

Quantitative structural analysis of $\text{Li}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ceramics prepared by high energy ball milling and sintered at 600 °C

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Abstract: $\text{Li}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ceramic powder was synthesized by high energy ball milling. The X-ray diffraction pattern of the sample was analyzed in a quantitative manner using rietveld analysis. X-rays being the finger print of a material and the diffracted intensity can be used to dig out a lot of information related to the material, size-strain rietveld analysis method is adopted to get quantitative information of the material. The phase of the material along with crystallite size, lattice strain of various planes and displacement of the particular plane is analysed. As the material is a good lead free energy harvester, it is tried to present a in-depth study of the material in term of its atomic positions, bond lengths, bond angles etc. Keywords: X-ray diffraction; Rietveld refinement; Structure

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1. Introduction

Lithium bismuth titanate ($\text{Li}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ or LBT) is considered to be one of the candidates of lead-free piezoelectric ceramics. This material is largely important because of its potential applications and interesting properties. Because of environment friendly nature and interesting behaviour, this material is widely studied by different researchers and presented in different platform. However, to our knowledge, the detailed structural analysis of this material is not available in the literature world. For the first time, a detailed structural analysis with crystallite size, lattice strain of various planes, atomic positions, bond lengths, bond angles etc. are presented in this work.

The mechanical synthesis of the material has a advantage to avoid the intermediate calcination step. So, here it is adopted to have fine grain and ease of fabrication with homogeneity as compared to conventional solid state reaction method. [1]

Lead oxide based ferroelectrics, represented by lead zirconate titanate $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$, (PZT) are widely used for piezoelectric actuators, sensors and transducers due to their excellent piezoelectric properties [2-3].

2. Materials and Methods

Powders reagent of Li_2O_3 (99 wt%), TiO_2 (99 wt%), and Bi_2O_3 (99 wt%) as starting materials were mixed according to their stoichiometric ratio to prepare $\text{Li}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ceramic. The prepared reactant was ball milled for 3 hours in a zirconia vial using 40 zirconia balls at a speed of 300 rpm in an ethanol medium. After ball milling, the obtained slurry was dried at 80°C for 6 h to remove the ethanol. The products were then grounded in an agate mortar for 1/2 hour. The fine powder was sintered at 600°C for 4 hours. Then the processed ceramic powder were structurally characterized by a PANalytical X'pert-MPD X-ray diffractometer (XRD). The XRD data were recorded using Ni-filtered Cu K_α radiation from a highly-stabilized and automated Philips X-ray generator (PW 1830) operated at 30 kV and 20 mA. The generator is coupled with a Philips X-ray powder diffractometer consisting of a PW 3040 mpd controller, PW 1050/51 goniometer of radius 240 mm, and a proportional counter with 1° divergence slit, and 1 mm receiving slit. The step-scan data of step size 0.017° and step scan 0.6 s were recorded for the entire angular range $10\text{--}90^\circ$.

3. Theory

Microstructure characterization of the ball-milled powder samples has been made by employing the Rietveld's whole-profile fitting method based on structure and microstructure refinement [5-6]. The experimental profiles were fitted with the most suitable pseudo-Voigt analytical function because it takes individual care for both the particle size and strain broadening of the experimental profiles. For both the $\text{K}_{\alpha 1}$ and $\text{K}_{\alpha 2}$ profiles, the line broadening function $B(2\theta)$ and the symmetric part of instrumental function $S(2\theta)$ may be represented by the pseudo-Voigt function

$$pV(x) = \sum I_n [\eta C(x) + (1 - \eta)G(x)] \quad (1)$$

where the Cauchyian component, $C(x) = (1 + x^2)^{-1}$ and the Gaussian component, $G(x) = \exp[-(\ln 2)x^2]$. The powder diffraction patterns were simulated providing all necessary structural information and some starting values of microstructural

parameters of the individual phases with the help of the Rietveld software, Fullprof [7-8].

Initially, the positions of the peaks were corrected by successive refinements of zero-shift error. Considering the integrated intensity of the peaks as a function of structural parameters only, the Marquardt least-squares procedures were adopted for minimization of the difference between the observed and simulated powder diffraction patterns and the minimization was carried out by using the reliability index parameter, R_{wp} (weighted residual error), R_{exp} (expected error) and R_B (Bragg factor) defined as:

$$R_{wp} = \left[\frac{\sum w_i (I_0 - I_c)^2}{\sum w_i I_0^2} \right]^{1/2} \quad (2)$$

$$R_B = 100 \frac{\sum |I_0 - I_c|}{\sum I_0} \quad (3)$$

and

$$R_{exp} = \left| \frac{N - P}{\sum w_i I_0^2} \right|^{1/2} \quad (4)$$

where I_0 and I_c are the experimental and calculated intensities, respectively, w_i ($1/I_0$) and N are the weight and number of experimental observations, and P is the number of fitting parameters.

