

Synthesis, Structural, Dielectrical Properties of Lead Free Ceramics by Solid State Reaction Method

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ABSTRACT: Lead free ceramics ($\text{Bi}_{1-x}\text{Na}_x\text{TiO}_3$) where $x=0.45$ was synthesized by Solid State Reaction technique. X-ray diffraction analysis reports single phase with rhombohedral structure. The lattice parameters obtained in BNT are $a=3.880\text{\AA}$ and $\alpha=89.78^\circ$. The sintering temperature increases the density of the material also increases to a maximum value. Further when the temperature increases the density of the material decreases and found to be more than 95% to that of the theoretical density. The average grain size in BNT is found to be $2.23\mu\text{m}$. The maximum temperature ($T_c=320^\circ\text{C}$). The room temperature $\tan\delta$ value has been found to be the order of 10^{-2} indicating low loss materials. When the temperature is increased above T_c , the $\tan\delta$ is found to increase.

KEYWORDS: Solid state reaction, XRD, SEM, Dielectric loss.

I. INTRODUCTION

Now a day the quest for environmental friendly materials had a brought a dramatic change. The main advantage of Lead free ceramics is no toxicity & environmental friendly. In 1880, Jacques and Pierre Curie discovered the piezoelectric effect. The ferroelectricity of this salt was discovered in 1917 by A. M. Nicolson, J. A. Andersen, and W. G. Cady, Valasek in 1921 discovered ferroelectric phenomenon [1]. The name ferroelectricity originates from the similarity of the fundamental concepts to those in ferromagnetic materials, such as magnetization, magnetic domains, and magnetic hysteresis loop. Busch and Scherrer discovered ferroelectricity in KH_2PO_4 and its sister crystals [2]. Devonshire theory [3] published in 1949 deepened the understanding of the transition mechanism of BaTiO_3 from a unified view point. $\text{A}'_{1-x}\text{A}''_x\text{BO}_3$ compounds have been proved to be very useful materials from the point of view of piezoelectric applications (Sakata Masuda 1974) [4]. The change of constituent elements in place of A' and A'' result in the control of properties. NBT or BNT and their solid solutions have been established as very promising materials for piezoelectric applications. BNT exhibits two structural phase transitions from ferroelectric rhombohedral to tetragonal of space group P_4/mmm [5] ($\sim 200\text{-}350^\circ\text{C}$) and to para electric high temperature cubic phase[6-7] of space group $\text{Pm}3\text{m}$ ($520\text{-}540^\circ\text{C}$). At about 320°C , NBT exhibits a broad maximum of electric permittivity. BNT doped with barium has been shown to exhibit an MPB near 7 mol % Ba reported by T. Takenaka et al [8].

II. MATERIAL AND METHODS

Fine particle size is desired for attainment of chemical equilibrium particularly in solid state of solid solution [9]. High purity (99.9 %) Na_2CO_3 , Bi_2O_3 , BaCO_3 and TiO_2 were used for the preparation of the composition. Stoichiometric quantities of the reagents were first dry mixed in an agate mortar. The composition was further wet-mixed for 2 h with suitable organic solvent media (Methanol). The well-grounded pale yellowish powder was taken in alumina crucibles covered with lid and then calcined at 850°C for 2 h for materials. This calcination process was repeated twice for each

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of the composition to increase homogeneity. An excess of Na_2CO_3 and Bi_2O_3 of 2-3 wt% was added to each composition to compensate the loss during high temperature treatment. The conventional ceramic method of dry pressing in a die punch assembly using a hydraulic press was employed to compress the powder into disc shape. To ensure good flow of the powder and a reproducible filling of the die, the powder was sieved and granulated using 5% polyvinyl alcohol (PVA). The granule were then pressed into discs at a pressure of 3-4 tonnes per sq.inch. The pressed discs were then placed on a platinum foil and closed with a crucible and the sintered in a silicon carbide heated furnace in air for a sintering at 1150°C for 2 to 4 hours for the preparation of different ceramic composition. The phase formation was confirmed by X-ray diffraction (XRD) studies of calcined materials. The X-ray diffractograms of the sample were taken using $\text{Cu K}\alpha$ radiation. For the dielectric characterization, the sintered pellets were polished and then coated with a conducting silver paste for making electrical contacts. Hewlett Packard LF impedance analyser model 4192A through an intermediary accessory model 16095A. Then the capacitance measurements were taken at 1khz from room temperature to 520°C .

