sent for calcinations to obtain the desired material. Various chemicals were used as starting materials. Water was used as solvent, resulting in each element obtaining its ionic form from the solution. Respective element was then mixed to produce homogeneous precursor.

Materials and Methods

There were four chemicals used as starting materials: Lead Nitrate ($PbNO_3$, Mallinckrodt, Mexico), Lanthanum Chloride ($LaCl_3$, Fluka, Switzerland), Zirconyl Nitrate ($ZrONO_3$, Fluka, Switzerland), and Potassium Titanium Oxalate ($KTiC_2O_2$, BDH, England) as the sources for lead, Lanthanum, Zirconate, and Titanate respectively. Each starting material was dissolved in water to produce aqueous solution at desired molarity.

Precursor Material Preparation

The prepared aqueous solutions of P-L-Z components were mixed and stirred to produce a clear homogeneous mixture. Aqueous solution of titanium component was then dripped into the P-L-Z mixture slowly with constant stirring. Precipitate was formed immediately after aqueous solution of potassium titanium oxalate was dripped into the mixture. The precipitate was then filtered and dried to obtain precursor material of PLZT.

Calcination And Characterization

Precursor material was then calcined using furnace. Calcination was performed at various temperatures and various soaking periods to examine the effect of temperature to phase and crystallite size of the material. Calcination temperatures and their respective soaking periods are listed in Table 1. Calcined powder was analysed using X-Ray Diffractometry (Philip PW1729 X-Ray Generator).

Table 1: Calcincation temperature and soaking time

Calcination Temperature	Soaking Period
650°C	1 Hour
850°C	1 Hour
850°C	6 Hours
850°C	12 Hours
950°C	1 Hour

RESULT AND DISCUSSION

Calcined sample analysis was performed using X-Ray Diffractometer (Philip PW1729 X-Ray Generator) with Cu-Kα radiation ($\lambda = 1.54056$ Å). The samples were scanned from 10 ° to 80° throughout 2θ angular regions. The diffractograms of the samples were tabulated in Figure 1 and 2 for comparison.

The x-ray diffractogram obtained are then compared to the standard diffractogram of PLZT and some literature [6-7] to confirm the phase of PLZT. From Figure 1, it is known that the powder is still in amorphous phase at 400°C. Major peaks start to form at 650°C. However, not all the peaks of PLZT perovskite phase are seen at this temperature. Almost every peak can be seen when the powder is calcined at 850°C. Although there are some minor phases appear in the diffractogram, perovskite structure of PLZT still remains as the major phase in the powders. Compared to sample calcined at 850°C, not much difference was observed in sample 950°C. Therefore, the best range of calcination temperatures remain between 650°C and 850°C in order to obtain single phase PLZT.

Other than calcinations temperature, variation in soaking time do not seem giving significant effect to the product. Figure 2 shows the diffratograms for precursor and sample calcined at 850°C for various soaking periods. Referring to Figure 2, the diffratograms for powder with different soaking periods were relatively similar compared to precursor material. From this result, it is known that the soaking period for the same calcination temperature did not affect the structure of the product very much compared to differences in calcination temperature.

Besides phase identification, the maximum peak of each x-ray diffractogram also allows calculation to be done via Sherrer's equation [8-9]:

