

# Synthesis and Structural properties of lanthanum doped Lead Titanate Prepared by Wet Chemical Method

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## Abstract:

In this work, we report the synthesis and characterization of Lanthanum doped pure Lead titanate  $La_{(x)}Pb_{(1-x)}TiO_3$  by ( $x = 0.0, 0.2, 0.4$ ) samples were synthesized using chemical route and were characterized for structural studies using X-ray diffraction studies, FTIR, TGA and TEM. The  $LaPbTiO_3$  samples were further studied for structural properties at different calcination temperature. The XRD spectrum analysis infers the samples to be crystalline in nature as well as single phased. The XRD spectral study of as synthesized samples further reveals their crystallization into the tetragonal structure with  $pmm4$  space group. The intense reflection peaks witness the crystallinity and narrow full-width at half maximum indicates the higher average particle size. The average particle size calculated using Scherrer's formula was 27.40nm, 27.44 nm, 35.84 nm at calcination temperature 600°C, 700°C and 800°C for pure lead titanate, 24.93 nm, 23.70 nm, 44.40 nm (for 0.2 lanthanum concentration) and 20.24 nm, 22.58 nm and 25.52 nm (for 0.4 lanthanum concentration) at calcination temperature 600°C, 700°C and 800°C respectively for Lanthanum doped Lead titanate. The lattice parameters and the  $c/a$  ratio calculated for doped and undoped  $LaPbTiO_3$  which witness acquired trigonal structure. The additional structural studies of  $La_{(x)}Pb_{(1-x)}TiO_3$  ( $x = 0.0, 0.2, 0.4$ ) samples were performed using FTIR spectrum. The peaks assigned to the lanthanum lead titanate confirm its formation by chemical route. The corresponding bonding of materials was shown by the wavelength. Also, TEM result show high crystallinity of the synthesized materials. It has strong agreements with XRD result when powder is calcined at 700°C and 800°C but shows agglomeration in the crystals to form larger sized particles for the powders calcined at 600°C.

**Keywords:** Wet Chemical Route,  $PbTiO_3$ ,  $LaPbTiO_3$  Structural Properties XRD, FTIR, TEM.

Date of Submission: 22-08-2022

Date of Acceptance: 05-09-2022

## I. Introduction

Nowadays, the ferroelectric materials has been made popular growing in scientific development and research that contribute to the benefit of many applications such as actuator, transducers, non-volatile ferroelectric memories, dielectric for microelectronics and wireless communication [1-3]. Pure Lead Titanate ( $PbTiO_3$ ) and Lanthanum lead titanate ( $LaPbTiO_3$ ) is an essential class of piezoelectric and ferroelectric that donate to the technology and devices [4]. Lanthanum lead titanate have a special characteristic where it has the % phase conversion ratio found to have optimal conversion at compositions near the morphotropic phase boundary separating of its parent material such that cubic to tetragonal  $PbTiO_3$ . The LPT structure merely will show structural properties at room temperature when its phase has a non-Centro-symmetric structure such as tetragonal [5-6].

However, high leakage current, high dielectric losses, low resistivity which restrict the lanthanum lead titanate to be used for many applications. Also, synthesis of single-phase  $LaPbTiO_3$  is not easy due to the volatilization of the lanthanum atoms at high temperature and crystallization of impurity phases such as  $PbTiO_3$ ,  $LaPbTiO_3$  etc. are unavoidable. Hence, the impurity phases, as well as the presence of oxygen vacancies due to the inter conversion from  $Pb^{2+}$  to  $La^{2+}$ , generate the high leakage current and low resistivity in  $PbTiO_3$ . One of the solutions is the substitution of different ions in the Pb sites of  $PbO$  [7-8]. In the present work, rare earth Lanthanum (La) and doped  $PbTiO_3$  at A-site were synthesized by the wet chemical reaction method to investigate its structural properties

## II. Experimentation

In the present work molar proportions of lanthanum doped and un-doped  $PbTiO_3$  were studied. The synthesis of lanthanum doped and undoped lead titanate prepared by dissolving solid lead nitrate and lanthanum nitrate [Make:Sigma Aldrich] powder in pure water and stirred for 1 hr. at 100° C in reaction flask, when the

lead nitrate and lanthanum nitrate were dissolved in water, then a stoichiometric amount of Titanium Isopropoxide [Make: Sigma Aldrich] was added to the solution and the solution was refluxed at 100°C for 1 h and the solution was kept at 100°C for 12 h to get nano-crystalline powder. Nanocrystalline powders with various crystallite sizes were obtained by the powder at different sintering temperatures at 600°C, 700°C and 800°C. Structure and phase transformation analyses were investigated by XRD 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.