III. RESULTS AND DISCUSSION

(a) X-RAY DIFFRACTION

It is observed from the Figure1 that as the sintering temperature increases the density of the material also increases to a maximum value. Figure 1 shows variation of density with respect to sintering temperature. Further when the temperature increases the density of the material decreases. The maximum density observed corresponding temperature in each of the system has been set as sintering temperature of the same. After removal of sample from the furnace, these disks have been found to change the colour from white to light brown as a function of exposure time.

Table 1: X-Ray diffraction of $\text{Bi}_{0.55}\text{Na}_{0.45}\text{TiO}_3$

Composition	Lattice Parameter		Density (ρ)(g/cm^3)			Avg. particle size (n m)	Volume (Cm^3)
	a (\AA)	α (angle)	ρ_{exptl}	ρ_{theor}	Density %		
BNT	3.880	89.78	5.95	6.05	98.3	54	60.18

The materials were scanned at the rate of $2^\circ/\text{min}$ for 2θ running from 10° - 70° . All the diffraction peaks obtained on from fig 2 were well matched with the literature values [10]. The maximum intensity peak in this material has been found at $2\theta = 32.27^\circ$ for which the d-spacing is 2.80, the assigned h k l values are 100, 110, 111, 200, 211, and 220. All the observed peaks have been indexed to be single phase with rhombohedral structure. The lattice parameters obtained in BNT are $a=3.880\text{\AA}$ and $\alpha=89.78^\circ$ which are very close to the reported [11]. Density of the materials is determined by Archimedes method and found to be more than 95% to that of the theoretical density. The tolerance factor (t) of the BNT ceramics is 0.985.

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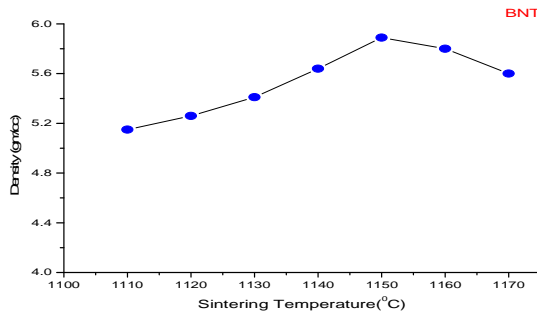


Fig 1: Density Vs Sintering Temperature

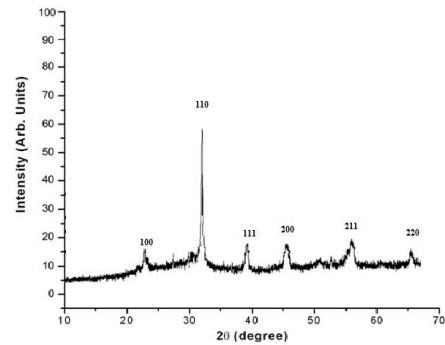


Fig 2: X-Rd of BNT ceramics

(b) SCANNING ELECTRON MICROSCOPY (SEM)

Scanning Electron Microscopy (SEM) is a powerful tool for unveiling important and useful information about the microstructure of solids. Average grain size in each of the specimen [12] has been calculated by line intercept method [13]. SEM analysis reveals detailed information about ceramic surface texture, grain sizes and shapes, and grain boundaries. A value of average grain size in BNT is found to be 2.23 μ m is shown from the Fig 3. (SEM image of BNT ceramics).