$$D = (0.9\lambda)/(\beta \mathrm{Cos}\theta) \qquad (1)$$

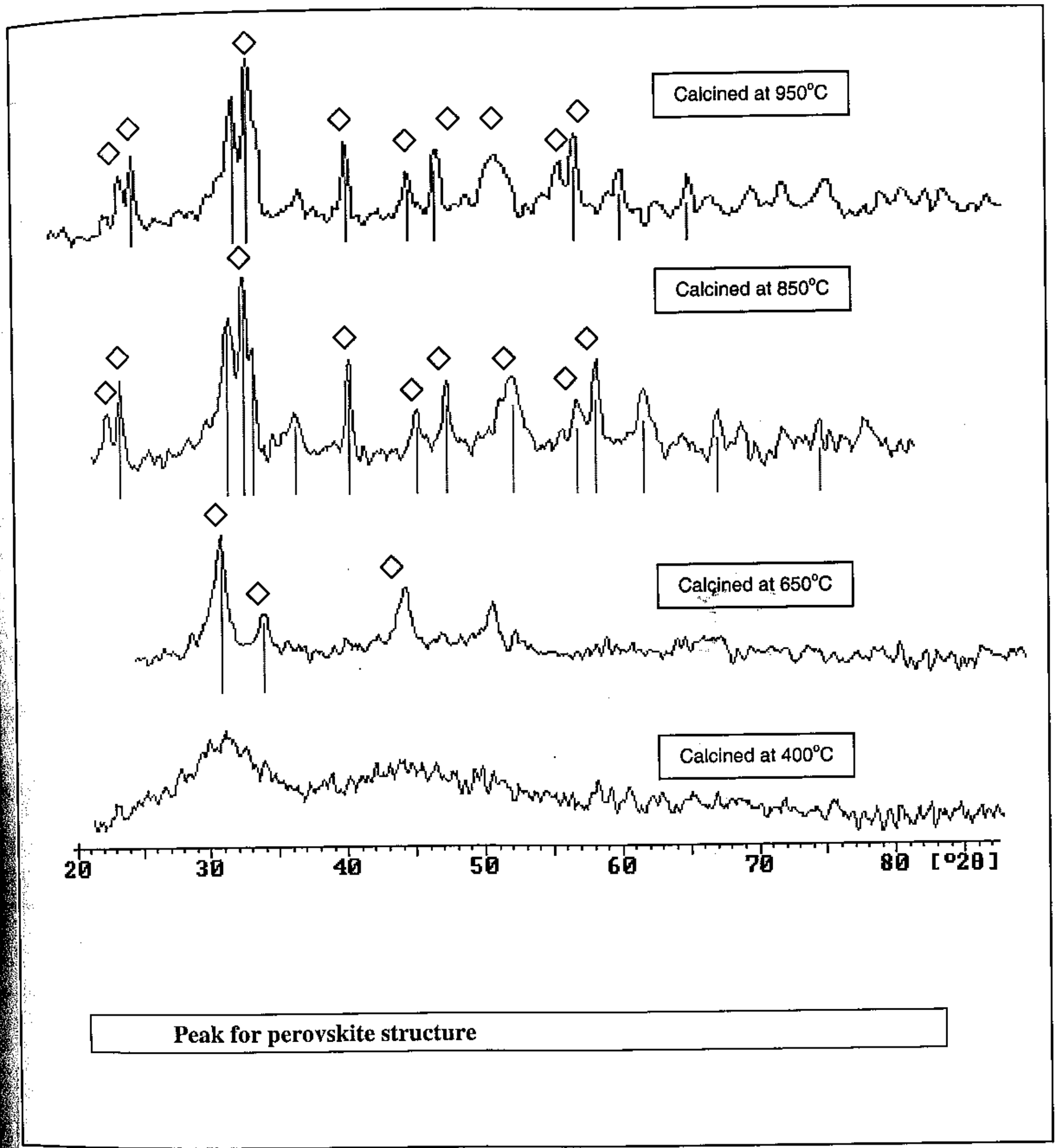

Figure 1. X-ray diffractograms for precursor and sample calcined at various temperatures

Crystallite size obtained from Sherrer's equation were plotted and shown in Figures 3 and 4. Graph patterns in Figures 3 and 4 show crystallite size of PLZT does not correspond to soaking period but much corresponds to different calcination temperatures. Crystallite size of PLZT increases, although still in the range of nanometer, as the calcination temperature rises. This however is limited to the temperature below 850°C. No significant changes other than a slight decrease in crystallite size when calcinatory rose above 850°C . Evaporation of lead could be the reason for this observation. On the other hand, crystallite size for samples soaked at 850°C for different periods (1, 6 and 12 hours) did not show much difference.