### III. Results And Discussions

#### X-RAY DIFFRACTION:

Structure of the samples was recorded at room temperature in the angular range of 2θ from 5° – 80°. The XRD result reveals that samples under study have trigonal perovskite structure with space group  $R\bar{3}c$ . According to the above results, it is observed that La ions are effectively assimilated into the crystal structure of  $PbTiO_3$ . Since, it is a big challenge to synthesize single-phase  $PbTiO_3$  because it mainly contaminated with secondary phases of  $PbO$  and  $TiO_2$ , we synthesized it with substitution to get its stable phase [9-12]. XRD pattern of the lanthanum doped and undoped  $PbTiO_3$  calcined at 600°C, 700°C and 800°C is shown in Fig.1, Fig. 2, and Fig. 3 respectively. At 600°C, the crystallization of tetragonal lanthanum doped lead titanate phase began along with impurity traces. At 600°C, all peaks can be indexed to the La doped  $PbTiO_3$  with a tetragonal structure. No peak corresponding to any of the source materials or allotropic forms was found, suggesting that a pure crystalline compound exists. The XRD diffraction pattern shows that the peak of 101 is decreasing and the peak of 110 is increasing. The peak 101 indicates a decrease in Pb and the peak 110 indicates an increase in the concentration of La. In pure lead titanate the peak related to the plane (100) is getting suppressed with the elevated sintering temperature. This peak may belong to the excess amount of  $PbO$  present in the material. As sintering temperature is increased, the peak belonging to  $PbO$  is vanished and pure phase  $PbTiO_3$  is obtained. The average crystallite size was calculated using Scherrer's formula [13-20]:

$$D = \frac{k\lambda}{\beta \cos(\theta)}$$

Where D is the crystallite size; k is a dimensionless shape factor with a value close to unity but typical value of about 0.9 for spherical particles;  $\lambda$  is the wavelength of X-ray used which is equal to 1.5406 Å;  $\beta$  is full width at half maximum (FWHM) in radian, and  $\theta$  is the Bragg angle. The average particle size calculated using Scherrer's formula was 27.40nm, 27.44 nm, 35.84 nm at calcination temperature 600°C, 700°C and 800°C for pure lead titanate and 24.93 nm, 23.70 nm, 44.40 nm for 0.2 lanthanum concentration and 20.24 nm, 22.58 nm and 25.52 nm for 0.4 lanthanum concentration at calcinated temperature 600°C, 700°C and 800°C for Lanthanum doped Lead titanate. The lattice parameters and the c/a ratio calculated for doped and undoped  $LaPbTiO_3$  which witness acquired trigonal structure. As shown in figure. The lattice parameters in c/a ratio calculated for  $PbTiO_3$  and  $LaPbTiO_3$ , which confirms the crystal structure of both the ceramics to be tetragonal.

Figure 4 shows the average grain size of the sample at calcination temperature 600°C, 700°C and 800°C at different doping concentrations. It can be seen that, when the sintering temperature is at 600°C and 700°C the average grain size decreased slightly as the lanthanum doping percentage is 0.2 moles. But slightly increases for the sintering temperature 800°C. When the sintering temperature at 600°C, 700°C and 800°C as lanthanum doping percent 0.4 mole the average grain size decreased.

