

## Structural analysis of Lead Titanate Prepared by Wet Chemical Method

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### ABSTRACT

While preparing  $\text{PbTiO}_3$  [usually referred as PT] nanocrystalline particles,  $\text{PbTiO}_3$  was prepared from Lead Nitrate [ $\text{Pb}(\text{NO}_3)_2$ ] and Titanium Isopropoxide [ $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$ ] by wet chemical technique. Thus synthesized  $\text{PbTiO}_3$  nanoparticles were kept at different temperatures of  $650^\circ\text{C}$ ,  $700^\circ\text{C}$ ,  $750^\circ\text{C}$  for 4 hours. The particle size of the sample was estimated to be between 25 and 55 nm by the Scherer's formula. Also  $\text{PbTiO}_3$  has been investigated using x-ray powder diffraction data to confirm the phase formations and phase purity. Also microscopic structural analysis of the sample was done using scanning electron microscopy. It showed that when the sintering temperature increases, the grain size of the particle decreases. Infrared Transmittance behavior with respect to sintering temperature of the samples sintered has been studied. The effect of sintering temperature on microstructure and other parameters have also been studied using TEM Analysis.

**Keywords :** Wet Chemical Route,  $\text{PbTiO}_3$ , XRD, FTIR, SEM, TEM.

### I. INTRODUCTION

In recent years, a large number of applications based on improved lead titanate have been widely used in applications such as piezoelectric, actuators and ultrasonic transducers continuously because of its high density and optimal piezoelectric properties [1].

Materials of the perovskite family, such as  $\text{PbTiO}_3$ ,  $\text{BaTiO}_3$ , and  $\text{SrTiO}_3$  etc. have been of constant interest because some of these materials show ferroelectric behavior and undergo structural phase transitions [2].  $\text{PbTiO}_3$  has been considered to be one of the most important members of this family. It has a high Curie temperature, high pyroelectric coefficient, low dielectric constant, and high spontaneous polarization. Lead titanate ( $\text{PbTiO}_3$ ), PT is a ferroelectric ceramic that has not only been proved to be a technologically important material but also it is a significant

component material in electronics such as capacitors, ultrasonic transducers, thermistors, and optoelectronics [3-5].

The conventional method of synthesizing  $\text{PbTiO}_3$  relies on the reaction between Lead Nitrate [ $\text{Pb}(\text{NO}_3)_2$ ] and Titanium Isopropoxide [ $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$ ] at high temperature. The conventional solid-state reaction has a tendency to produce a coarse  $\text{PbTiO}_3$  powder with compositional inhomogeneity and a degree of particle agglomeration if the processing parameters are not carefully optimized. Therefore, many chemistry-based processing routes, including co-precipitation, sol-gel synthesis, hydrothermal and citrate routes have been devised for the preparation of an ultrafine, sintering-reactive  $\text{PbTiO}_3$  powder [6-8]. However, almost all these chemistry routes require calcinations of the precursors at an elevated

temperature to develop the desired  $\text{PbTiO}_3$  phase [9]. Furthermore, most of these chemistry-based processing routes require high purity inorganic or organo-metallic chemicals as the starting materials, which are many times more expensive than the widely available oxides and carbonates. It has been observed that the synthesis of a mechanically robust, high density, monolithic ceramic pure  $\text{PbTiO}_3$  is not simple [10]. Problems typically encountered include loss of lead (Pb) due to the volatility of  $\text{PbO}$  at elevated temperatures, porosity, and micro cracking, in extreme cases leading to spontaneous fracture. The main hurdle in the PT fabrication is the synthesis of a single phase with required perovskite structure [11-15]. The primary difficulty is due to the volatility of  $\text{PbO}$  at elevated temperatures [16]. The  $\text{PbTiO}_3$  structure can only tolerate minor loss of lead (Pb), higher levels of which effectively promote second phase formation and the degradation of piezoelectric properties. An example is the formation of a PT phase with the pyrochlore structure observed during a coprecipitation synthesis experiment. A more common occurrence is the formation of a two-phase mixture Ti-O with Titanium Isopropoxide [ $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$ ] [17-20]. The volatilization of  $\text{PbO}$  is known to increase markedly at temperatures above  $750^\circ\text{C}$  though the critical temperature is debated. It has been observed that a PbO-rich PT in liquid phase is formed above  $750^\circ\text{C}$ , Alguero et al. found that at  $650^\circ\text{C}$  an excess of 20%  $\text{PbO}$  was required because of Pb-loss during thermal treatments of wet method prepared a modified PT, whereas Ananta and Thomas found that Pb volatility in PMN-PT could be minimized by careful sintering up to  $750^\circ\text{C}$  [21]. What is clear is that the loss of lead depends on particle size of constituent oxides, processing conditions, and chemical stability. The degree of Pb incorporation into the presintered crystal structure affects the volatility enormously. Many groups report that loss of lead (Pb) may be minimized by sintering compacted powders in a surrounding lead-based powder or a  $\text{PbO}$  vapor

