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Synthesis of Ferroelectric $Bi_{1/2}Na_{1/2}TiO_3$ Fine Powder through the Solid State Reaction Technique

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Abstract:
Solid solutions of $Bi_{1/2}Na_{1/2}TiO_3$ (symbolized as BNT) were successfully prepared by means of solid state reaction technique. The effects of processing parameters on the growth and morphology of derived $Bi_{1/2}Na_{1/2}TiO_3$ powders were investigated. The BNT powders were synthesized in a stoichiometric ratios of raw oxide and carbonate powers (Bi_2O_3, TiO_2, and Na_2CO_3) at an optimized temperature of 850-900 ^0C. X-ray diffraction pattern of NBT compounds revealed the hexagonal crystal structure. The lattice parameters vary with optimization condition of sintering temperature. Density of the prepared samples was found to be average 84-90 % of their theoretical values. The relationship between temperature & frequency dependent dielectric constant and loss studies are also investigated in this research paper.
Keywords: *$Bi_{1/2}Na_{1/2}TiO_3$ Powder; Ferroelectrics; Crystal Structure; X-ray Diffraction; Dielectric studies.*

1. INTRODUCTION

Now a days, the environmental destruction has been a serious issues worldwide. One of the serious problem is subjected to the release of harmful ingredients (like as Pb, Hg, Cd) from the electrical industries. Therefore, further restriction on the hazardous materials/substances will be required soon to avoid the release of harmful waste [1, 2]. The lead–based ferroelectric materials/ceramics denoted as Pb $(Zr,Ti)O_3$ (symbolized as PZT), which have been extensively utilized for the development of sensors, actuators, piezoelectric transducers and so on just because of their outstanding piezoelectric features. On the other hand, evaporation of the harmful ingredients of lead oxide during synthesis process causes a crucial environmental issues. For that reason, it is an essential need to develop the eco-friendly/lead-free piezoelectric materials to replace the PZT-based materials. This significant approaches has become one of the suitable approaches for the present development of piezoelectric specimens. Bismuth sodium titanate (symbolized as $Bi_{1/2}Na_{1/2}TiO_3$ or BNT) discovered in 1960 (Smolenskii et al.), which is considered to be a promising applicant of eco-friendly piezoelectric specimen [3, 4]. BNT belongs to the perovskite kinds of ferroelectric compound with a relatively high remanent polarization ($P_r = 38\mu C/cm^2$) and Curie temperature ($T_c = 320$

^{0}C) at room temperature [5, 6]. It show ferroelectricity at room temperature. The perovskite symmetry of the compound structure is adopted through the existence of numerous oxides that having ABO_3-types chemical formula. Said symmetry of the structure are very useful in several technological applications like ferroelectrics, sensors, catalysis, superconductors, thermo-power and so on. Main attractive features of the BNT-based ceramics materials are multiple phase transition that makes it much possible to control the temperature stability of their electrical features by means of compositional modification, free control of toxic atmosphere during sintering process and lack of air pollution from the lead volatilization [7].

The ferroelectric ceramic powders was also reported by the sol-gel synthesis method. This synthesis process are generally long, complex and starting materials cost is also high [8]. So we used to prepare BNT powder by the conventional solid-state reaction method. In this paper, $Bi_{1/2}Na_{1/2}TiO_3$ powders were prepared by the SSR method with the initial ingredients of Bi_2O_3, Na_2CO_3 and TiO_2 powders.

The main tasks of the research work are as follows:-

- Preparation of $Bi_{1/2}Na_{1/2}TiO_3$ powder by the solid state reaction method and to perform its structural characterization.
- To identify the X-ray diffractogram of calcinated powder & sintered pellets and it's indexing by the PowdMult software.
- Density of the prepared pellets is measured experimentally and compared with theoretical one.
- The dielectric characterization from room temperature to high temperature.
- To identify the optimal conditions for the synthesis and further studies of the materials.

2. RELATED THEORY

2.1 Perovskite structure

More suitable ferroelectrics, like barium titanate (BT), lead zirconate titanate (PZT), lead titanate ($PbTiO_3$) and lead lanthanum zirconate titanate (PLZT) belongs to the perovskite symmetry structure. Perovskite belongs to the special mineral family of the calcium titanate ($CaTiO_3$). Its common formulation as the ABO_3 type and it consist of a closed-packed anion lattice in which every fourth anion is replaced by a divalent cation (Figure.1), with a quadravalent cation in the octahedral site at the centre of unit cell. Perovskites are able to accommodate a large number of cation combinations as long as the overall crystal is neutral. The modified versions usually occur when the larger cation is small, which tends to tilt the axis of the B-octahedra with respect to their neighbor. This result is puckered networks of linked B-octahedra which are the basis for one of the unusual electrical behaviour, namely piezoelectricity. Another perovskite was discovered from the barium titanate in the year 1945 [9]. In 1950's the solid solution of the $Pb(Ti,Zr)O_3$ (PZT) ceramics system has also perovskite symmetry, which found to be ferroelectric. The compositions of the PZT based ceramics system are now the most widely exploited of all piezoelectric specimen in both industry and research. The current detailed description of the BT and PZT based systems can

