# STRUCTURAL, MORPHOLOGICAL AND OPTICAL PROPERTIES OF LEAD CALCIUM TITANATE ($PbCaTiO_3$) THIN FILMS FOR SOLAR CELL APPLICATION

Khine Khine Linn[1], Ohn Mar Swe[2], Khin Phyu Win[3]

## Abstract

In this work, the structural, morphological and optical properties of lead calcium titanate ($PbCaTiO_3$) thin films were reported for solar cell application. The $PbCaTiO_3$ thin films deposited on indium doped tin oxide (ITO) glass substrates were prepared by spin coating method. PbO, CaO and $TiO_2$ were used as starting materials to obtain $PbCaTiO_3$ powders by solid state reaction method. The films of $PbCaTiO_3$ were coated on ITO glass substrates by spin coating method. The phase formation, structural properties and surface morphology of $PbCaTiO_3$ samples were characterized by X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The XRD patterns of $PbCaTiO_3$ specimens were perovskite type with tetragonal structure According to SEM analysis, the smallest grain size of $PbCaTiO_3$ powder was found to be about 0.27 μm at 700 ºC. Ultraviolet-Visible (UV-Vis) spectroscopy was used to observe the optical properties of $PbCaTiO_3$ films.

**Keywords:** $PbCaTiO_3$ thin films, XRD, SEM, UV-Vis.

## Introduction

The thin film is a thin layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness (Georgakopoulos T, et al.,). The controlled synthesis of materials as thin films (a process referred to as deposition) is a fundamental step in many applications (Wang C, et al.,). A thin-film solar cell is a second generation solar cell that is made by depositing one or more thin layers or thin films of photovoltaic materials on a substrate such as, glass, plastic or metal. Ferroelectric materials are a class of materials that possess high dielectric constant, relatively low dielectric loss, high electrical resistivity, moderate dielectric breakdown strength and strong electromechanical and electro optical behaviors (Kim K E, et al.,) Ferroelectrics with perovskite structure ($ABO_3$) such as barium titanate ($BaTiO_3$), calcium titanate ($CaTiO_3$) and lead titanate ($PbTiO_3$) are the most studied ferroelectric oxides materials because of their versatile properties for use in thin films applications (Tian J, et al.,). Solar cell is an important application of thin film technology from the point in view of global energy crunch, which converts the energy of the solar radiation into useful and constructive electrical energy. The properties of the thin films and aspects of growth mechanism can be well understood by its characterization of the films. Materials with different optical band gaps can be easily combined to form multiple stacks that exploit a larger part of the solar spectrum increasing the efficiency of the photovoltaic device (Giannouli M and Spiliopoulou F).

## Experimental Procedure

### $PbCaTiO_3$ Powder Preparation

The sample preparation of $PbCaTiO_3$ powders were prepared by solid state reaction method. Lead oxide (PbO), Calcium oxide (CaO), and Titanium dioxide ($TiO_2$) were weighed with digital balance with their molar ratio. Mixtures of homogeneous $PbCaTiO_3$ were synthesized by mixing of three oxide powders and then they were grinded vigorously with agate motor for 48 hr. Ethanol was used as solvent and poured drop by drop in this mixture

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powders. In the next step, the reaction mixture was applied with mesh-sieving process to reduce particle size. The mesh-sieving steps were 100 mesh, 250 mesh and 400 mesh. After that, the dried mixture powders were annealed in a muffle furnace at 500 °C, 600 °C and 700 °C respectively for 2 hr. The formation of $PbCaTiO_3$ powders were characterized by XRD and SEM for phase formation, morphological and structural properties. The block diagram of sample preparation of $PbCaTiO_3$ powder was shown in figure1.