The goodness of fit (GoF) is established by comparing R_{wp} with the expected error, R_{exp} . This leads to the value of goodness of fit [9-10]:

$$GOF = \frac{R_{wp}}{R_{exp}} \quad (5)$$

Refinement continues till convergence is reached.

4. Results and discussion

In the present study rietveld profile matching and integrated intensity refinement analysis of X-ray of powder diffraction data is adopted to obtain the refined structural parameters, such as atomic coordinates, occupancies, lattice parameters, microstructural parameters, and energy density using Fullprof version 2.50 Rietveld software. The XRD pattern of NBT ceramic is shown in

fig.1. The refinements were conducted without refining the isotropic atomic thermal parameters.

The x-ray pattern shows 2 different major phases, namely, Lithium bismuth titanate(94.9%) and another polymorph of sodium bismuth titanate(5.1%) matched with JCPDS data card (98-000-9961), respectively. During refinement process the different structural parameters obtained are enlisted here as, Tip Width, 3.79468 Å, Obs. Lorentz B [$^{\circ}2\theta$]=6.01523, Obs. Gauss B [$^{\circ}2\theta$]=0.102916, Obs. B [$^{\circ}2\theta$]=6.04347, Instr. Lorentz B [$^{\circ}2\theta$]=0.07471, Instr. Gauss B [$^{\circ}2\theta$]=0.063278, Instr. B [$^{\circ}2\theta$]=0.11856, Struct. Lorentz B [$^{\circ}2\theta$]=5.94034, Struct. Gauss B [$^{\circ}2\theta$]=0.08009, Struct. B [$^{\circ}2\theta$]=5.94167, Universal Shape=0.52327, Micro Strain [%]=0.16448, Crystallite Size [Å]=15.19054. Different structure factor are estimated to be, F observed=170.1591, F calculated=141.3979 and F esd=15.21154 with multiplicity 8.

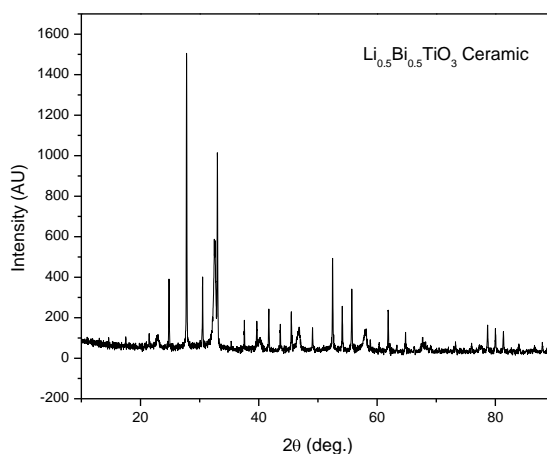


Fig.1: X-ray diffraction of $\text{Li}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ceramic sintered at 600 °C.

Different refined parameters are calculated to be, $R_p=36.0654$, $R_{wp}=60.9821$, $R_{exp}=14.3425$ with $GOF = 18.0782$. After refinement a crystal structure with the following data was obtained. crystal system: tetragonal, space group=I 41/a c d and space group no.=72. The lattice parameters (Å) are found to be, $a=b=7.191(4)$, and $c=5.06(2)$ with $\alpha=\beta=\gamma=90^{\circ}$. Volume per unit cell is estimated to be $V=261.46 \text{ \AA}^3$ with figure of merit 4.76.

