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Rietveld Analysis of a single phase $PbTiO_3$

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Abstract

$PbTiO_3$ compound was prepared by following the solid state route. X-ray diffraction (XRD) pattern was recorded at room temperature. Sample is found to be in single phase form. All the observed peaks could be indexed to P4mm space group with tetragonal symmetry. The XRD pattern has been analyzed by employing Rietveld method. The unit cell parameters are found to be a=b=3.8987(0.0008)Å and c=4.1380(0.0009)Å. The axial ratio c/a and unit cell volume is found to be 1.0614 and 62.896(0.023)Å respectively. Bond lengths and bond angles have been calculated using the cell parameters

Keywords: Rietveld analysis; *$PbTiO_3$; XRD; Ferroelectric; Oxides;*

1. Introduction

Lead titanate ($PbTiO_3$, PT), has drawn considerable interest in fundamental research due to its rich physical properties. This material shows high Curie temperature and possesses high spontaneous polarization. It is a ferroelectric material that presents a Curie temperature of 490^0C and displays pyroelectric and piezoelectric properties [1-8]. This material is being considered for applications in different kinds of devices, such as storage information, piezoelectric actuators, infrared sensors and ultrasonic transducers in medical and solar applications [9-11]. Recently lots of effort has been given to prepare the bulk as well as thin film of $PbTiO_3$. However, a large tetragonality (c/a=1.063) of tetragonal phase PT resulting in a high stress within the lattice leads to a frangibility and brings difficulty to prepare corresponding ceramics [12]. Recently, the isomorphic substitution of lead with lanthanum gives rise to a decrease in the tetragonality, and the material with a formula of $Pb_{0.7}La_{0.3}TiO_3$ (PLT30) has a pseudo cubic perovskite structure [13-15]. However, according to our knowledge, the detailed structural analysis for $PbTiO_3$ prepared at different temperatures and method is lagging to short out the synthesis of stable $PbTiO_3$. We have prepared PT by solid state route 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 and the help of Fullprof software.

2. Experimental Procedure

$PbTiO_3$ compound was prepared by following solid state route. Stoichiometric ratio of $Pb(NO_3)_2$ and TiO_2 with 99.9% purity were weighed by using a high precision electronic balance with 5 digit accuracy (Avon, Gr 202). The above materials were mixed thoroughly with the help of agate mortar and pestle. The grinding was carried out under acetone till the acetone evaporates from the mortar. The mixture was presintered at 600^0C for 36hrs with intermediate grindings. The sintering in pellet form was carried out at 1000^0C for over 40hrs with intermediate grindings and repelletizing. All the above sintering processes were carried out in air. The scanning electron micrograph was recorded using LEO SEM. The compositional analysis was carried out by SEM EDS. XRD pattern at room temperature for the sample was recorded by using Bruker D 8 Advance XRD machine. The CuK_α radiation was used as X-Ray source. The machine was

operated at 40KV and 40mA. The data was collected with step size of 0.01^0 and time constant of 1 second.

3. Results and discussions

XRD patterns were recorded at room temperature using a BRUKER D-8 ADVANCE XRD machine by employing CuK_α radiation. The XRD patterns recorded for $PbTiO_3$ compound is shown in Fig. 1. One can see that the sample is essentially in single phase form within the instrumental error. All the observed peaks could be indexed to *P4mm* space group with tetragonal symmetry.

The XRD pattern was refined by Rietveld method and by using the fullprof program [16]. The refined XRD pattern is shown in Fig. 2. The experimental points are given as plus (+) and theoretical data are shown as solid line. Difference between theoretical and experimental data is shown as bottom line. The vertical lines represent the Bragg's allowed peaks. The XRD peaks were generated by using *P4mm* space group, i.e. in tetragonal symmetry. The pseudo-voight function was chosen for the profile shape refinement. The refinement was carried out by allowing the variation of different parameters such as, cell parameters, scale factors, position parameters, and isotropic thermal parameters. The position of the Pb, Ti and O atoms are given in table – 1. Two oxygen positions were taken for the refinement. The occupancy was taken as fixed as it is a lighter atom; hence it is not very sensitive to the XRD. It is difficult to refine the oxygen occupancy from XRD data.