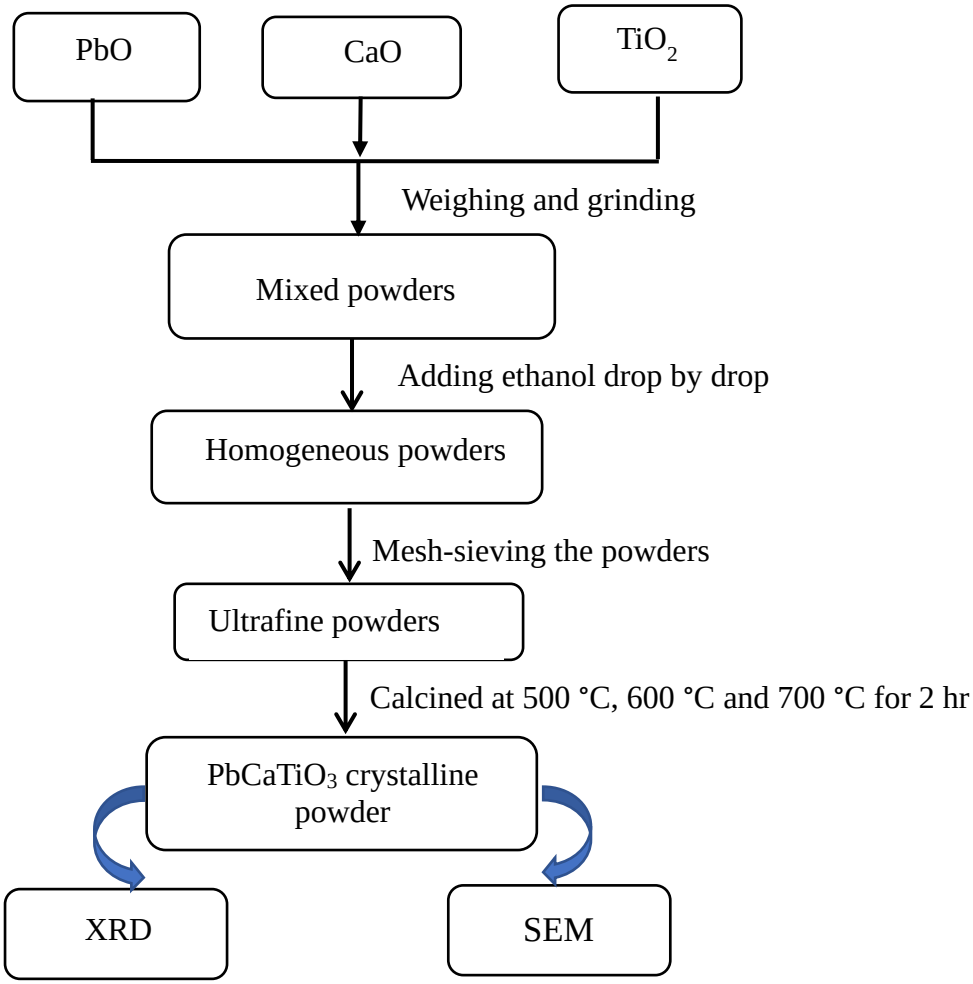


Figure 1 Block diagram of preparation of $PbCaTiO_3$ powder

**$PbCaTiO_3$ Thin Films Preparation**

The sample preparation of $PbCaTiO_3$ thin films was described as follow. The substrates used in this study were ITO glasses. Before film fabrication, ITO substrates were cleaned step by step. The $PbCaTiO_3$ powders were dissolved by using 2-Methoxyethanol. The mixed solution was stirred with glass rod for 4 hr. After that, the precursor solutions which were then coated on ITO glass by using spin coating technique. The well dissolved precursor solutions were poured onto the cleaned ITO substrate which was placed on substrate holder of spinner. The spin speed was 3000 rpm, the substrate temperature was at room temperature and the spinning time was 30 s. After fabrication, $PbCaTiO_3$ thin films were dried at 120 °C respectively for 30 min. Finally, $PbCaTiO_3$ thin films were successfully obtained. Surface morphology and grain size of the thin films were investigated with Scanning Electron Microscope (SEM). The absorption spectrum for energy band-gap was measured by UV-Vis Spectroscopy. The block diagram of $PbCaTiO_3$ thin films was shown in figure 2.