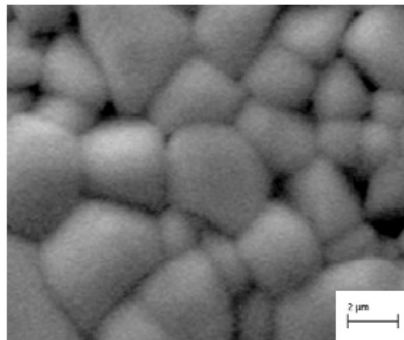


Fig 3: SEM image of BNT ceramics

(c) DIELECTRIC PROPERTIES

The variation of dielectric constant and dielectric loss ($\tan\delta$) as a function of temperature. It can be seen from the Fig.4 showed the ferroelectric to paraelectric phase transition at Curie temperature (T_c). Further, the dielectric constant at T_c decreases with increase in frequency, which is a characteristic feature of ferroelectric materials. The value of dielectric constant (ϵ') increases with increasing in temperature attaining a maximum value at T_c . The maximum temperature (T_c)=320 $^{\circ}$ C have been observed in BNT material, these values are well matched with the reported values[14]. The dielectric constant at room temperature (ϵ'_{RT}) at 1kHz and the maximum dielectric constant at 1kHz are observed to be 450 and 1225 respectively. The room temperature $\tan\delta$ value has been found to be the order of 10^{-2} indicating low loss materials. When the temperature is increased above T_c , the $\tan\delta$ is found to increase [15] is shown in Fig.5.

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Table 2: DIELECTRIC PROPERTIES BNT CERAMICS

Composition	Dielectric constant (ϵ') at (1kHz)		T_d 1kHz ($^{\circ}$ C)	T_c 1kHz ($^{\circ}$ C)	Tan δ at (1kHz)	
	ϵ'_{RT}	ϵ'_{T_c}			RT	T_c
$\text{Bi}_{0.55}\text{Na}_{0.45}\text{TiO}_3$	450	1225	200	320	0.03	0.05

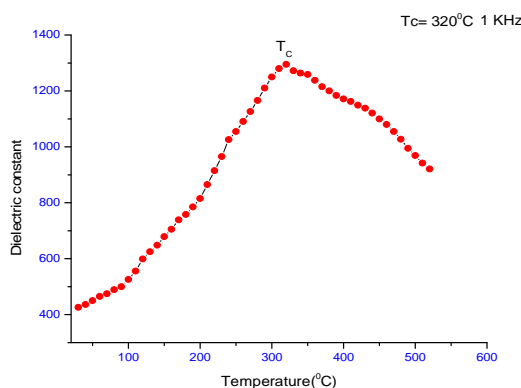


Fig 4: Dielectric constant Vs Temperature.

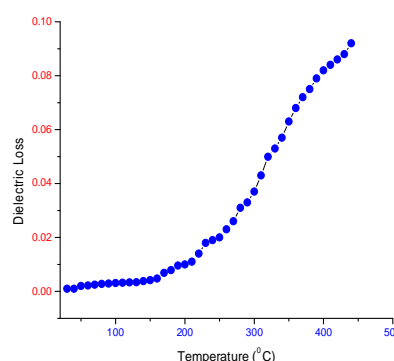


Fig.5: Dielectric loss Vs Temperature

IV. CONCLUSIONS

Lead free ceramics ($\text{Bi}_{1-x}\text{Na}_x\text{TiO}_3$) where $x=0.45$ was synthesized by Solid State Reaction technique. X-ray diffraction analysis reports single phase with rhombohedral structure. The lattice parameters obtained in BNT are $a=3.880\text{\AA}$ and $\alpha=89.78^{\circ}$. The sintering temperature increases the density of the material also increases to a maximum value. Further when the temperature increases the density of the material decreases and found to be more than 95% to that of the theoretical density. When the temperature is increased above T_c , the $\tan\delta$ is found to increase.

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