atmosphere although this may lead to a Pb gradient in the final sintered product. The problem of porosity has largely been addressed through particle size control of the starting powder [22]. A careful and systematic study optimization of the synthesis parameters provides an alternative means of minimizing the problem of cracking, porosity, and Pb volatility. Careful sintering at lower temperatures may restrict grain growth and on cooling internal strains are reduced. In addition, sintering at low temperatures, the problem of volatility of lead is minimized. It has been shown that homogeneous powders with a fine grain size can be produced by the ceramic process on the optimization of synthesis parameters. The electrical properties result from the different contributions made from various components and processes present in the material [23].

## II. METHODS AND MATERIAL

Nanocrystalline  $\text{PbTiO}_3$  powders, denoted PT, were prepared by the a solid mixture of Lead Nitrate [ $\text{Pb}(\text{NO}_3)_2$ ], Titanium Isopropoxide [ $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$ ] in liquid, and pure water stirred for 3 hr at  $100^\circ\text{C}$  by using the wet chemical route and first, lead nitrate was dissolved in pure water on a stirred for 1 hr at  $100^\circ\text{C}$  in reaction flask and then the lead nitrate was dissolved in water. When the temperature of the water reaching the oxidation and Secondly a stoichiometric amount of titanium Isopropoxide was added to the solution and the solution was refluxed at  $100^\circ\text{C}$  for 3 hr. After cooling the Pb-Ti complex alkoxide solution to room temperature, a stoichiometric amount of the lead titanate. Thereby forming a  $\text{PbTiO}_3$  complex alkoxide solution.

By controlling the hydrolysis condition of the solution and adjusting the pH value of the solution about 11 during the polymerization and precipitation of metal alkoxide, the gel was then dried at a designated temperature and time. PT nanocrystalline powder

with various crystallite sizes was obtained by calcining the gel powder at different temperatures between 600 and 750 °C. Structure and phase transformation analyses were investigated by XRD using a radiation in the range of 0°–90°. The average crystallite size was calculated from the full width at half maximum of the diffraction lines using Scherrer's relation which assumes the small crystallite size causes line broadening, the diffraction peak and  $K$  the Scherrer constant.

### III. RESULTS AND DISCUSSION

#### i) X-RAY DIFFRACTION

XRD pattern of the  $\text{PbTiO}_3$  calcined at 600°C, 650°C and 700°C and 750°C is shown in Fig.1. The XRD pattern shows the integrity of the synthesized material and the formation of single phase compound. The crystallite size of the particles calcined at various temperatures could be calculated by the Scherrer's equation:  $t = k\lambda/\beta\cos\theta$  (where  $t$  is the average size of the particles, assuming particles are spherical,  $k=0.9$ ,  $\lambda$  is the wavelength of X-ray radiation,  $\beta$  is the full width at half maximum of the diffracted peak and  $\theta$  is the angle of diffraction). The average crystallite size obtained from XRD data at 600°C, 650°C and 700°C and 750 °C were 30.875, 29.665, 25.155, 25.64 nm, respectively. The peak around 30° is getting suppressed with the elevated sintering temperature. This peak belongs to the  $\text{TiO}_2$  present in the material. As sintering temperature is increased, the peak belonging to  $\text{TiO}_2$  is vanished and pure phase  $\text{PbTiO}_3$  is obtained. That means with increase in sintering temperature,  $\text{TiO}_2$  gets attached to the  $\text{PbO}$  to form single phase crystalline  $\text{PbTiO}_3$ .

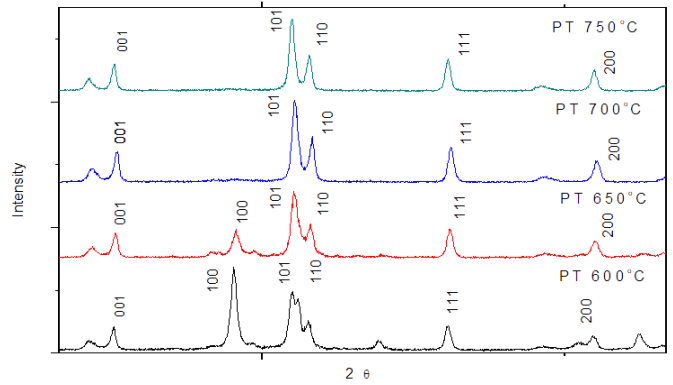


Fig 1.

