RIETVELD REFINEMENT OF CALCIUM MODIFIED LEAD TITANATE (PCT) SAMPLE USING FULLPROF SUITE

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Abstract – The Lead Titanate (PT) and Calcium modified Lead Titanate (PCT) sample was synthesized by adopting the standard method of preparation like the Solid-State reaction. At room temperature, the structural analysis was done by utilizing the X-ray diffraction (XRD) method. The careful Rietveld refinement of Calcium modified Lead Titanate done using the FULLPROF Programming suite. The direct lattice parameter discovered to be a = b = 3.9015 Å and c = 4.1280 Å. The investigated crystal system is tetragonal with a space group discovered to be P4mm and the ATZ value is 303.078. The microstructural analysis done using Scanning Electron Microscopy (SEM) also Composition analysis was done with EDX analysis.

Keywords: Lead Titanate, Calcium modified Lead Titanate, XRD, Rietveld refinement, SEM, EDX

I. INTRODUCTION

Ceramics are the important class of materials exploited for significant technological applications. Lead Titanate ($PbTiO_3$) sample is one of the class of material that possesses a perovskite (ABO3) kind of structure under the ferroelectric category. It possesses high Curie temperature, high pyroelectric coefficient, and low dielectric constant. It also suggests high spontaneous polarization. It is the most appropriate material used in electronics gadgets like capacitors, thermistors, ultrasonic transducers, and optoelectronics. The ferroelectric ceramic that has not been ended up being an innovatively tremendous material. As a consequence of its large pyroelectric coefficient and reasonably low permittivity. It additionally suggests the application in a pyroelectric infrared detector Lead Titanate ($PbTiO_3$) is broadly shown applications as a piezoelectric material because of ferroelectric perovskite arrangement, for example, PbZr, Pb(x)Ca(1-x), and Pb, etc [1, 2]. The Lead Titanate material highlights a sturdy anisotropy at 490°C temperature, which creates all through cooling via the cubic to tetragonal phase change. The anisotropy of the Lead Titanate sample as envisioned as c/a ratio is ~1.06 which leads to tetragonality of the unit cell. It is suggested that a c/a large will be best for advanced structural study and electrical characterization [3]. It has been seen that this problem may be diminished with the aid of editing the Lead Titanate ($PbTiO_3$) with different additives, for example, Ca, Sn, Sr, Ba and so forth to reap a crack-free ceramics. This additionally enhances the electrical and structural properties of the Lead Titanate. It has been observed that the substitute of Ca^{2+} brings about reducing cubic to tetragonal phase transformation temperature and with an appropriate amount, it is able to be brought down to room temperature. The exact crystal structure of the prepared sample has been studied at room temperature by studying the X-ray Powder diffraction (XRD) pattern. XRD pattern investigation was done with the help of Fullprof suite programming software by applying Rietveld approach [4, 5].

II. EXPERIMENTAL WORK

Synthesis of Calcium modified Lead Titanate [PCT] Sample

To hold out the examination, the standard method of solid-state synthesis was employed for the preparation of calcium modified Lead Titanate (PCT) sample. Stoichiometric amounts of high purity calcium oxide powder, CaO (all over ~ 99.9% purity) were cautiously weighted and was doped in a proportion of x = 0.00, 0.05, 0.10, 0.15, 0.20, 0.25 with synthesized Lead Titanate ($PbTiO_3$) the powder has given within the equation. This powder mixture was mixed in an agate mortar for two hours. To scale back the impurities and acquire homogeneity of the ultimate compound the samples were calcined in silica crucible at 850°C for 5 hrs followed by furnace cooling. The calcined material was once more ground thoroughly in the required stoichiometric proportion. The following are the series of PCT compounds that had been prepared.

