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Structural characterization of Lead Titanate ($PbTiO_3$) sample using FULLPROF

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Abstract: *Lead Titanate ($PbTiO_3$) sample was prepared using Solid State reaction method. The structural analysis done using X-ray diffraction (XRD) at room temperature. The crystal structure has been refined using FULLPROF program by employing Rietveld analysis. The direct lattice parameter found out to be a = b = 3.9015 Å and c = 4.1280 Å. The crystal system is tetragonal with space group found out to be P4mm and the ATZ value is 303.078. The micro structural analysis done using Scanning Electron Microscope (SEM).*
Keywords: *Lead Titanate, XRD, Rietveld analysis, SEM*

I. Introduction

Crystals of the perovskite family, such as PbTiO3, SrTiO3 and, have been of constant interest because some of these materials show ferroelectric behavior and undergo structural phase transitions [1]. PbTiO3 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 [2]. Lead titanate (PbTiO3, PT) is a ferroelectric ceramic that has not been proved to be a technologically important material by itself but is a significant component material in electronics such as capacitors, ultrasonic transducers, thermistors, and optoelectronics [3–7]. It is also a promising material for pyroelectric infrared detector applications because of its large pyroelectric coefficient and relatively low permittivity [8, 9]. PbTiO3 (PT) has also been extensively used in a range of piezoelectric applications, as well as being the end member of technologically significant, ferroelectric perovskite series such as PbZr (PZT), Pb(x)Ca(1-x) (PZN-PT), and Pb and so forth. At ambient temperature, the material has a strong anisotropy which develops during cooling through the cubic-tetragonal phase transition of approximately 490°C. The anisotropy as measured by the tetragonality of the unit cell, c/a, may be as high as ~1.06. A large c/a ratio is considered favorable for enhanced electrical properties [10]. Here we have prepared PT by solid state reaction method to study its crystal structure. The detailed crystal structure has been studied by analyzing the XRD pattern recorded at room temperature. The XRD pattern has been analyzed by employing Rietveld method with the help of Fullprof suite software.

II. Experimental Work

Synthesis of pure Lead Titanate [$PbTiO_3$]

The starting materials were commercially available Lead Carbonate, PbCO3 (GR) and Titanium dioxide, TiO_2 (GR) with 99% purity. The two oxide powders exhibited an average particle size in the range of 3.0 to 5.0 µm. $PbTiO_3$ powder was synthesized by the solid state reaction of thoroughly ground mixtures of $PbCO_3$ and TiO_2 powders that were milled in the required stoichiometric ratio. The milling operation was carried out for 5h. High purity (99%) agate mortar was used as the milling media. After milling powder sample was calcinated at 900^{o}C for 5h in silica crucible, in order to investigate the formation of $PbTiO_3$ powders were conventionally synthesized by solid state reaction between $PbCO_3$ and TiO_2 at 900^{o}C. The phase identification and quantification was performed of the starting oxides mixture and calcined samples by X – ray powder diffraction method on X –Ray Diffractometer (D – 8 Advance Bruker axs) over a wide range of Bragg angles ($20^o \leq 2\theta \leq 80^o$) at room temperature. The scanning electron micrographs of sintered samples show the uniform distribution and densely packed grains over the entire surface.

III. Characterization

The crystalline phase of the sample have been examined by powder X-ray diffraction pattern using Cu-rotating anode based X –Ray Diffractometer (D – 8 Advance Bruker axs) using Cu-K_α radiation (λ = 1.542 Å) operating over a wide range of Bragg angles ($20^o \leq 2\theta \leq 80^o$) at room temperature. The surface morphology of the sample has been studied using JEOL 6360A Analytical Scanning Electron Microscope.

IV. Result And Discussion

The XRD patterns recorded for $PbTiO_3$ sample at room temperature has been shown in Fig. 1. The diffraction pattern consists of well resolved peaks which have been indexed to P4mm space group with tetragonal symmetry. All the diffraction peaks are well matched with JCPDS. The observed diffraction peaks corresponding to reflection planes (001), (100), (101), (110), (111), (002), (200), (102), (201), (210), (112), (211) and (202) provide a clear evidence for the formation of single phase with tetragonal symmetry for the $PbTiO_3$ sample under study.

The XRD pattern has been analyzed by employing Rietveld method using Fullprof Suite program [11] using the P4mm space group. The X-ray diffraction patterns along with Rietveld refined data has been shown in the Fig. 2.