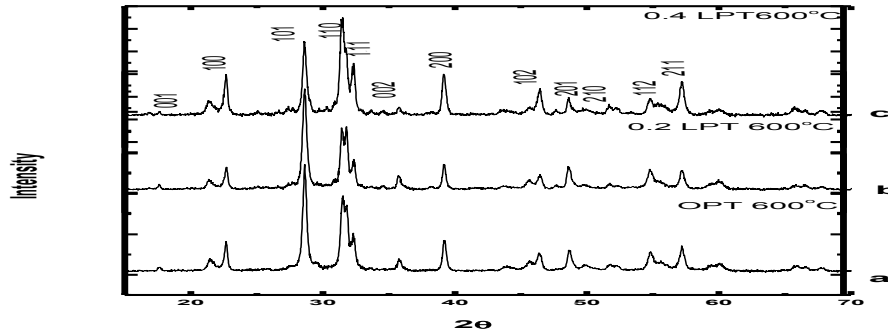
Figure 5 shows the c/a ratio of the sample at calcination temperature 600°C, 700°C and 800°C at different doping concentrations. The c/a ratios slightly decreases for sintering temperature at 600°C and 700°C and lanthanum doping 0.2. But for sintering temperature at 800°C and lanthanum concentration 0.2, the c/a ratio is very low which may be due to temperature and doping percentage. Also, when the sintering temperature is at 600°C and 700°C and doping concentration 0.4 mole, the c/a ratio slightly decreases and for the sintering temperature at 800°C, the c/a ratio is seen to increase. From this it is concluded that the material can be said to have changed from cubic structure to tetragonal structure.

Figure 6 show that lanthanum doped lead titanate at sintering temperature 600°C shows a decrease in cell volume as the doping concentration is increased from 0.0 to 0.2 and increases sharply when the doping concentration further increased from 0.2 to 0.4. Also, when the sintering temperature is 700°C, the cell volume decreases for increase in doping concentration from 0.0 to 0.2 and 0.2 to 0.4. Also when the sintering temperature is 800°C the cell volume increases for lanthanum concentration 0.0 to 0.2 and decreases at 0.4 concentrations.

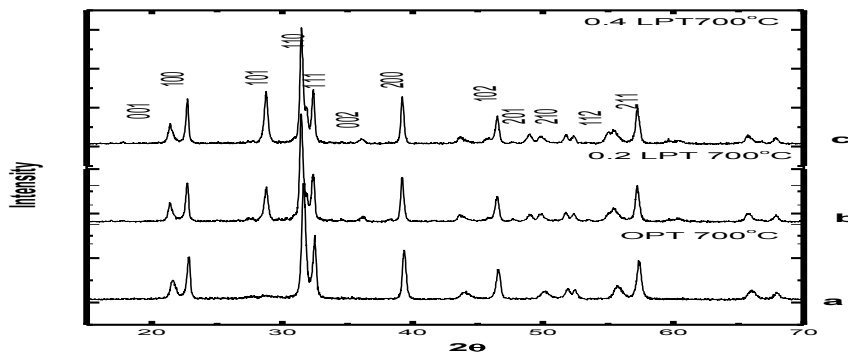
Figure 7 show that lanthanum doped lead titanate at sintering temperature 600°C shows an increase in cell density as the doping concentration is increased from 0.0 to 0.2 and decrease sharply when the doping

concentration further increased from 0.2 to 0.4. Also, when the sintering temperature is 700°C, the cell density increases for increase in doping concentration from 0.0 to 0.2 and 0.2 to 0.4. Also when the sintering temperature is 800°C the cell density decreases for lanthanum concentration 0.0 to 0.2 and increases at 0.4 concentrations.

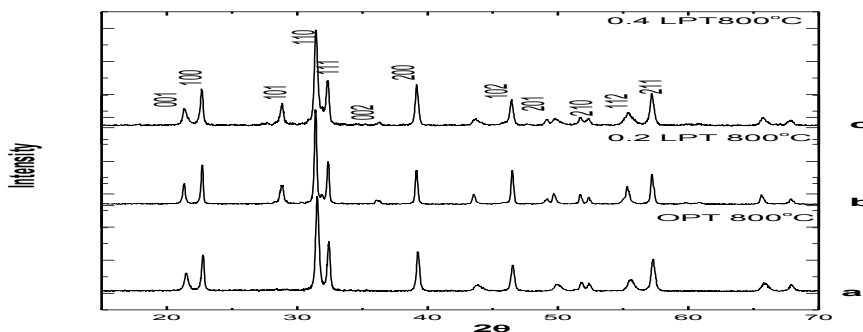
Sintering temperature affects material cell volume and material cell density. Sometimes low sintering temperature and increasing doping concentration lead to an increase in the impurity phase of the material, resulting fluctuations of cell volume and cell density.