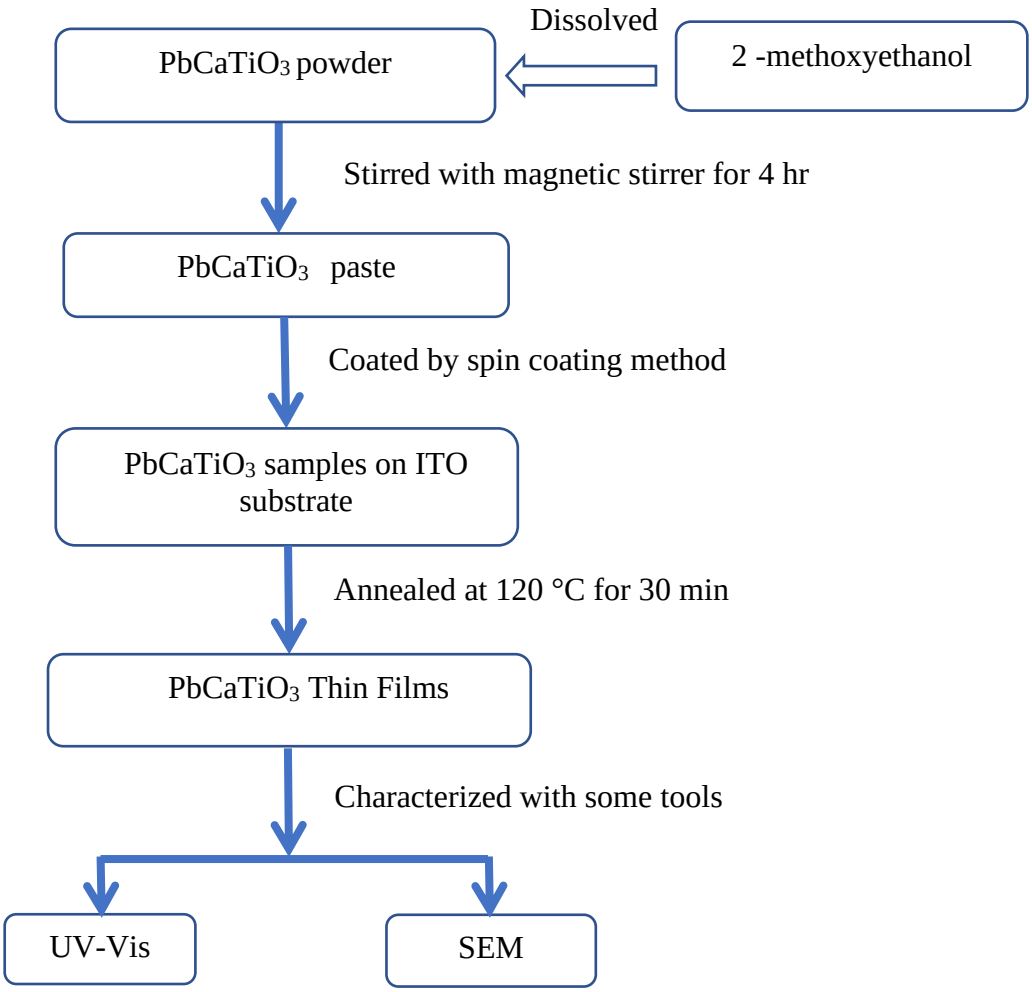


Figure 2 Block diagram of preparation of $PbCaTiO_3$ thin films

## Results and Discussion

### XRD Analysis of $PbCaTiO_3$ powder

X-ray diffraction technique (XRD) is a powerful technique for determination of crystal structure. It provides simple nondestructive information on the nature of intermetallic and crystal phase usually in a very short time. The great deal of information about the crystallographic information of crystalline $PbCaTiO_3$ powder has been studied by crystallite size. The XRD patterns of $PbCaTiO_3$ specimens were perovskite type with tetragonal structure as shown in figure 3(a-c). There are several diffractions of the standard peaks were scanned within the diffraction angles range from 10° to 70°. Some extra peaks were formed on all XRD profile and they could not be identified. PCT powders were obtained and examined its phase formation by X-ray diffractometer using Cu-$K_\alpha$ radiation with wavelength of 1.54056 Å. All the peak heights and peak positions were in good agreement with the JCPDS (Join Committee on Powder Diffraction Standards) in 49-0863 > $PbCaTiO_3$ library file. The average crystallite-sizes were 29.872nm at 500 ° C, 25.253 nm at 600 ° C and 24.827 nm at 700 ° C. The lattice parameter (a, b and c) and lattice distortion (lattice strain) c/a of dominant peaks were described in Table 1. Thus, the PCT powders were successfully obtained by solid state reaction method with tetragonal structure. The crystallite size was calculated using a well-known Debye Scherrer's formula: $G = \frac{0.899 \times \lambda}{FWHM \times \cos\theta}$ , where G = crystallite size, λ = 1.54056 Å for Cu $K_\alpha$, FWHM = full width at half maximum at dominant peak, θ = Bragg angle.