1. $Pb_{1-x}Ca_xTiO_3$ (x=0.00) - PCT100
2. $Pb_{1-x}Ca_xTiO_3$ (x=0.05) - PCT101
3. $Pb_{1-x}Ca_xTiO_3$ (x=0.10) - PCT102
4. $Pb_{1-x}Ca_xTiO_3$ (x=0.15) - PCT103
5. $Pb_{1-x}Ca_xTiO_3$ (x=0.20) - PCT104
6. $Pb_{1-x}Ca_xTiO_3$ (x=0.25) - PCT105

The phase identification and quantification have been executed of the starting oxides mixture and calcined samples via X-ray diffraction method for powder sample on X-ray Powder Diffractometer (D – 8 Advance Bruker axs) over an extensive range of Bragg angles ($20^o \leq 2q \leq 80^o$) at room temperature. The scanning electron micrographs of sintered samples show the uniform distribution and densely packed grains over the complete surface [6].

CHARACTERIZATION

The analysis of the crystalline phase at room temperature is done by an X-ray powder diffraction pattern by using X-ray powder Diffractometer of Cu-rotating anode primarily based with make D – 8 Advance Bruker axs using Cu-K_α radiation of wavelength λ = 1.542 Å operating over a range of Bragg angles ($20^o \leq 2\square \leq 80^o$) [7]. The microstructural analysis of the prepared sample has been contemplated utilizing JEOL 6360A Analytical Scanning Electron Microscopy. The composition of prepared material analysis was done using Energy-Dispersive X-Ray (EDX), to investigate the presence of all elements within the grown material [8].

III. RESULT AND DISCUSSION

The XRD patterns recorded for Lead Titanate ($PbTiO_3$) sample at room temperature has been shown in Figure 1. The X-ray powder diffraction pattern accommodates well-resolved peaks and the calculation shows tetragonal symmetry with indexing to the P4mm space group. All the diffraction peaks are compatible with JCPDS. The result shows peaks relating to reflection planes (001), (100), (101), (110), (111), (002), (200), (102), (201), (210), (112), (211), and (202) provide confirmation of the development of single-phase with tetragonal symmetry for the $PbTiO_3$ the sample under investigation [9].

The Analysis of the XRD pattern done by means of utilizing the Rietveld technique using Fullprof Suite programming software [10] using the P4mm space group. The Rietveld refined X-ray powder diffraction patterns of the Lead Titanate sample have been shown in Figure.2.