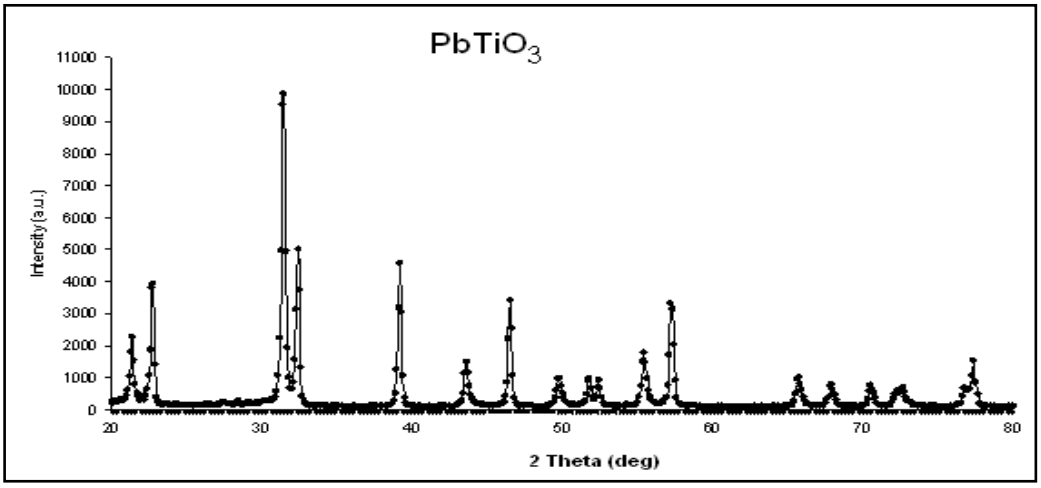

Fig. 1. The XRD pattern of $PbTiO_3$ sample.

It could be seen that the profiles for observed and calculated ones are matching to each other and all the experimental peaks are allowed Bragg 2θ positions for P4mm space group. The oxygen positions have been taken as free parameters during the refinement. The atomic fractional positions for Lead and Titanium have been fixed. Isothermal parameters and occupancies are fixed for Lead, Titanium and Oxygen. Other parameters such as lattice constants, scale factors and shape parameters have been taken as free parameters during the fitting.
The global parameters such as background and scale factors were refined in the first step of refinement. In the next step, the structural parameters such as lattice parameters, profile shape, width parameter, preferred orientation, asymmetry and atomic coordinates were refined in sequence.

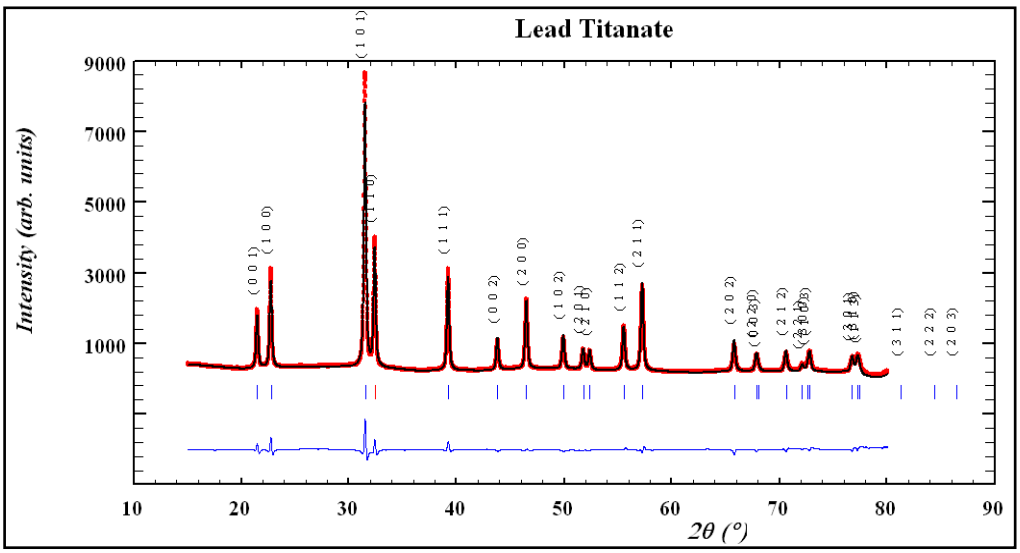

Fig. 2: Rietveld refined XRD pattern for the $PbTiO_3$ sample. The circles represent experimental points and the solid line represents Rietveld refined data. The bottom line shows the difference between the experimental and refined data. The marked 2θ positions are the allowed Bragg peaks.