Table 1 Lattice parameters and c/a ratios of $PbCaTiO_3$ at different temperatures

| Temperature (°C) | Lattice Parameter (Å) | | Latice Distoration c/a |
|---|---|---|---|
| | a = b | c | |
| 500 | 3.9162 | 4.1804 | 1.0674 |
| 600 | 3.9170 | 4.1602 | 1.0621 |
| 700 | 3.9218 | 4.1624 | 1.0613 |

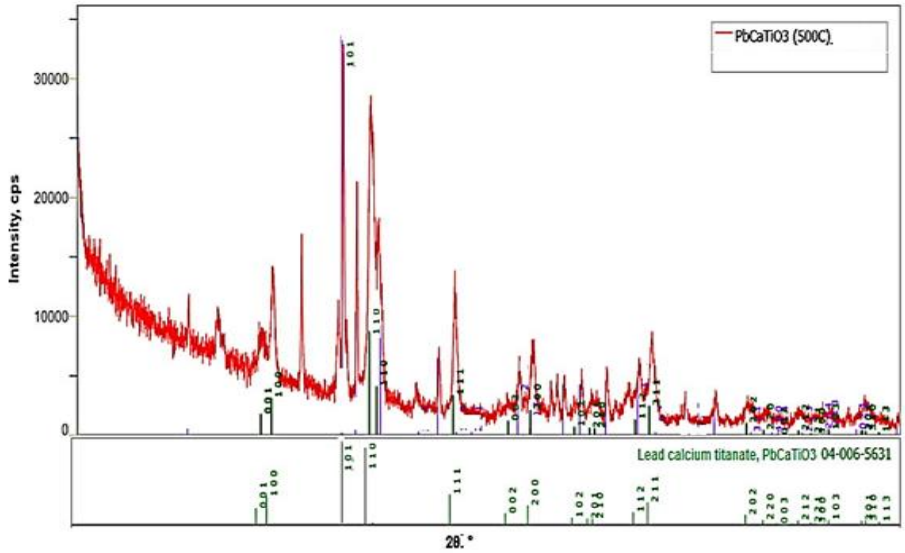


Figure 3 (a) XRD patterns of $PbCaTiO_3$ powders at 500 ° C

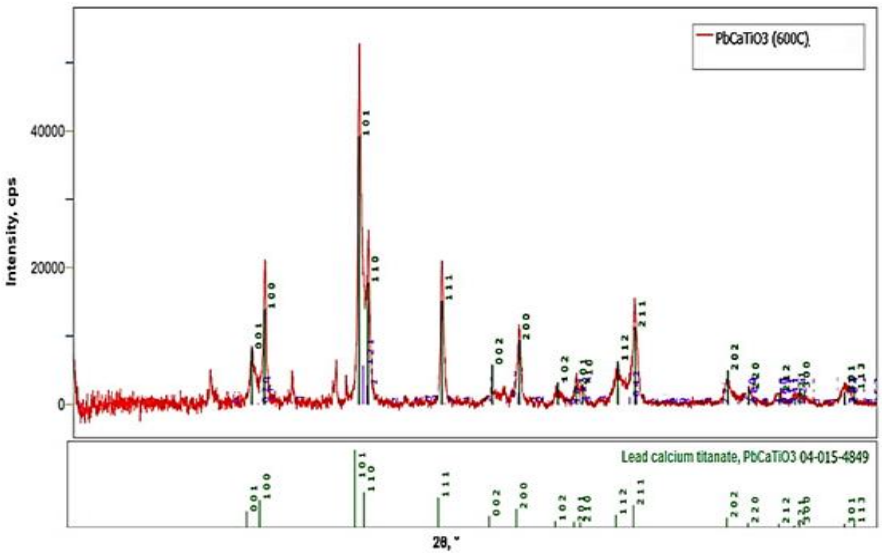


Figure 3 (b) The XRD patterns of $PbCaTiO_3$ powders at 600 ° C

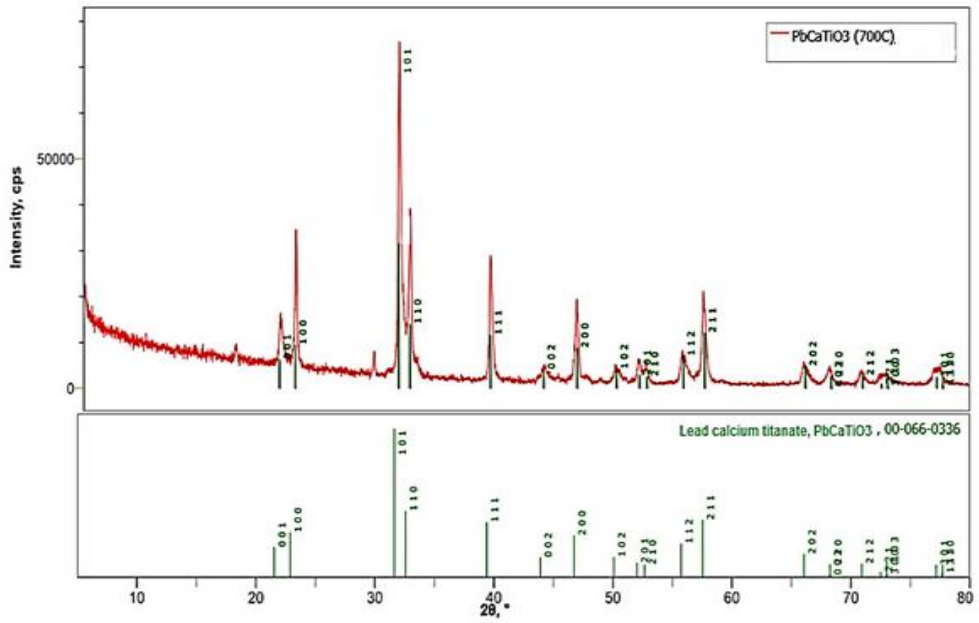


Figure 3 (c) The XRD patterns of $PbCaTiO_3$ powders at 700 ° C

**SEM Analysis of $PbCaTiO_3$ powder**

The Scanning Electron Microscopy (SEM) is an important tool capable of producing high-resolution images of a sample surface. SEM images of $PbCaTiO_3$ powders at different temperatures at 500 ºC, 600 ºC and 700 ºC were shown in figure 4 (a-c). As the detail analysis of SEM image, it was found that small grain sizes crack free and uniform particle size. This image consisted of circular features known as rosette structure in microstructure. The grain sizes were calculated by using well known bar code system. Bar code size was 5μm with magnification of 4 k. The average grain size of $PbCaTiO_3$ powders was found to be 0.39 μm at 500 ºC, 0.31 μm at 600 ºC and 0.27 μm at 700 ºC respectively. With increasing temperature, more obvious pores were generated, but the size of the pores became smaller and sharper. From the images, it was clearly found that the little amount of pores and grain growth were examined with the increase in process temperatures. The surface morphology and the formations of grains were changed by the varying different temperatures. According to SEM analysis, the smallest grain size of $PbCaTiO_3$ powder was found to be about 0.27 μm at 700 ºC.