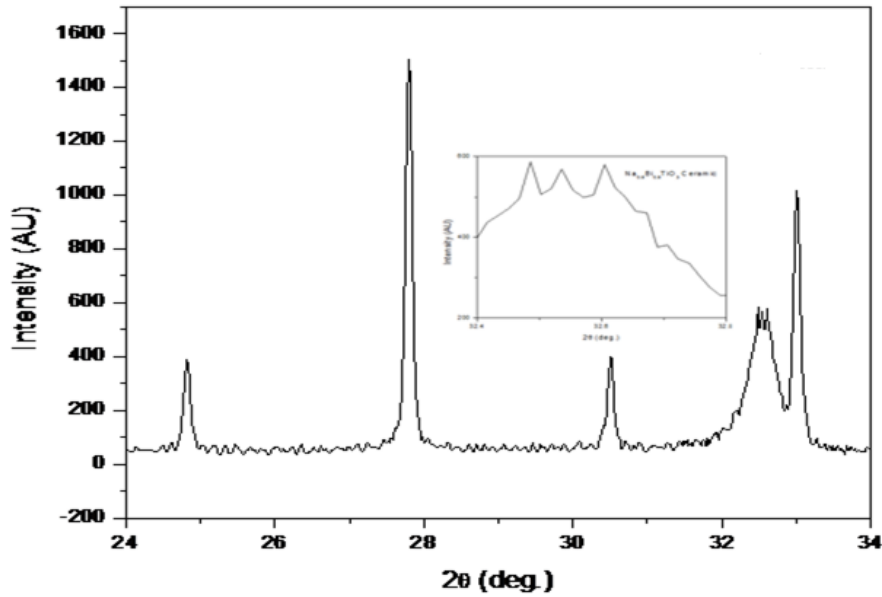


Fig.2 : X-ray Diffraction of $\text{Li}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ceramic and normalised diffractogram (inset)

Table-1 shows the x-ray diffraction data of $\text{Li}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ceramic with inter-planner spacing, crystallite size and (h k l) parameters of individual planes. FWHM and intensity(cts) is also mentioned for the individual planes. From the normalised diffractogram it is seen that, one or more new peaks may evolve if we increase the sintering temperature. Because the presence of the splitting of peaks confirms the very very diffuse minor phase, which is not refined due to the insufficient peak heights by quantitative analysis, which will be our further course of study. If such will be the case then this material will be a very good substitute for lead free ferroelectric material as $\text{K}_{0.5}\text{Na}_{0.5}\text{TiO}_3$. This is the requirement of the present day environment friendly, high dielectric constant, ferroelectric material for versatile application in the field of electronics.

Table-1: Structural analysis of $\text{Li}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ceramic sintered at 600 °C

Sl. No.	Diffraction Angle (deg)		FWHM (2 θ)	Inter planner Spacing (Å)		Lattice Plane			Integral Breadth (2 θ)	Crystallite Size (nm)	Lattice strain
	(2 θ) (C)	(2 θ) (O)		d (c)	d (o)	h	k	l			
1	21.4667	21.4685	0.1224	4.136093	4.135753	1	0	1	0.1632	65.98	0.008213
2	24.8132	24.8311	.102	3.585329	3.582777	1	1	1	0.136	79.75	-0.15824
3	27.7174	27.8043	0.1224	3.215905	3.206047	2	1	0	0.1632	66.86	0.008748
4	30.4827	30.5038	0.0816	2.930167	2.928191	2	0	1	0.1088	100.91	-0.0405
5	32.9829	33.0084	0.3672	2.713538	2.711501	2	1	1	0.4896	22.57	0.092152
6	37.4904	37.5844	0.0816	2.396994	2.391214	3	0	0	0.1088	102.85	-0.19477
7	39.6475	39.6660	0.1224	2.271411	2.270393	2	2	1	0.1632	69.00	0.020782
8	41.6658	41.6906	0.102	2.165928	2.164700	3	0	1	0.136	83.35	-0.01116
9	43.6072	43.6500	0.102	2.073896	2.071961	3	1	1	0.136	83.90	-0.13437
10	45.4399	45.4921	0.0816	1.994419	1.992252	3	2	0	0.1088	105.57	0.02285
11	49.0624	49.0888	0.1224	1.855300	1.854362	3	2	1	0.1632	71.36	-0.04458
12	52.4207	52.4789	0.1224	1.744069	1.742270	4	1	0	0.1632	72.37	0.016447
13	54.0988	54.1019	0.102	1.693863	1.693774	4	0	1	0.136	87.46	-0.00919
14	55.7060	55.7188	0.1428	1.648740	1.648392	4	1	1	0.1904	62.93	-0.07966
15	57.5664	58.1277	0.4896	1.599800	1.585682	1	1	3	0.6528	18.57	0.219406
16	58.9372	58.8485	0.2448	1.565818	1.567968	3	2	2	0.3264	37.26	0.024198
17	60.3572	60.3461	0.2448	1.532332	1.532589	4	2	1	0.3264	37.54	-0.0212
18	62.1296	61.8822	0.1428	1.492806	1.498179	2	1	3	0.1904	64.87	-0.09746
19	64.7693	64.8022	0.1632	1.438196	1.437545	5	0	0	0.2176	57.66	0.028037
20	67.6760	67.6986	0.1224	1.383323	1.382916	4	3	1	0.1632	78.16	-0.03492
21	73.2590	73.2921	0.2448	1.291066	1.290564	5	2	1	0.3264	40.45	-0.03353
22	78.9258	78.6843	0.1632	1.211965	1.215079	4	1	3	0.2176	62.95	-0.00797
23	80.0203	80.0197	0.1632	1.198119	1.198127	5	3	1	0.2176	63.59	-0.03727
24	81.3226	81.3697	0.1224	1.182190	1.181626	6	1	0	0.1632	85.60	-0.16873
25	84.0045	84.0063	0.2448	1.151144	1.151124	6	1	1	0.3264	43.67	0.026545
26	87.9597	87.9631	0.2448	1.109293	1.109259	6	2	1	0.3264	45.10	-25.0086
27	89.2751	89.2295	0.2448	1.096325	1.096766	5	4	1	0.3264	45.59	0.079633