Fig.2. shows the variation of  $c/a$  ratio with the sintering temperature, which clearly indicates decrease in  $c/a$  ratio along with sintering temperature. Decrease in  $c/a$  ratio indicates dispersion from tetragonality and an approach to the cubic phase with higher sintering temperature. Fig.3 shows the variation of average grain size with sintering temperature indicating decrease in average grain size with increasing sintering temperature.

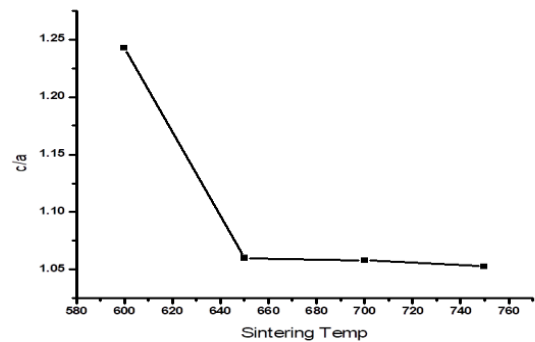


Fig. 2

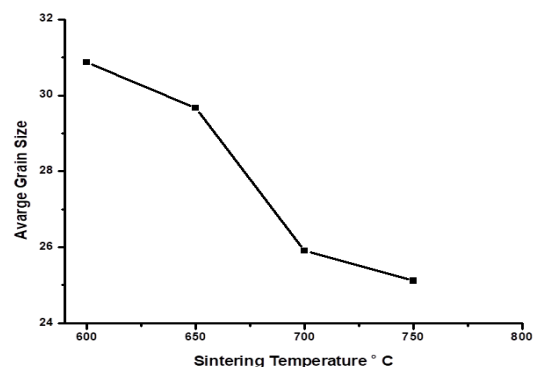


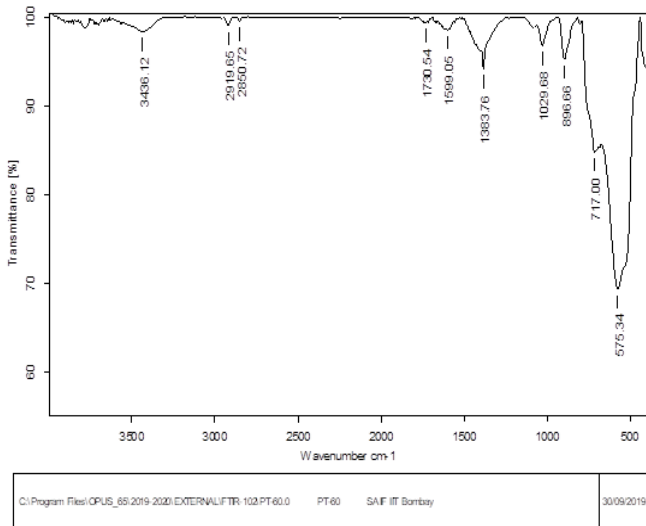
Fig. 3

**ii) FTIR (Fourier transform infrared spectrum)**

FTIR is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high spectral resolution data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time.

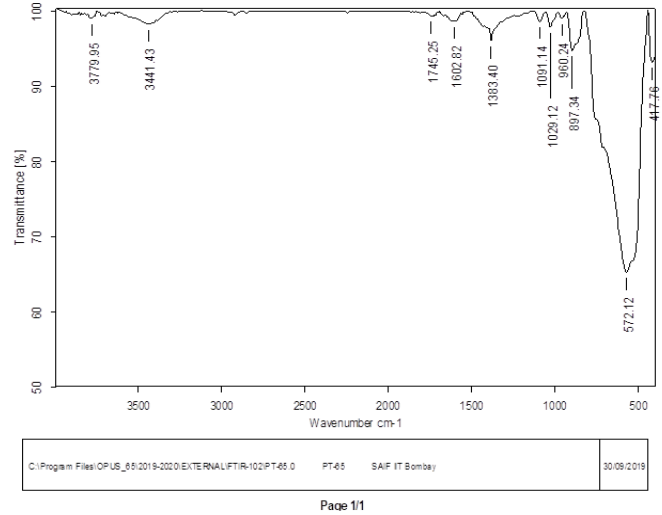
Fig. (4 to 07) illustrates the FTIR spectra for PbTiO<sub>3</sub> powders derived via the wet chemical method and calcined at various temperatures ranging from 600°C, 650°C, 700°C and 750°C for 4 hours. The IR spectrum of the sample calcined at 650 °C clearly indicates the presence of Ti–O band characterized by the absorption bands at nearly 600, 700 cm. The broad band at 4000 cm was assigned to stretching vibration of weakly bound water. It was reported that absorption bands over the range of 1000–1700 cm are mainly related to the organic groups. Increasing the calcination temperature to 750°C results in decrease in intensity of the organic absorption bands and increased intensity of the absorption Ti–O band. The organic residuals were completely eliminated when the derived powders were calcined at 650°C.