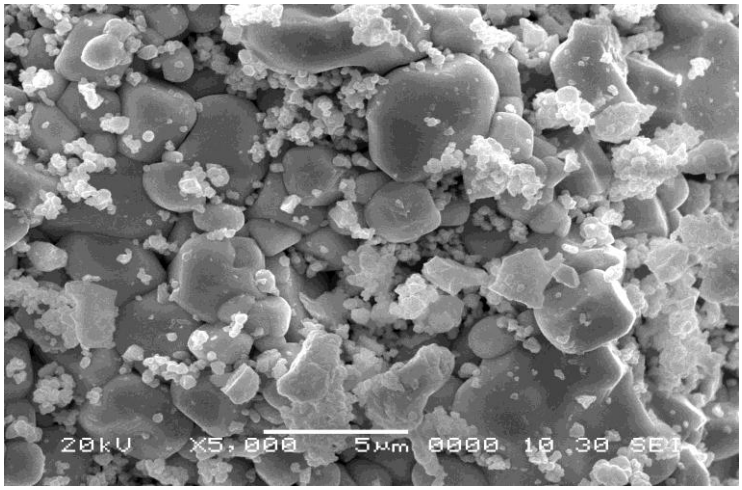

Fig. 3: Scanning Electron Microscopy of pure Lead Titanate sample

Background has been fitted with sixth order polynomial while the peak shapes have been described by pseudo-voigt profiles. The fractional atomic positions and isothermal parameters of the atoms obtained from Rietveld refinement are given in Table 1.

The fitting quality of the experimental data have been assessed by computing the parameters such as the "goodness of fit" χ^2, and various R-factors such as R_p (profile factor), R_{wp} (weighted profile factor), R_{exp} (expected weighted profile factor), R_B (Bragg factor) and R_F (crystallographic factor) which are defined as follows[12]

Profile factor,

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

Where, 'y_i' is the observed point (experimental) and '$y_{c,I}$' is the calculated point and n represents the number of data points.

Table 1: Fractional atomic coordinates and isothermal parameter of different atoms obtained from the Rietveld analysis of XRD pattern for the $PbTiO_3$ sample.

Sample	**$PbTiO_3$**			
Parameters → Atoms ↓	**X**	**Y**	**Z**	**B**
Pb1	0.00000	0.00000	0.00580	0.70300
Ti2	0.50000	0.50000	0.55387	0.05900
O3	0.50000	0.50000	0.14343	0.35100
O4	0.50000	0.00000	0.59452	0.47600

Weighted profile factor,

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

where $\omega_i = \frac{1}{\sigma i^2}$, σi^2 is the variance of observation

Expected weight factor,

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

Here (n – p) is the number of degrees of freedom. 'n' is the total number of experimental points and 'p' is the number of refined parameters.

Reduced chi-square,

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

Bragg factor,

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

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

Crystallographic R_F factor,

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

The Reliability factors (R factors) R_p, R_{wp}, R_{Bragg}, R_F and χ^2 obtained from refinement are listed in the Table 2. The low value of χ^2 (goodness of fit) has been observed which justifies the goodness of refinement. The Rietveld refinement yields lattice parameters and unit cell volume which are tabulated in Table 2 along with the errors (in brackets). The observed lattice constant is in good agreement with those reported in literature [13]. The axial ratio found out to be 1.05804 which less than the earlier reported value 1.0614 [14].The low axial value shows the material is more compact and structure is more stable.

Table 2: Reliability factors (R_p, R_{wp}, R_{Bragg}, R_F and χ^2), lattice constant, ATZ and Grain size for the $PbTiO_3$ sample. Errors of the lattice parameters have been shown in bracket.

Parameters	**Values**
R_p	11.6
R_{wp}	14.2
R_{Bragg}	4.67
R_F	4.39
χ^2	2.62
a = b (Å)	3.901577 (0.000035)
c(Å)	4.128031 (0.000062)
ATZ	303.078
Grain size (μm)	1 – 2
Volume (Å)	62.838 (0.001)

V. Conclusions

We have prepared a single phase $PbTiO_3$ compound by following the solid state route. All the observed peaks could be indexed to P4mm space group with tetragonal symmetry. From Rietveld analysis the unit cell parameters are found to be a=b= 3.901577 Å and c = 4.128031 Å. The axial ratio c/a is found to be approximately 1.06 which very closes to the reported value.

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