**Figure 1: X-Ray Diffraction Patterns for Lanthanum doped and Undoped PbTiO<sub>3</sub> annealed in air at 600°C with varying Lanthanum in mole a) 0.0, b) 0.2 and c) 0.4**



**Figure 2: X-Ray Diffraction Patterns for Lanthanum doped and Undoped PbTiO<sub>3</sub> annealed in air at 700°C with varying Lanthanum in mole a) 0.0, b) 0.2 and c) 0.4**



**Figure 3: X-Ray Diffraction Patterns for Lanthanum doped and Undoped PbTiO<sub>3</sub> annealed in air at 800°C with varying Lanthanum in mole a) 0.0, b) 0.2 and c) 0.4**

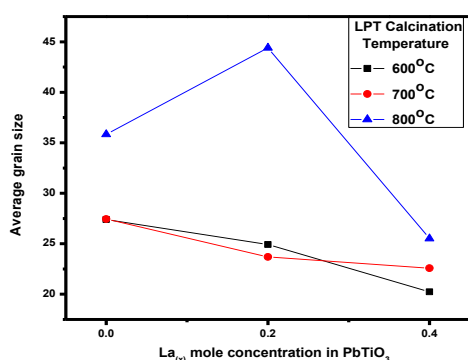


Fig.4: Variation of average grain size with doping concentration

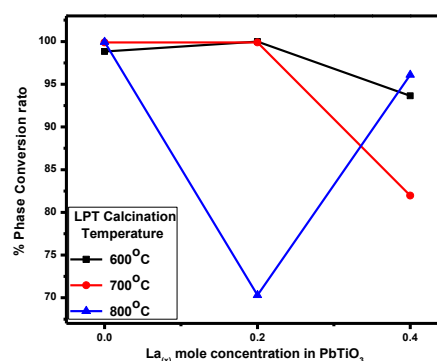


Fig.5: Variation of c/a with doping concentration

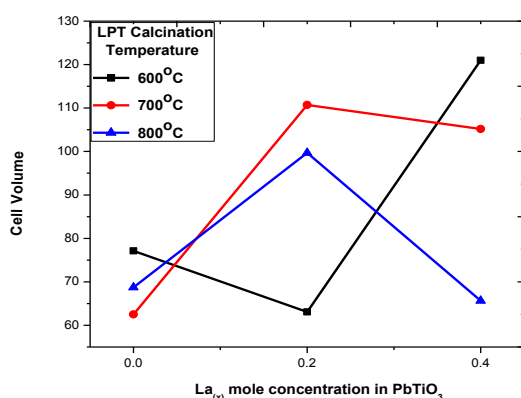


Fig.6: Variation of cell volume with doping concentration

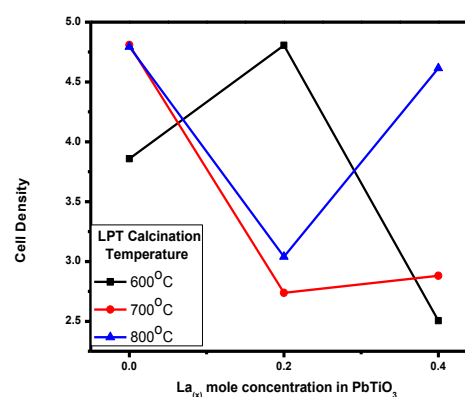


Fig.7: Variation of cell density with doping concentration

#### Fourier Transmission Infrared Spectroscopy Study (FTIR)

In figure 8 a, the sintering temperature is constant at 600°C and the doping concentration of lanthanum increases at the rate of 0.0, 0.2 and 0.4. When the lanthanum concentration is 0.0, the emission peaks are at 575.34, 1383.86 cm<sup>-1</sup>. Considering this, since the molecular vibration is slightly lower, the emission peaks are not sharp, which suggests that the vibration is reduced due to some impurity during doping of La with Pb. As the doping ratio increased and the impurity decreased, the molecular vibration increased and the peak became sharper. Also confirms the formation of lanthanum doped lead titanate sintering temperature at 600°C. Some assignments are general and show a hydrogen bonded O-H stretch, indicating moisture.