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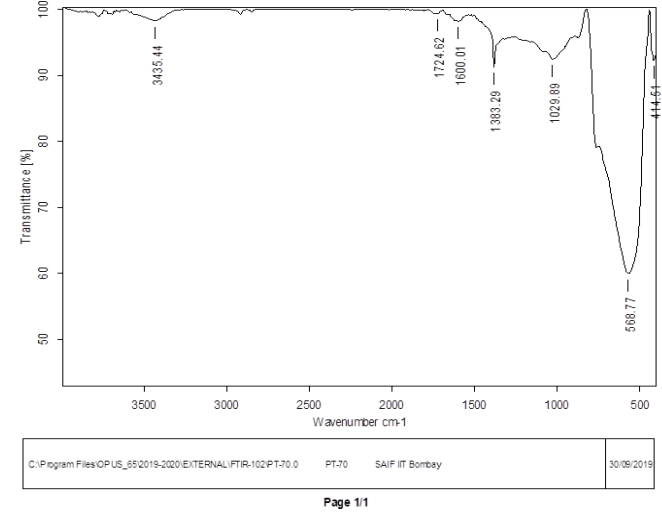
**Fig.4 (Temp.600OC)**

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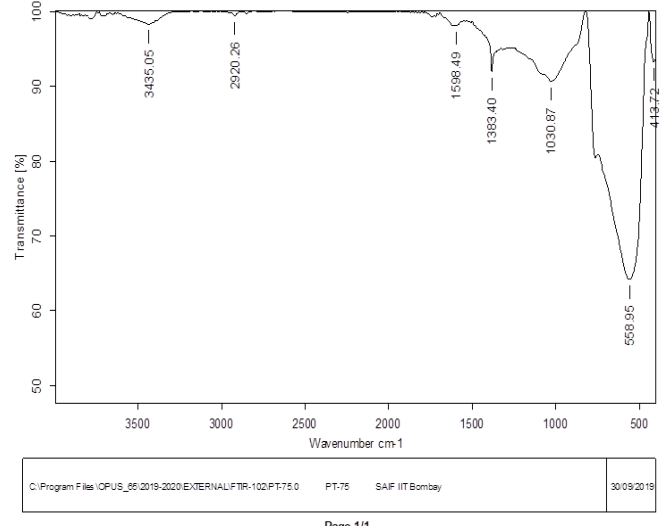
**Fig.5 (Temp.650OC)**

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**Fig.6 (Temp.700OC)**

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**Fig.7 (Temp.750OC)**

### iii) SEM (scanning electron microscope)

SEM micrographs of  $\text{PbTiO}_3$  with magnification  $\times 100000$  sintered at various temperatures have been presented in Fig.(08 to 11) It can be observed from the figure that the microstructure of the sample sintered at low temperature ( $600^\circ\text{C}$ ) is homogeneous whereas the microstructure of the sample becomes heterogeneous at higher sintering temperatures ( $600^\circ\text{C}$  and  $750^\circ\text{C}$ ). It is also observed that the grain size decreases with increasing sintering temperature. Further it may be noticed that the porosity of the samples sintered at  $750^\circ\text{C}$  is predominately inter-granular, whereas the porosity of the samples sintered at  $650^\circ\text{C}$  and  $750^\circ\text{C}$  is located at grain boundaries and many of the very small pores disappear through diffusion kinetics as sintering temperature decreases. That's why the grain size increases and the number of grain boundaries decreases and consequently the porosity decreases and results in the homogeneous grain size distribution