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also be found [10]. After it an enormous number of ferroelectrics doped with the different ions at A, B or AB sites is investigated to search new materials for device applications. The complex perovskite structure has a general formula is as following types $(A_1\ldots\ldots\ldots\ldots An)(B_1\ldots\ldots\ldots\ldots..Bn)O_3$. It could only be synthesized if they fulfill the general conditions.

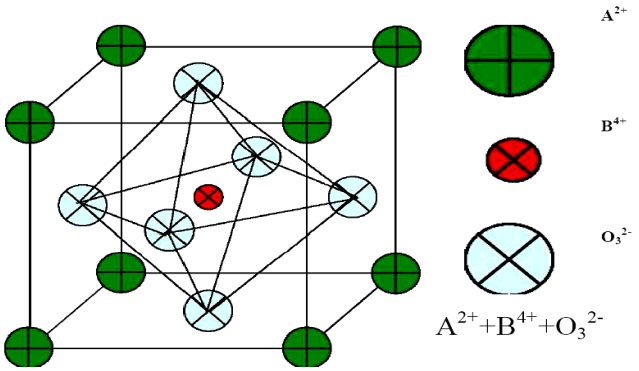

Fig. 1: A cubic ABO_3 perovskite-type unit cell.

2.2 Charge Neutrality:

$$\sum_{i=1}^{k} X_{Ai}\, n_{Ai} + \sum_{i=1}^{j} X_{Bi}\, n_{Bi} = 6$$

Herein, X_{Ai} and X_{Bi} are the fractions of cations A & B.

$\sum_{i=1}^{k} X_{Ai} = 1$: $\sum_{i=1}^{l} X_{Bi} = 1$ where $0 \leq X_{Ai} \leq 1, 0 \leq X_{Bi} \leq 1$, $n_{Ai} = 1,2,3$ and $n_{Bi} = 2,3,4,5,6$.

2.3 Goldschmidt Tolerance Factor:

$$t = \frac{(\langle r_A \rangle + r_O)}{\sqrt{2}\ (\langle r_B \rangle + r_O)} \qquad (1)$$

Where, the term r_A represents an average ionic radius of the A-site atoms, r_B represents an average ionic radius of B-site atoms and r_0 represents ionic radius of oxygen. For a common perovskites specimen, the value of t lies between 0.8-1.05. For an ideal cubic perovskite symmetry, the tolerance factor value is equal to one. In exercise, the cubic structures whose tolerance factor value is about 0.95-1 with lower t values are slightly distorted represents non-ferroelectric, and those values slightly over one tend to be ferroelectric.

2.4 Synthesis of Ferroelectric ($Bi_{1/2}Na_{1/2}TiO_3$):

Chemically raw powders of Bi_2O_3, Na_2CO_3 and TiO_2 were utilized as a starting materials. The $Bi_{1/2}Na_{1/2}TiO_3$ (BNT) was prepared through the following chemical reactions:

$$½\ Bi_2O_3 + ½\ Na_2CO_3 + 2\ TiO_2 \rightarrow 2\ Bi_{1/2}Na_{1/2}TiO_3 + CO_2\ (gas) \qquad \text{Eq. (1)}$$

In Eq. 1, the starting raw powder materials were weighed in the stoichiometric amount/proportion to yield the BNT and mixed through acetone an agate mortar & pestle for 5 h. The dry mixture of the BNT precursors are in the equal stoichiometric composition.

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2.5 Density Measurement:

We calculate the experimental density and theoretical density of the pallet, using the formula given below –

Experimental density ρ_{exp} = Mass of pellet M (gm) / Volume of pellet V (cm^3)

Theoretical density $\rho_{x\text{-}ray} = A * n / V * N_A$

Where, A = formula weight or molecular weight of the compound formed,

V = Unit cell volume,

n = Number of atoms per unit cell,

N_A = Avogadro's number (=$6.023*10^{23}$)