In Figure 8 b, the sintering temperature is constant at 700°C and the doping concentration of lanthanum increases at the rate of 0.0, 0.2 and 0.4. When the concentration of lanthanum is 0.0, the emission peak at 568.77, 1033.29 cm<sup>-1</sup> is obtained. Considering this, since the molecular vibration is slightly lower, the emission peaks are not sharp, which indicates that some impurity during doping of La with Pb reduces the vibration. As the doping amount increased and impurities decreased, the molecular vibration increased and the peak became sharper. Also agree to produce lanthanum doped lead titanate sintering temperature at 700°C. Some assignments are general and show a hydrogen bonded O-H stretch, indicating moisture.

Figure 8 c centering temperature is 800°C and the doping concentration of lanthanum increases as 0.0, 0.2 and 0.4. When the lanthanum concentration is 0.0, the emission peak are at 558.95, 1383.40 cm<sup>-1</sup>, while for 0.2 lanthanum concentration, the emission peak is 570.03, 1222.46 cm<sup>-1</sup> and for 0.4 lanthanum concentration, 576.18 yielding 1088.31 cm<sup>-1</sup>. This shows that in molecular vibration when lanthanum concentration is 0.0 it vibrates with PbO. When the lanthanum concentration is 0.2 it shows that the vibration increases due to overlapping of La with Pb. Also, when the doping ratio is 0.4, the Pb decreases due to the increase in the amount of lanthanum, Also vibration decreases due to the bonding structure. But the emission peak is sharp. This confirms the formation of lanthanum doped lead titanate. Also in figure 8 a, b & c peak 3368.88 cm<sup>-1</sup>, 3462.84 cm<sup>-1</sup> and 3472.91 cm<sup>-1</sup>. confirms hydrogen bonded O-H stretch, which may be due to the presence of moisture in the powder while analysis of sample in the instrumental laboratory in the formation of pure and doped lead titanate at different sintering temperature. [21-25]

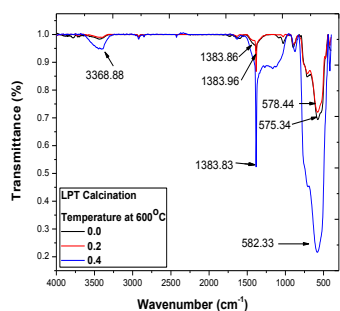


Fig. 8 (a)

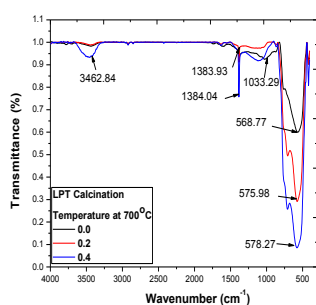


Fig. 8 (b)

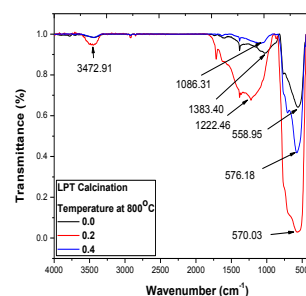


Fig. 8 (c)

### Transmission Electron Microscope Study (TEM)

Figures 9 (a, b & c), 10 (a, b & c) and 11 (a, b & c) reveal the TEM diffraction spot patterns of tetragonal structure of 0.0, 0.2 and 0.4 lanthanum doped lead titanate powder calcined at 600°C, 700°C and 800°C indicate that the nano-particles are highly crystalline and are in agreement with the XRD data. Some of the selected images are shown here. The observed grain size and its deviation from crystallite size depict agglomerations of the crystals to form the clusters of larger size. The grains within the range of 9.51 to 280.21 nm are observed, with comparable size of the agglomerations with the values calculated for nano-crystallites from XRD. The average crystalline size calculated from XRD is 28.00 nm.

TEM images for 0.4 lanthanum concentration doped lead titanate powder calcined at 600°C, 700°C and 800°C show grain growth in the range of 9.18 nm to 394.62 nm. The average crystallite size calculated from XRD is 20.24 nm; the diffraction pattern has an average crystals. Some variations show crystals dispersed to form aggregates.