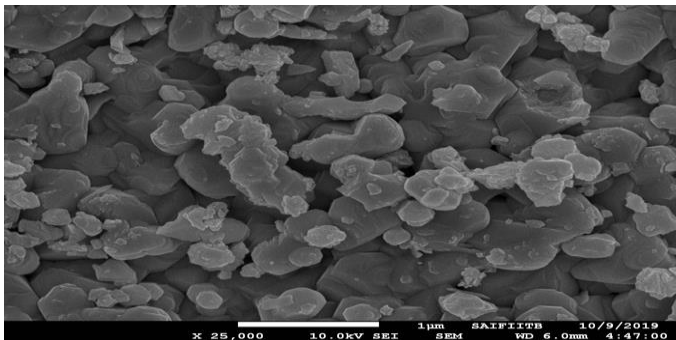


Fig.8 Temp. 600oC

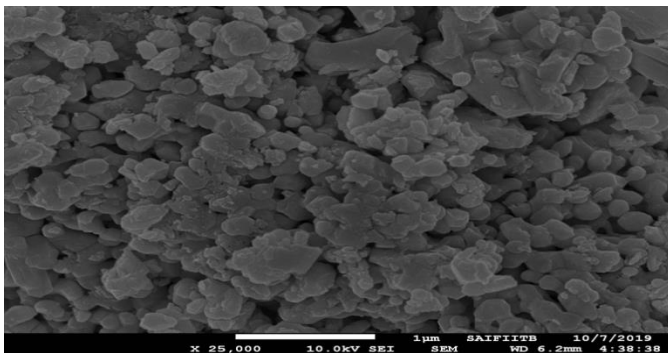


Fig.9 Temp. 650oC

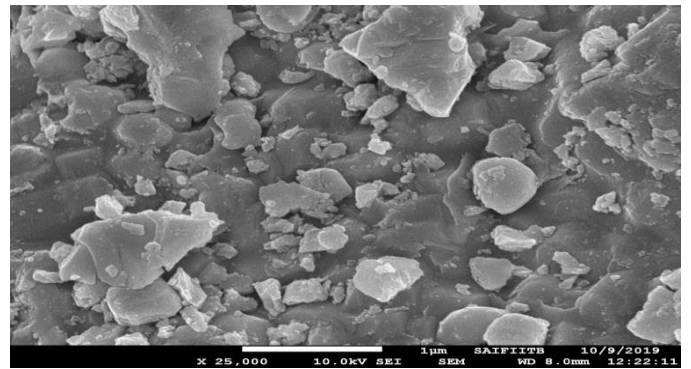


Fig.10 Temp. 700oC

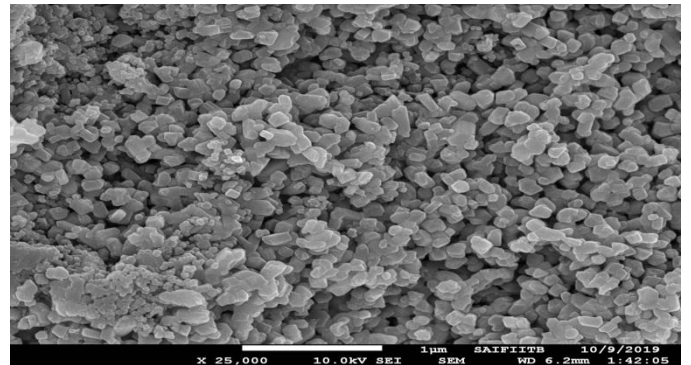


Fig.11 Temp. 750oC

### iv) TEM (Transmission electron microscopy)

Fig. (12 to 15) The established multi-spot rings of selected area diffraction patterns clearly indicate the single crystalline nature of the powder. The diffraction pattern also indicates decrease in grains size with increase in sintering temperature. It also confirms that homogeneity of the material decreases with increase in sintering temperature.