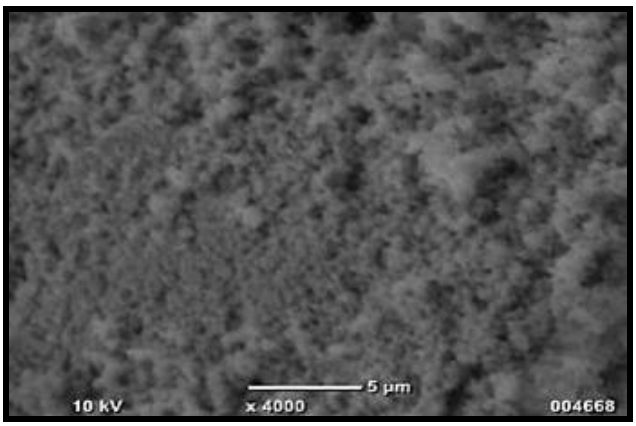


Figure 4 (a) The SEM image of $PbCaTiO_3$ powders at 500 ° C

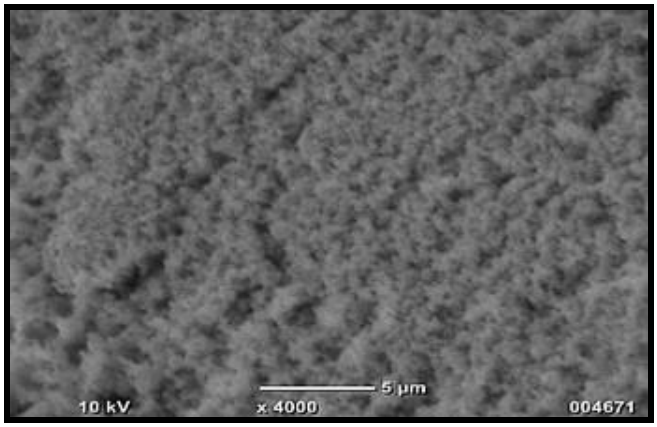


Figure 4 (b) The SEM image of $PbCaTiO_3$ powders at 600 ° C

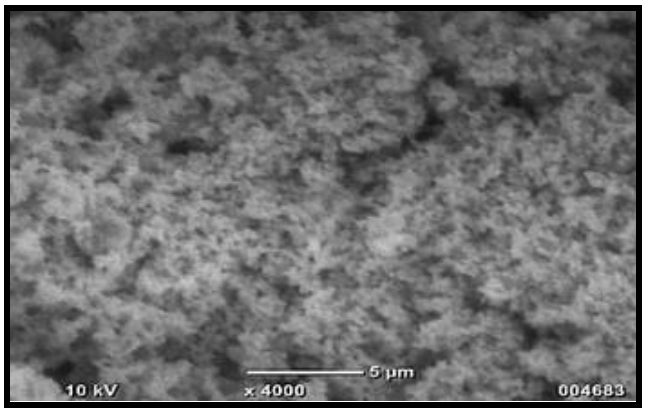


Figure 4 (c) The SEM image of $PbCaTiO_3$ powders at 700 ° C

**SEM Analysis of $PbCaTiO_3$ thin films**

Figure 5 (a-c) showed the SEM images of $PbCaTiO_3$ thin films annealed at 120 °C for 30 min. According to SEM analysis, the surface morphology of $PbCaTiO_3$ thin films at three temperatures were seemed to be well defined, crack free and uniform distribution but the surface morphology at 700 °C was smoother than that of other two temperatures. The average grain size of thin films was about to be 0.57 μm, 0.43 μm, and 0.38 μm at 500 °C, 600 °C and 700 °C. As a result, it was concluded that the minimum grain size of the $PbCaTiO_3$ thin film was found to be about 0.38 μm at 700 °C.