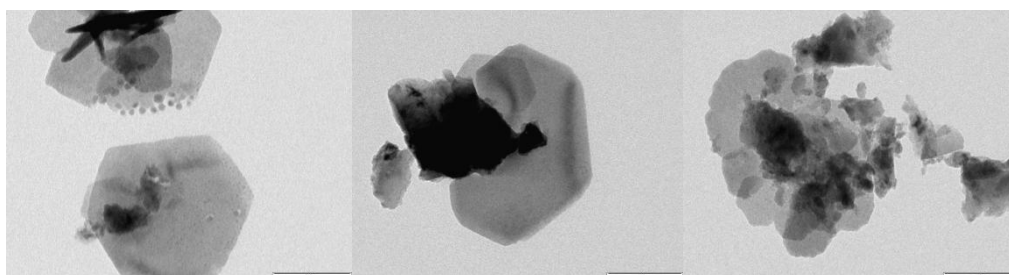


Fig. 9 (a)

Fig. 9 (b)

Fig. 9 (c)

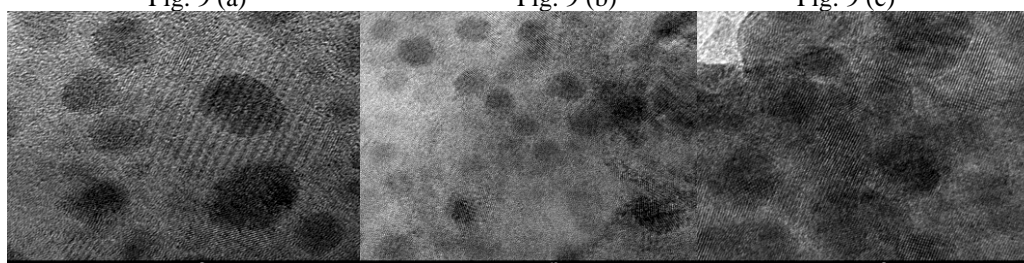


Fig. 10 (a)

Fig. 10 (b)

Fig. 10 (c)

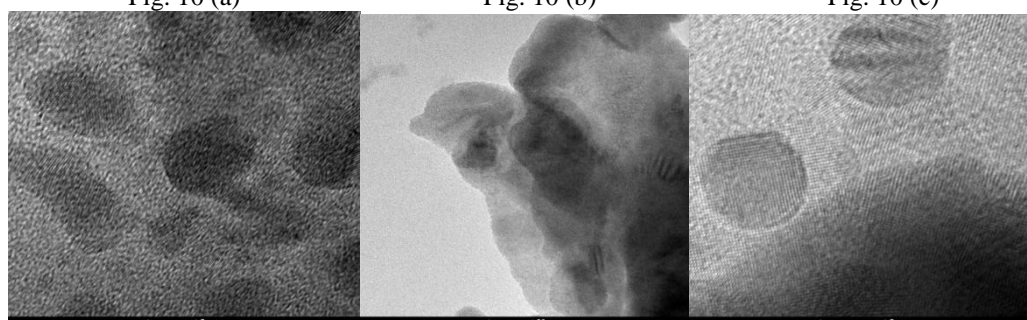


Fig. 11 (a)

Fig. 11 (b)

Fig. 11 (c)

#### IV. Conclusions:

XRD confirms lowest crystallite size 20.24 nm and average crystallite size 28.00 nm. C/a ratio calculated shows lattice anisotropy and hence tetragonal structure. The highest value of c/a for 0.4 molar concentration of lanthanum strongly agrees with the tetragonal phase conversion of the doped lead titanate. The % phase conversion ratio for the tetragonality is 99.99% which is less than 100 % since it is compared with pure lead titanate synthesized experimentally.

FTIR spectrum and peaks associated to the lanthanum lead titanate show its confirmation with the structure. The corresponding bonding of materials shows the wavelength and it confirms synthesis of lanthanum doped lead titanate.

Also, TEM result show high crystallinity of the synthesized materials. It is in strong agreement with XRD result when powder is calcined at 700°C and 800°C but shows agglomeration in the crystals to form larger sized particles for the powders calcined at 600°C. It may affect the properties of the materials.

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N. V. Galande, et. al. "Synthesis and Structural properties of lanthanum doped Lead Titanate Prepared by Wet Chemical Method." *IOSR Journal of Applied Physics (IOSR-JAP)*, 14(5), 2022, pp. 13-18.