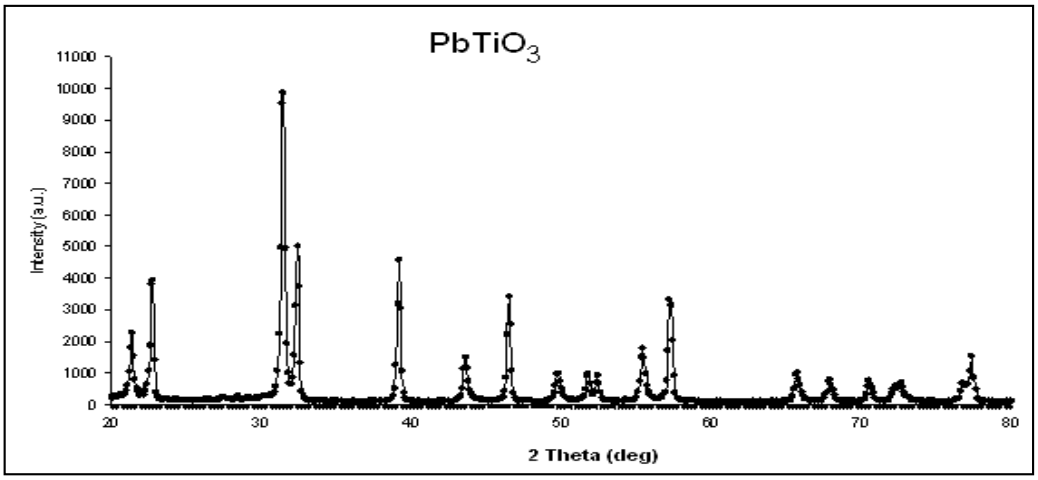


Fig. 1: The XRD pattern of the $PbTiO_3$ (PCT100) sample

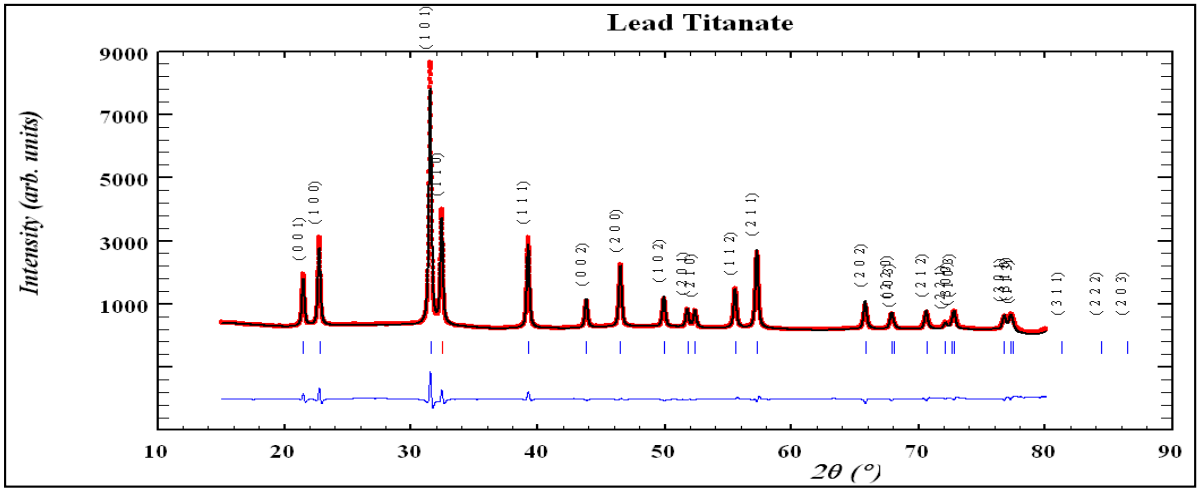