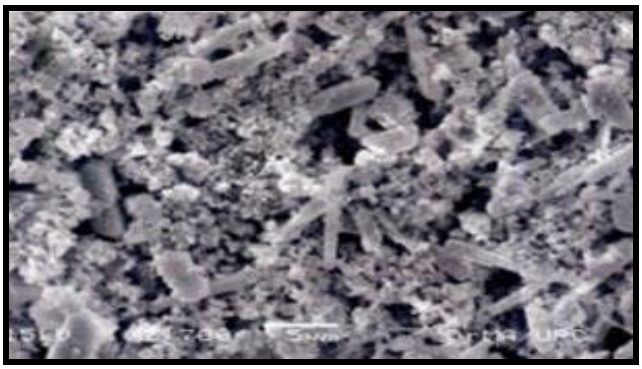

Figure 5 (a) The SEM image of $PbCaTiO_3$ thin film at 500 ° C

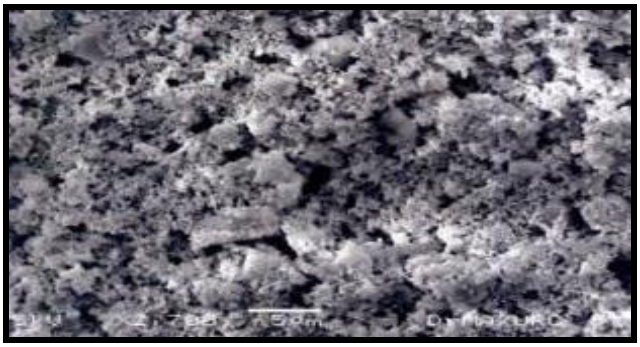

Figure 5 (b) The SEM image of $PbCaTiO_3$ thin film at 600 ° C

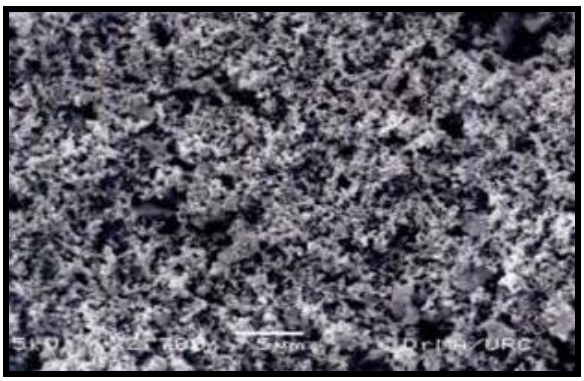

Figure 5 (c) The SEM image of $PbCaTiO_3$ thin film at 700° C

**UV-Vis Analysis of $PbCaTiO_3$ thin films**

The UV-Vis spectra of all films were obtained on UV-1800 Spectrometer (Shimadzu) in the range of 190 nm -700 nm. Figure 6 (a-c) showed that the UV-Vis absorption spectrum of $PbCaTiO_3$ thin films at 500 ˚C, 600 ˚C and 700 ˚C. It was found that the maximum absorption of wavelength obtained by coating onto ITO is in the UV-visible region. The alternative method to observe the band gap is Beer-Lambert law. From Tauc's plot relation $\alpha h\upsilon = A(h\upsilon - E_g)^n$ , the $(\alpha h\upsilon)^2$ and $h\upsilon$ characteristic curve of $PbCaTiO_3$ thin films at 500 ˚C, 600 ˚C and 700 ˚C were shown in figure 6 (a-c). On the characteristic curve, the extrapolating the straight line onto horizontal axis ($(\alpha h\upsilon)^2 = 0$), give the values of band gap and the obtained thin films had a direct band gap 3.95 eV at 500 ˚C, 3.50 eV at 600 ˚C and 3.44 eV at 700 ˚C respectively. Table 2 showed the observed energy band gap of $PbCaTiO_3$ thin films at different temperatures. The optical energy gap of $PbCaTiO_3$thin film was calculated by the formula given below: $E_g = \frac{hc}{\lambda}$ , where $E_g$ = energy band gap (eV), h= Planck's constant ($6.625\times10^{-34}$Js),c= speed of light ($3\times10^{8}ms^{-1}$), $\lambda$ = wavelength (nm).

Table 2 The observed energy band gap of $PbCaTiO_3$ thin films at different temperatures

| Sr No. | Temperature (°C) | Observed energy band gap (eV) | Standard energy band gap (eV) |
|---|---|---|---|
| 1 | 500 | 3.95 | 3.20-5.00 |
| 2 | 600 | 3.50 | 3.20-5.00 |
| 3 | 700 | 3.44 | 3.20-5.00 |