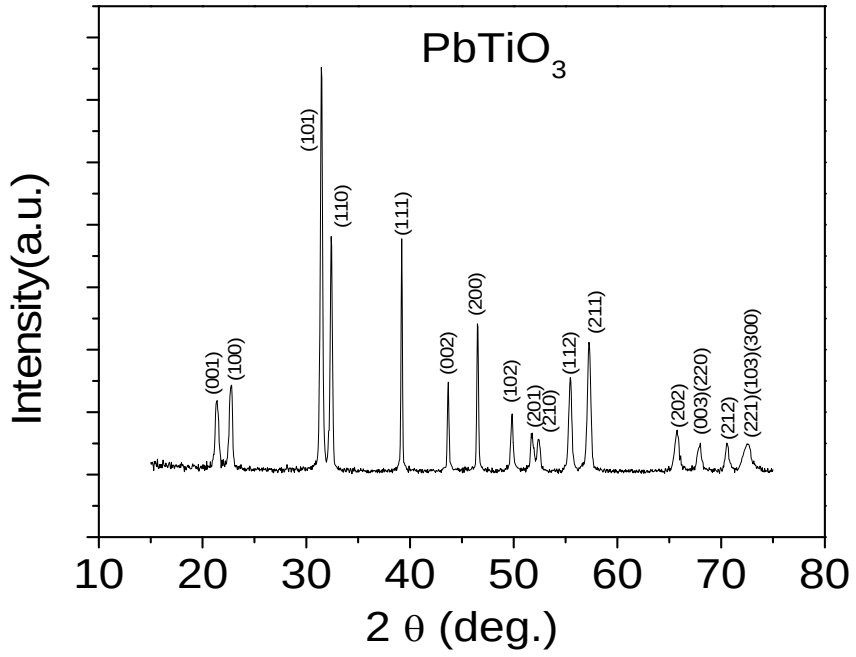

Figure 1. The XRD pattern of $PbTiO_3$. Observed peaks are indexed to *P4mm* space group

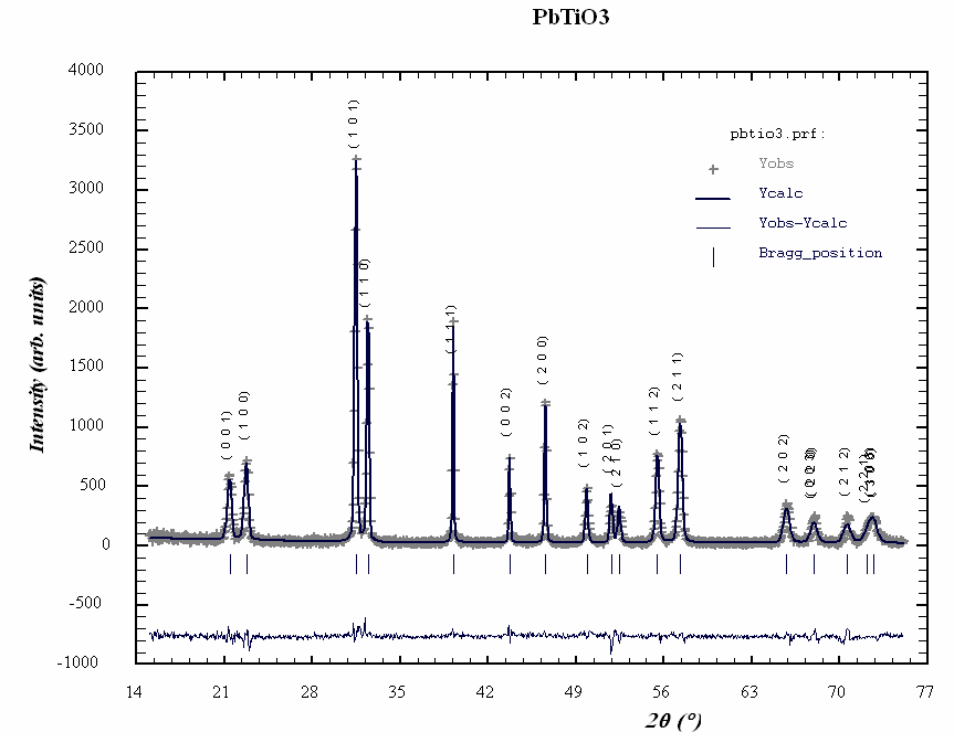

Figure 2. XRD pattern for $PbTiO_3$ with refined data obtained by Rietveld method.

The experimental points are given as plus (+) and theoretical data are shown as solid line. Difference between theoretical and experimental data is shown as bottom line. The vertical lines represent the Bragg's allowed peaks.

Table 1. Position parameters of Pb, Ti, O1 and O2.

Atom	X	Y	Z
Pb	0.00000	0.00000	0.00000
Ti	0.50000	0.50000	0.53000
O1	0.50000	0.50000	0.07410
O2	0.50000	0.00000	0.64090

The refined cell parameters are found to be a = b = 3.8987(0.0008) Å and c = 4.1380 (0.0009) Å. These values are found to be comparable to those of in ref. 12. The unit cell volume is found to be 62.896(0.023) Å. The goodness of fit parameters are found to be R_p=3.70, R_{wp}= 4.20, R_{exp}=3.91, R_{Bragg}= 5.63, R_f = 3.20 and χ^2 = 1.32. The axial ratio c/a is found to be 1.0614 which is less then that of earlier reported value 1.063 [12]. The low axial value shows that the material is more compact and structure is more stable. Hence we could prepare the material with less axial ratio by following the solid state route.