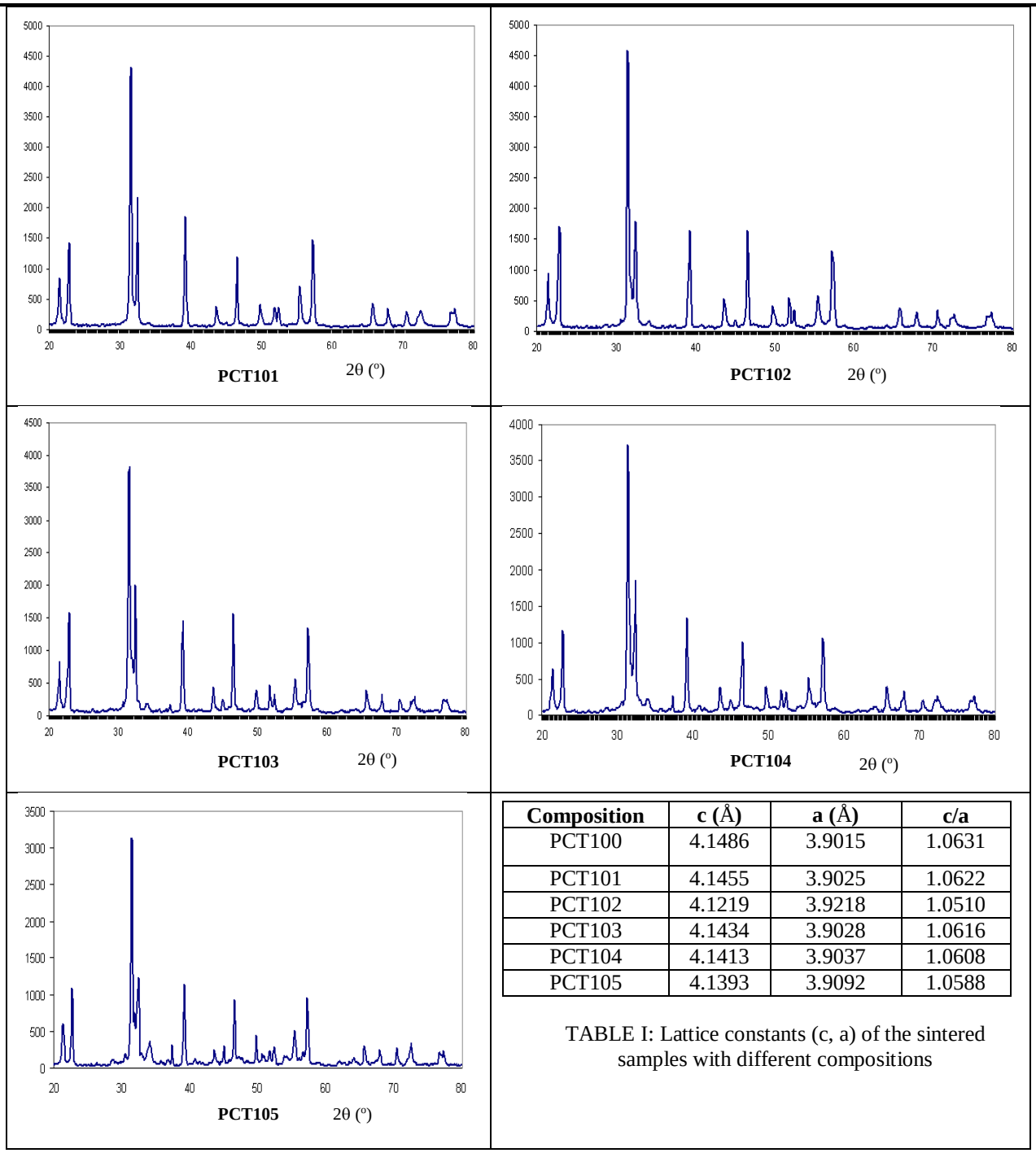
Fig. 2: Rietveld refined X-ray powder Diffraction (XRD) pattern for the $PbTiO_3$ (PCT100) sample.