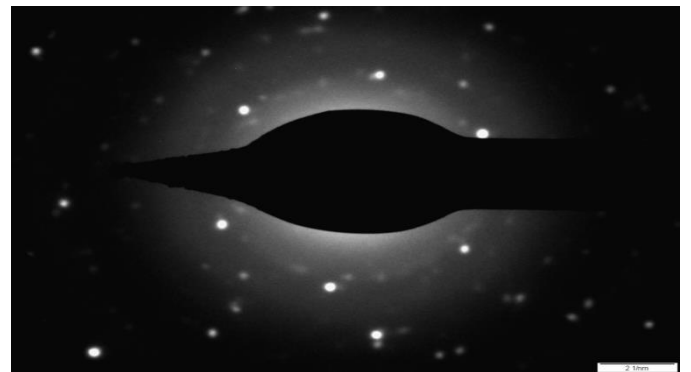


Fig.12 Temp. 600oC



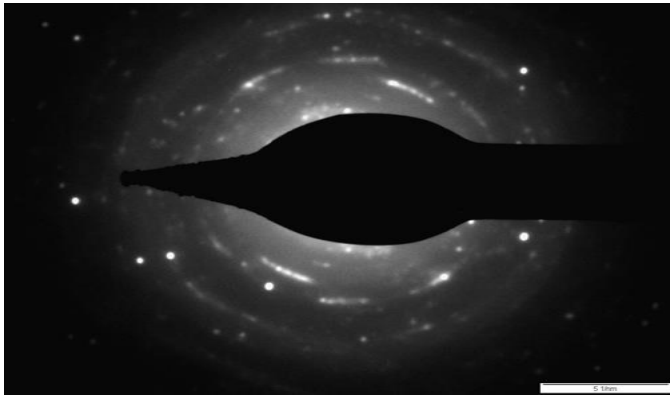


Fig.13 Temp. 650oC

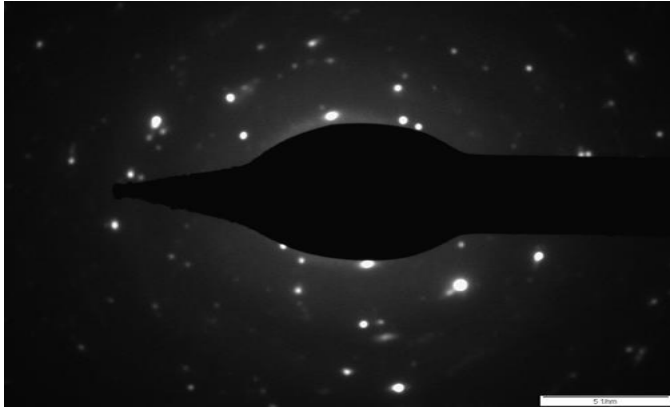


Fig.14 Temp. 700oC

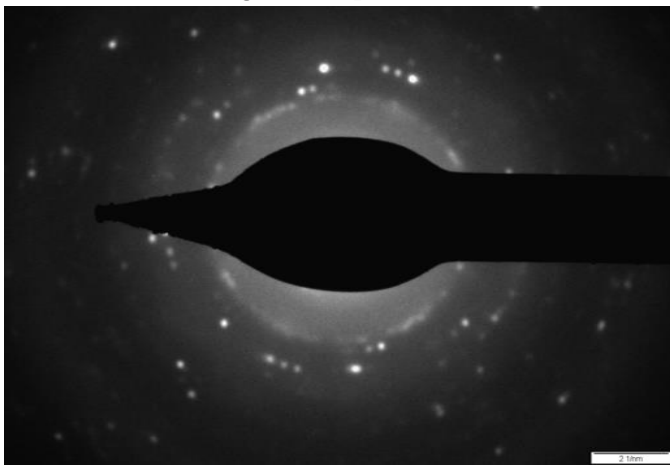


Fig.15 Temp. 750oC

#### IV. CONCLUSION

The  $\text{PbTiO}_3$  (Lead Titanate) has been successfully synthesized using wet chemical method. The effect of sintering temperature on various properties have been investigated. XRD Analysis shows that with increase in sintering temperature,  $\text{TiO}_2$  gets attached to the  $\text{PbO}$  to form single phase crystalline  $\text{PbTiO}_3$ . The

variation of  $c/a$  ratio with the sintering temperature clearly indicates decrease in  $c/a$  ratio along with sintering temperature. Decrease in  $c/a$  ratio indicates dispersion from tetragonality and an approach to the cubic phase with higher sintering temperature. The variation of average grain size with sintering temperature indicates decrease in average grain size with increasing sintering temperature. A slight increase in density is observed as sintering temperature increases up to  $750^\circ\text{C}$ . However, a density jump occurs at  $650^\circ\text{C}$ , and almost dense materials are achieved. Increasing the calcinations temperature to  $750^\circ\text{C}$ , results in decrease in intensity of the organic absorption bands and increased intensity of the absorption  $\text{Ti-O}$  bond. The organic residuals were completely eliminated when the derived powders were calcined at  $700^\circ\text{C}$ . SEM Analysis reveals that increase in sintering temperature results in shift from homogeneous material to heterogeneous material which has also been confirmed by TEM. Moreover, TEM reveals the single crystalline nature of the synthesized material.

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