3. EXPERIMENTAL

For obtaining the solid solutions of sodium bismuth titanate ($Bi_{1/2}Na_{1/2}TiO_3$), ceramic samples were prepared by the traditional method of solid state synthesis. As starting materials for preparing the ceramics reagent- grade oxide and carbonate powers, Bi_2O_3 (99.0 % SD fine Chem. Ltd), TiO_2 (99.5 % Laba, Chem. Pvt. Ltd. India), and Na_2CO_3 (99.99 % Merck) were used as starting materials stoichiometric amount of the power were mixed in wet medium (acetone) for five hours. Pure NBT powder calcined at 850 ^{0}C for four hours. After calcination, the mixture was granulated with PVA (added 2%) solution, as binder. The powders (granulated) were made into disc shaped pellets (diameter 10-12 mm and thickness 1.2 mm). Doping composition compacted discs were sintered at 900 ^{0}C for six hours. As sintered disc were electrode using silver paste on both faces of disc and fired at 500 ^{0}C for 2 hours. The X-ray diffraction pattern were recorded on (Philips) differactometer with CuKα radiation (λ =1.5418 A^0). Dielectric and impedance measurement were carried on advanced LCR Meter and LCR-Hi-Tester respectively. Temperature was controlled through computer and µp- based temperature controller.

4. RESULTS AND DISCUSSIONS

4.1 X-ray analysis

Fig. 2, displays the X-ray diffraction (XRD) configurations of as prepared pure NBT ($Bi_{1/2}Na_{1/2}TiO_3$) ceramics powder, which obtained in a wide range of Bragg angles in the 2θ range of 20° to 80° at a slow scan using CuKα radiation (λ=1.540500 A^0) at room temperature.

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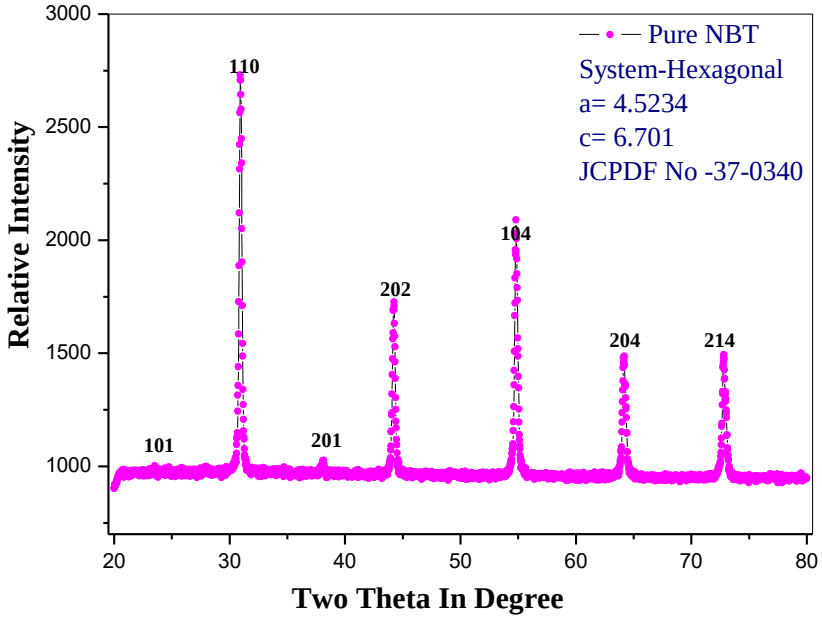

Fig. 2: The XRD picture of bismuth sodium titanate

At room temperature the symmetry of pure BNT ceramic, shows hexagonal phase. All the diffraction peaks positions and lattice parameters have been indexed and calculated using a computer program package POWD [11] software. These obtained diffraction peaks positions and lattice parameters matches with JCPDF No- (36-0340) [12]. Brief results are shown in table -1.

Compound details: $Bi_{1/2}Na_{1/2}TiO_3$

System –Hexagonal a = 5.5234 c = 6.7011 SD = 0.0009

JCPDF No- (36-0340)

S. No	d-spacing		h	k	l
	d_{obs}	d_{cal}			
1.	3.9207	3.9012	1	0	1
2.	2.7642	2.7620	1	1	0
3.	2.2531	2.2536	2	0	1
4.	1.9513	1.9497	2	0	2
5.	1.5893	1.5878	1	0	4
6.	1.3753	1.3761	2	0	4
7.	1.2306	1.2317	2	1	4

Table-1: Comparison of observed and calculated d-values of their major reflections for $Bi_{1/2}Na_{1/2}TiO_3$ powder at room temperature.

4.2 Dielectric Study

Pure BNT (Fig. 3), shows dual abnormal dielectric peaks trends that originate as of the phase transition from ferroelectric to anti-ferroelectric (at a particular point of T_f) and anti-ferroelectric to paraelectric stage (at a particular point of T_m). The trends of the plot nature is also consistent with our earlier reported results of the sodium bismuth titanate lead

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based/lead-free based ceramics systems [13]. The dielectric description of the relaxors has mostly focused on examining the temperature dependence above T_m used for further dielectric relaxation [14-16]. Temperature dependence of dielectric constants and dielectric losses (tanδ) for pure BNT powder at different frequency are displayed in Fig. 3.