In profiles it has been concluded that for observed results and calculated results are coordinating with each other and each one allowed Bragg 2θ positions through experimental peaks result to the P4mm space group. All through the refinement, the positions of oxygen are taken as free parameters to urge extra refined values and the Exceptional parameters like lattice constants, shape parameters and scale factors are taken as free parameters in the course of the appropriate fitting.

The atomic fractional positions for Lead and Titanium are fixed. For Lead, Titanium, and Oxygen the occupancies and the Isothermal parameters are kept constant.

The global parameters like background and scale factors had been refined inside the initiative of refinement. In succession the structural parameters like profile shape, width parameter, lattice parameters, preferred orientation, atomic coordinate's asymmetry and have been refined [10-12].

From the observation, it was clear that an experimental point represented by the circles and the solid-line indicates Rietveld data through refinement process. The differentiation of experimental and refined data through the FULLPROF suite given by bottom line in the Figure 2. The permitted Bragg peaks were marked with 2θ positions.

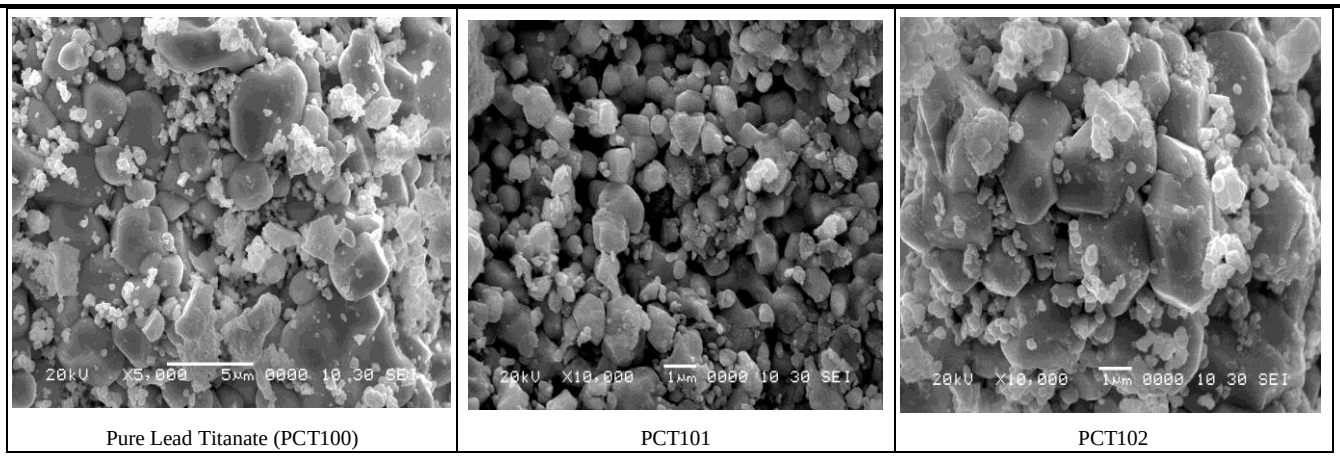


Composition	c (Å)	a (Å)	c/a
PCT100	4.1486	3.9015	1.0631
PCT101	4.1455	3.9025	1.0622
PCT102	4.1219	3.9218	1.0510
PCT103	4.1434	3.9028	1.0616
PCT104	4.1413	3.9037	1.0608
PCT105	4.1393	3.9092	1.0588

TABLE I: Lattice constants (c, a) of the sintered samples with different compositions

Fig. 3: X-Ray diffraction of PCT with varied Ca proportion (where, x = 0.05, 0.10, 0.15, 0.20, 0.25)

Figure 3 shows that with the rise in Ca^{2+} substitution% the XRD peak intensity decreases, recommending the decrease in homogeneity and crystallization with the increase in Ca^{2+} fraction in pure Lead Titanate sample. All peaks are sharp and particular in Ca^{2+} modified Lead Titanate sample suggesting the higher solubility of Ca^{2+} in the Lead Titanate system [13]. From the intensity peak the full-width half maximum (FWHM) indicates that the polycrystalline highlights a homogeneous perovskite structure. All the peaks were indexed with care and the lattice constants 'a' and 'c' were determined by utilizing hkl values as mentioned in Table I. These results attribute that the Ca^{2+} ions (A – site substitution) occupying Pb^{2+} ions site having lesser ionic radius (Ca^{2+} = 0.99 Å, Pb^{2+} = 1.20 Å). From the observation it is suggested that the reduction in c/a ratio indicates good mechanical stability and a perovskite-phase with a tetragonal structure [14, 15].



Pure Lead Titanate (PCT100) | PCT101 | PCT102

Fig. 4: Scanning Electron Microscopy of pure Lead Titanate (PCT100) and PCT101, PCT102 sample

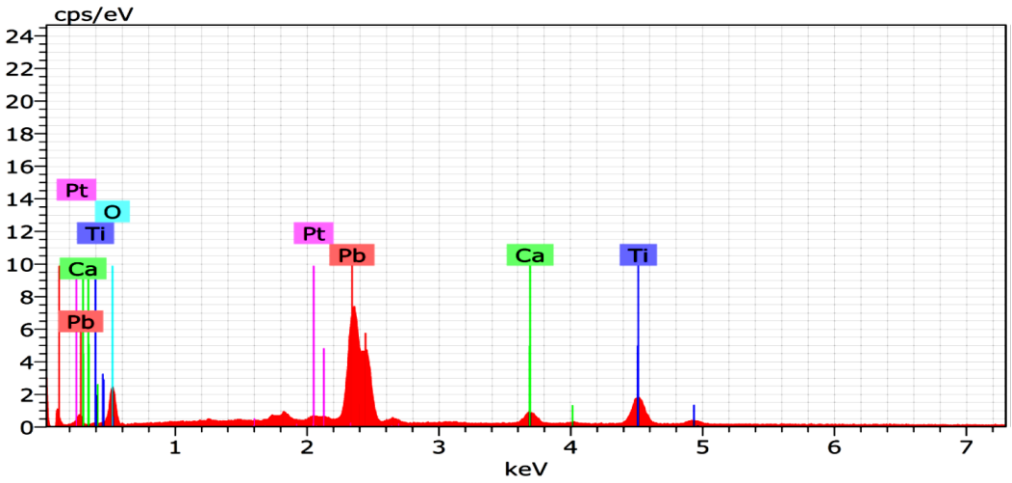


Fig. 5: Elemental Analysis of Ca modified $PbTiO_3$ sample

Figure 4, shows that the uniform distribution and densely packed grains over the total surface as Calcium content is increased typical characteristics of exaggerated grain growth, a duplex microstructure is ascertained. The average grain size of the sample determined by exploitation Contrell's methodology was found to be within the range of 1 – 2 µm.