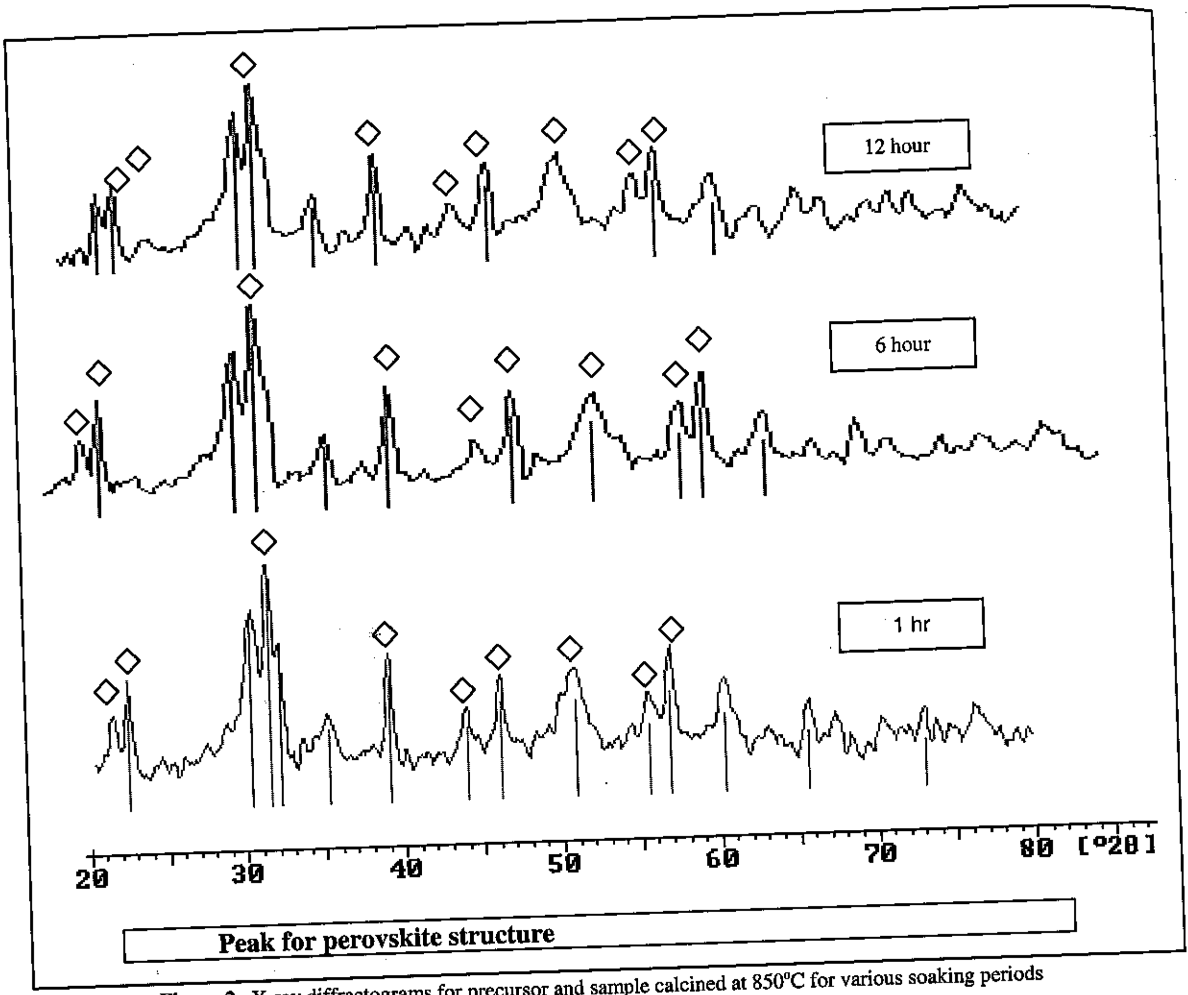

Figure 2. X-ray diffractograms for precursor and sample calcined at 850°C for various soaking periods

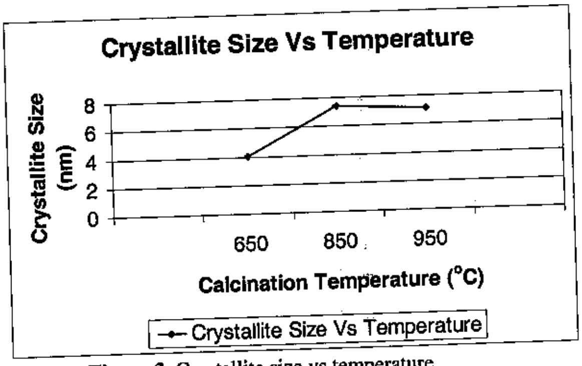

Figure 3. Crystallite size vs temperature

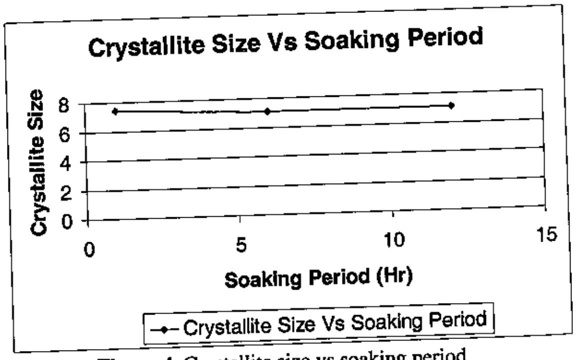

Figure 4. Crystallite size vs soaking period

Table 2: Temperature vs crystallite size

Temperature	Crystallite Size
400°C	Amorphous
650°C	4.0484 nm
850°C	7.4112 nm
950°C	7.1069 nm

Table 3: Soaking Period vs crystallite size

Soaking Period	Crystallite Size
0 hour	-
1 hour	7.4112 nm
6 hours	7.1028 nm
12 hours	7.1050 nm

CONCLUSION

From the XRD result, coprecipitation technique can be a technique to produce PLZT but single phase PLZT cannot be obtained without proper calcinations. Besides, it is found that the calcination temperature has much affected the phase formation and crystallite size of PLZT compare to the soaking period at temperature as high as 850 °C

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Abbreviation

Pb or P - Lead
La or L - Lanthanum
Zr or Z - Zirconium
Ti or T - Titanium

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