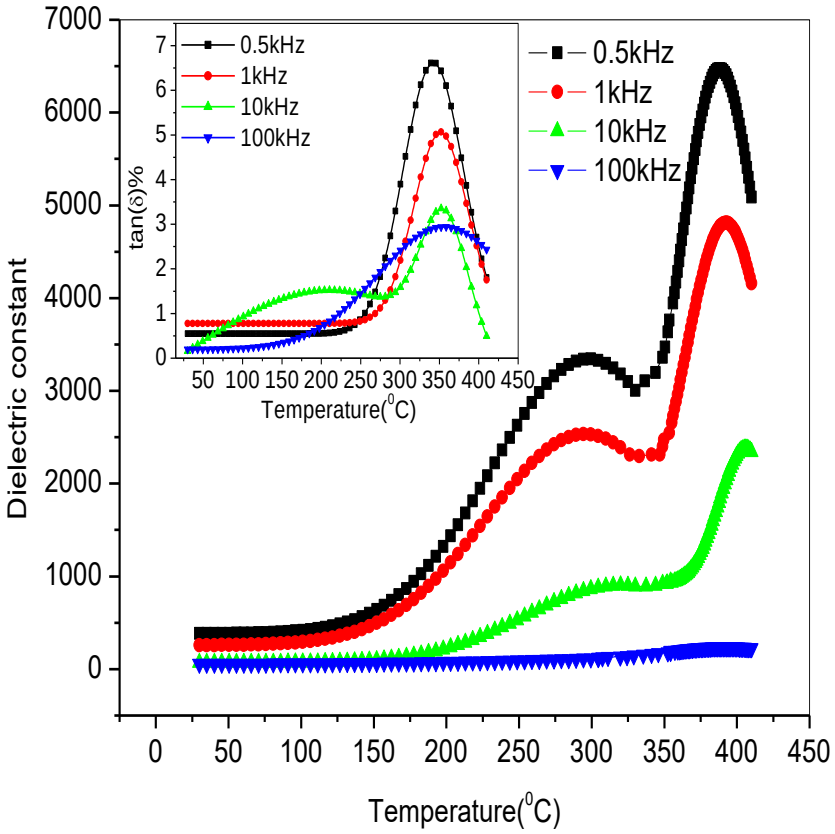

Fig. 3: Dielectric studies of the bismuth sodium titanate

The dielectric losses (tanδ) of the BNT powder displays higher values at lower temperature. It could be explained through the use of macro-domain to micro-domain transition theory [17]. The tangent/dielectric loss in the BNT–based ferroelectrics specimen rises from the domain walls and increasing temperature. Therefore, the macro-domains trends shift to micro-domain and the domain walls suddenly rises that leads to rise further tangent loss at lower temperature. Additional rise of the temperature, the micro-domains trend changes to polar micro-zone and domain-walls drops. Hereafter the tangent/dielectric loss decrease that leads distinguished peak in loss tangent-temperature plot corresponding to T_f.

Improved Curie law is utilized to describe the dielectric trend nature of the complex ferroelectrics with diffuse phase transition. It is well-defined as the following mathematical expression [18].

$$\frac{1}{\varepsilon'} - \frac{1}{\varepsilon'_m} = \frac{(T - T_m)^\gamma}{C'}$$

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Herein, the terms γ and C' are measured to be constants, the magnitude of the γ lies between one and two. The term of γ provides an information related to the phase transition character. If the value of γ is one that signifies the classical ferroelectric phase transition, in which common Curie-Weiss rule is followed and if the magnitude of γ is two that signifies the quadratic dependence. It also defines the whole diffuse phase transition behavior.

5. CONCLUSION

In summary, large-size and high-quality $Bi_{1/2}Na_{1/2}TiO_3$ (symbolized as BNT) solid solution with hexagonal crystal structure was grown by the solid state reaction route technique. Using XRD analysis, BNT perovskite system crystallizes in the form of solid solution across a wide concentration range. X-ray diffraction patterns indicates that the lattice parameter investigation revealed that $Bi_{0.5}Na_{0.5}TiO_3$ is in single phase only. The rise of temperature and soaking time of preparation/synthesis could develop plate-like grains of the BNT powder more distinct and discrete. The BNT particles, as developed in this experiment could utilized to synthesized ceramics with additional uniform grain orientation, i.e., textured ceramics for enhanced piezoelectric features. The density of BNT was optimized at different temperatures and optimum density was 91 % at 950 ^{0}C. Presently, we are preparing these materials through wet chemical route in order to understand the influence of grain characteristics over the physical properties. Works on these lines are in progress.

Conflict of interest

The authors declared that there is no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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