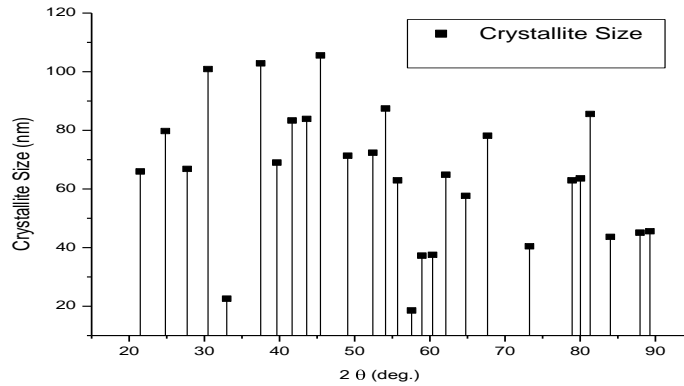
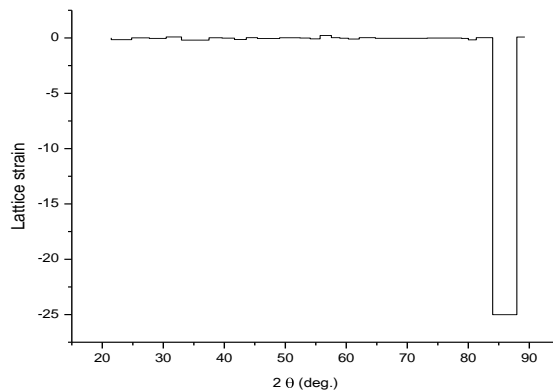


Fig. 3: Variation of crystallite size w.r.t. diffraction angle

Fig. 3 shows a variation of crystallite size with the diffraction angle. It is observed that the crystallite as estimated from the well known Scherrer formula is max. at diffraction angle ($2\theta = 30.48, 37.49$ and 44.45°), minimum at diffraction angle ($2\theta = 32.98, 57.56^\circ$). The mean crystallite size is observed to around 84 nm. For all most all plane the average crystallite size is varying from approx. 44 nm to 87 nm. Fig. 4 represents the variation of lattice strain w.r.t. diffraction angle. It is observed that the lattice strain remains almost same (constant) for all the planes and it is negligible except for the deepest plane at around $2\theta = 85^\circ$. This speaks that there is not much defect in the material synthesis so far strain is concerned, so strain induced broadening can be neglected for this material. Also it indicated that as there is no much mis orientation of the atoms in the material, the material may be very dense without much porosity and planar orientation of the material may be very good.

Fig. 4: Variation of Lattice strain w.r.t. diffraction angle



5. Conclusion

$\text{Li}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ceramics is prepared by mechanical milling in mixed oxide route. A detailed structural analysis of the material is conducted quantitatively and presented here. It is observed that the mean crystallite size (D_v) is nearly 84 nm and lattice strain is very negligible for all the planes except at the deeper planes. The normalization of the spectrum reveals that with further increase in sintering temperature, the material may give a new phase and so, may be suitable for high dielectric constant lead free ferroelectric materials.

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