Figure 5, shows the Energy-dispersive X-ray (EDX) investigation of one of the representative graphs for Calcium modified Lead Titanate ceramics of composition with x = 0.05. This EDX result confirm the existence of the desired element within the composed material and the elements are seen within the spectrum like Lead (Pb), Calcium (Ca), and Titanium (Ti), and so on which gives associated peaks [16]. The experimental and calculated observation of prepared sample is given in the Table II.

TABLE II: Experimental observation of EDS Wt% and Calculated Wt % of Ca modified Lead Titanate ($PbTiO_3$)

Element	Cal Wt %	at %	Error	EDS Wt %
Pb	73.12	21.60	2.60	69.28
Ti	17.64	22.56	0.54	16.72
O	14.47	55.37	1.86	13.71
Ca	0.31	0.48	0.04	0.38

Figure 6 represents the Rietveld refined XRD pattern of calcium substituted Lead Titanate with Ca proportion x = 0.05. The sixth-order polynomial used for background fitting and pseudo-Voigt profiles are depicted for peak shapes [17].

The evaluation of the calculated data for fitting quality is resolved by Profile factor (R_p), Weighted-profile factor, expected weight factor, Bragg factor, reduced chi-square factor and crystallographic R_F factor which are characterized as follows [18].

Profile factor,

$$R_p = 100 \frac{\sum_{i=1,n} |y_i - y_{c,i}|}{\sum_{i=1,n} y_i} \quad \text{----------} \quad (1)$$

Where, 'y_i' = experimental observed point

'$y_{c,I}$' = calculated point

'n' = number of data points.

Weighted-profile factor,

$$R_{wp} = 100\left[\frac{\sum_{i=1,n}\omega_i|y_i - y_{c,i}|2}{\sum_{i=1,n}\omega_i yi^2}\right]^{1/2} \quad \text{----------} \quad (2)$$

Where, $\omega_i = \frac{1}{\sigma i^2}$, σi^2 = observation variance

Expected-weight factor,

$$R_{exp} = 100\left|\frac{n-p}{\sum_{i=1,n}\omega_i yi^2}\right|^{1/2} \quad \text{----------} \quad (3)$$

where, (n – p) = number of degrees of freedom
'n' = total number of experimental points
'p' = number of refined parameters [19].

Reduced chi-square (χ^2),

$$\chi^2 = \left[\frac{R_{wp}}{R_{exp}}\right]^2 \quad \text{----------} \quad (4)$$

Bragg factor (R_B),

$$R_B = 100\frac{\sum_h|I_{obs,h} - I_{calc,h}|}{\sum_h I_{obs,h}} \quad \text{----------} \quad (5)$$

where, 'h' = vector which levels the Bragg reflections.
$I_{obs,h}$ = observed integrated intensities
$I_{cal,h}$ = calculated intensities.

Crystallographic-R_F factor,

$$R_F = 100\frac{\sum_h|F_{obs,h} - F_{cal,h}|}{\sum_h F_{obs,h}} \quad \text{----------} \quad (6)$$

The Rietveld refinement yields unit cell parameters and volume which is arranged in Table 3 alongside the errors (in brackets). The refinement parameters like reliability factors (R-factors) and chi-square obtained are recorded inside the Table 3 [20]. The low value of goodness of fit (χ^2) ascertained that the goodness of refinement obtained. The observed lattice constant is in full coordination with cited results in the review papers. The axial ratio acknowledged being 1.05804 but the earlier reported value is 1.0614. The c/a value investigated that the material is more stable and compact [21].