The bond lengths and bond angles were calculated from the refined data with the help of Powdercell programme. The average axial and in plane bond lengths are found to be 1.8886Å and 2.0026Å respectively. All the bond lengths are listed in table 2. These values are found to be comparable with those reported in the literature. All the calculated bond angles are listed in table 3 and these are comparable with that of earlier literature values. The structure of the compound is shown in fig. 3. This structure has been drawn using the refined parameters.

Table 2. Bond Length using the parameters obtained from Rietveld analysis.

No	atom1	Atom2	Distance	quant
1	PB	TI	3.5228	4
2	TI	O1	1.8865	1
3	TI	O2	2.0026	4
4	TI	PB	3.3738	4
5	O2	PB	2.4511	8

Table 3. Bond angles calculated using the parameters obtained from Rietveld analysis.

No	atom1	atom2	atom3	angle	quant	No	atom1	atom2	atom3	angle	quant
1	PB	TI	O1	51.4957	3	18	O2	TI	PB	46.0119	2
2	PB	TI	O2	66.6733	6	19	O2	TI	PB	115.4878	6
3	PB	TI	PB	67.1950	4	20	TI	O2	PB	97.9855	6
4	PB	TI	O2	132.9454	6	21	PB	TI	O2	66.6742	2
5	PB	TI	PB	102.9922	2	22	PB	TI	PB	73.7068	2
6	PB	TI	PB	73.7063	2	23	PB	TI	PB	176.6984	3
7	PB	TI	PB	111.0323	8	24	O2	TI	O2	86.9893	1
8	PB	TI	PB	176.6986	1	25	O2	TI	PB	115.4871	2
9	O1	TI	O2	103.2468	2	26	TI	O2	PB	97.9861	2
10	O1	TI	O2	103.2477	2	27	PB	TI	PB	70.5908	2
11	O1	TI	PB	51.4965	1	28	PB	TI	PB	109.5952	2
12	O1	TI	PB	125.2020	1	29	TI	PB	O2	36.0032	8
13	O1	TI	PB	125.2026	3	30	PB	TI	PB	70.5904	2
14	O2	TI	O2	86.9897	3	31	PB	O2	PB	105.3639	4
15	O2	TI	PB	132.9445	2	32	O2	PB	O2	68.4369	3
16	O2	TI	O2	153.5056	2	33	O2	PB	O2	68.4363	1
17	O2	TI	PB	46.0113	6						

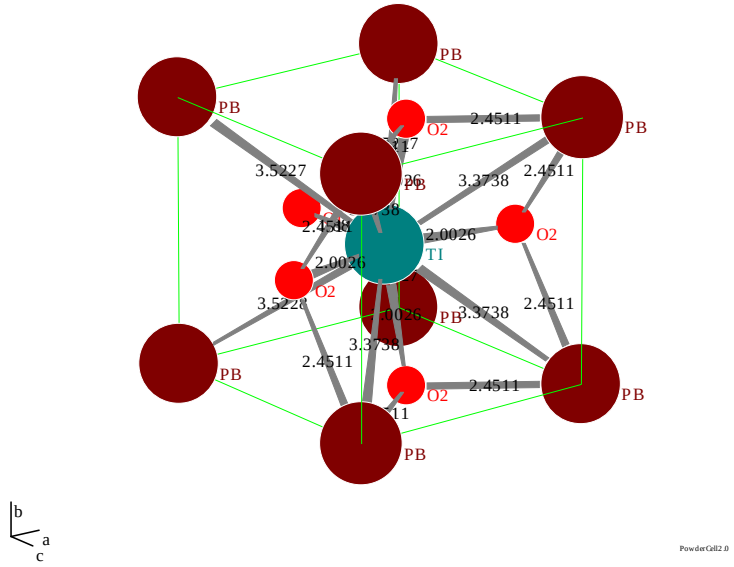

Figure 3. Structure of $PbTiO_3$ obtained from the Rietveld analysis parameters.

4. 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=3.8987(0.0008)Å and c=4.1380(0.0009)Å. The axial ratio c/a is found to be 1.0614 which is less then that of reported value 1.0630. Hence, we could prepare with low axial ratio compound by following solid state route. The average axial and in plane bond lengths are found to be 1.8886Å and 2.0026Å respectively.

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