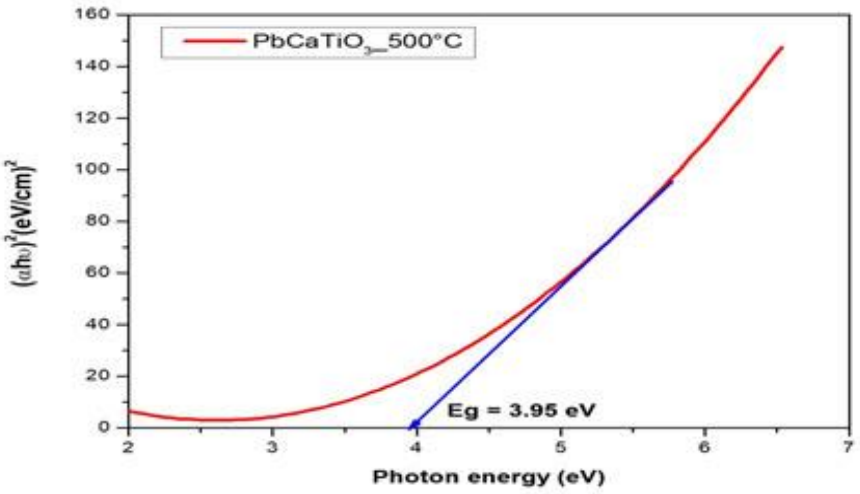


Figure 6 (a) The UV-Vis analysis of $PbCaTiO_3$ thin film at 500 ° C

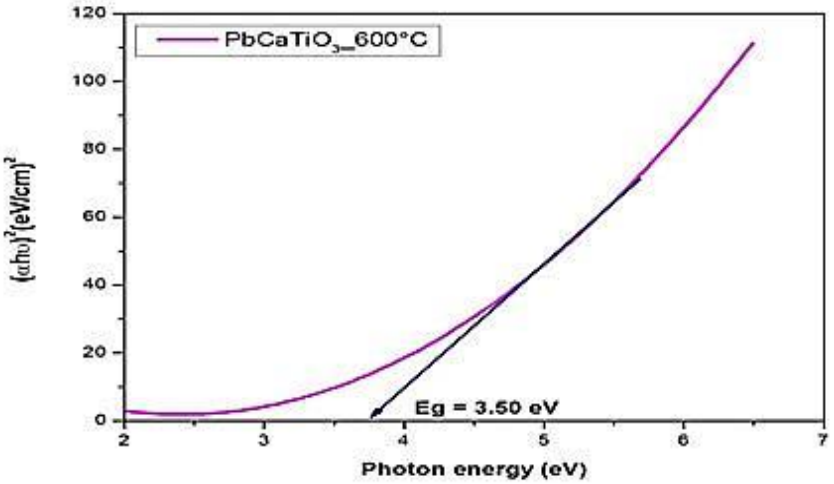


Figure 6 (b) The UV-Vis analysis of $PbCaTiO_3$ thin film at 600 ° C

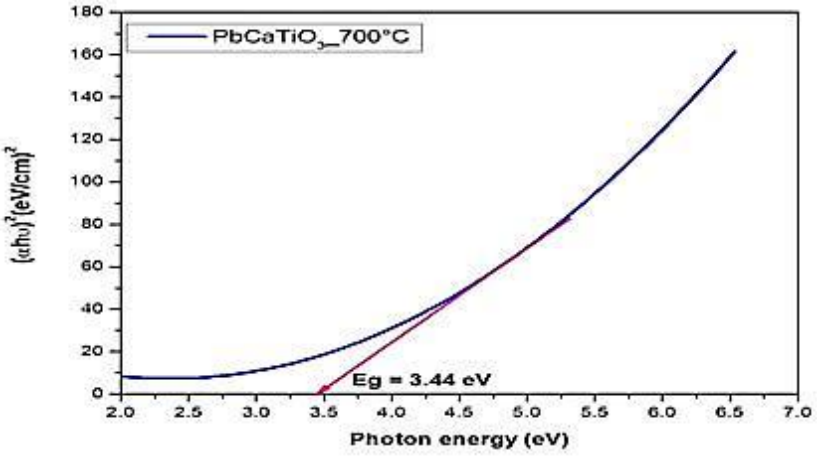


Figure 6(c) The UV-Vis analysis of $PbCaTiO_3$ thin film at 700 ° C

## Conclusion

In this research work, the preparation and characterization of $PbCaTiO_3$ powders have been firstly investigated by solid state reaction method. Then, the preparation of $PbCaTiO_3$ thin films were successfully implemented by spin coating methods. According to XRD analysis, all the peak heights and peak positions of different temperatures were in good agreement with library files of XRD machine. The XRD pattern revealed that these powders were tetragonal structure. According to XRD analysis, the smallest crystallite size of $PbCaTiO_3$ powder was found to be about 24.827 nm at 700 ºC. According to SEM analysis, the surface morphology and the formations of $PbCaTiO_3$ powders were changed by the varying different temperatures. The smallest grain size of $PbCaTiO_3$ powder was found to be about 0.27 μm at 700 ºC. SEM analysis was examined to be smooth, uniform, crack free and agglomerated spread layers of $PbCaTiO_3$ thin films onto the ITO glass substrates. This suggested that agglomerated grain size decreases with increasing process temperatures**.** The experimental finding resulted from this research work indicated that the crystal structure, phase formation and surface morphology of $PbCaTiO_3$ thin films were influenced by annealing different temperatures. It was concluded that the minimum grain size of the $PbCaTiO_3$ thin film was found to be about 0.38 μm at 700 °C. UV-Vis showed that the dominant sharp band of $PbCaTiO_3$ thin films were observed around UV-visible range. All the band gap energies of $PbCaTiO_3$ thin films were in the range between 3.2 eV to 5 eV. Therefore, these $PbCaTiO_3$ thin films can be used as the electron transporting layers for solar cells.

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