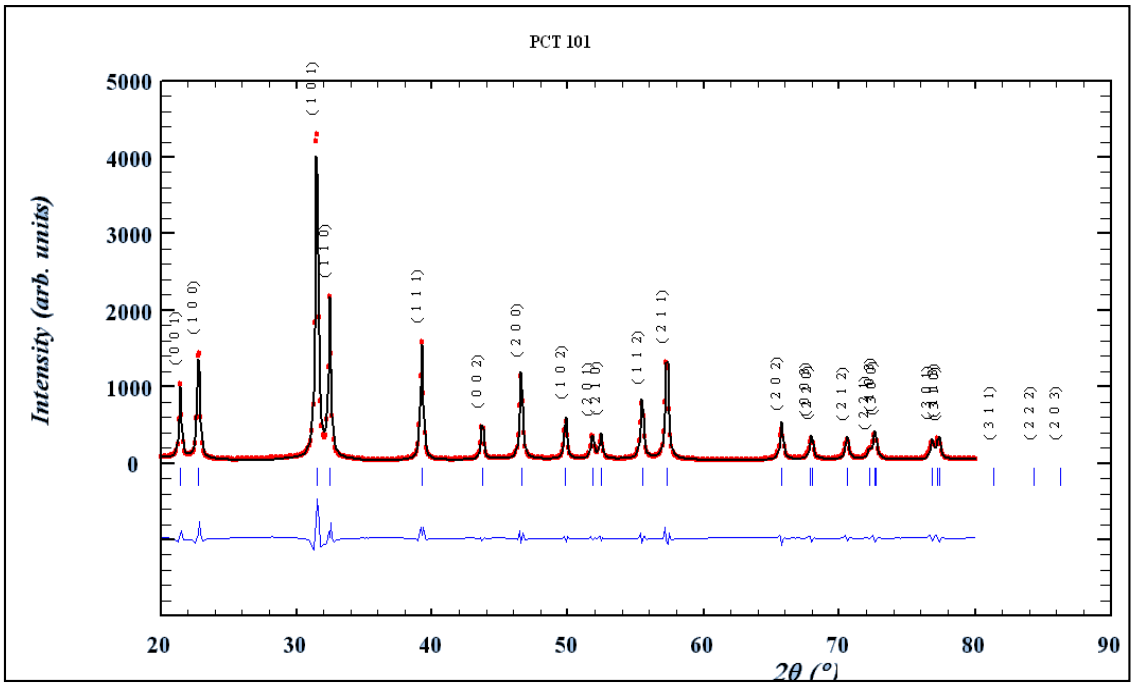


Fig. 6: Rietveld refined XRD pattern of calcium substituted Lead Titanate (with x = 0.05)

Throughout the fitting, the Lattice constants, fractional atomic positions, occupancy, and so forth were taken as free parameters. The listing of lattice constants, the goodness of the fitting is given in Table 3.

TABLE III: Reliability factors and chi-square, lattice constant, ATZ and Grain size for the Calcium modified $PbTiO_3$ sample. The bracket terms in the table indicate the errors of the lattice constants.

Parameters	**PCT101 x = 0.05**	**PCT102 x = 0.10**	**PCT103 x = 0.15**
R_p	11.6	11.0	10.9
R_{wp}	14.2	12.7	12.4
R_{Bragg}	4.67	1.84	2.17
R_F	4.39	1.34	1.66
χ^2	2.62	1.80	1.54
a = b (Å)	3.901577 (0.000035)	3.897781 (0.000130)	3.897943 (0.000123)
c (Å)	4.128031 (0.000062)	4.139768 (0.000221)	4.140274 (0.000209)
ATZ	303.078	303.078	303.078
Grain size (µm)	1.18	1.52	0.99
Volume (Å)	62.838 (0.001)	62.894 (0.004)	62.907 (0.004)

IV. CONCLUSIONS

X-ray powder diffraction of all prepared samples shows a single-phase Calcium modified Lead Titanate (PCT) sample synthesized by following the standard preparation method like solid-state reaction technique. It's been observed the sample is having tetragonal symmetry with space group discovered to be P4mm [22]. From the Rietveld investigation, it was found that for x = 0.05 of Ca substitution, unit cell lattice constants are a = b = 3.901577 Å and c = 4.128031 Å. The c/a ratio obtained through analysis is approximately 1.06 which is very close to the reported value and the ATZ value obtained through investigation is 303.078.

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