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# Structural and Dielectric Properties of $ZrO_2$ Added $(Na_{1/2}Bi_{1/2})TiO_3$ Ceramic

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Polycrystalline samples of  $ZrO_2$  added  $(Na_{1/2}Bi_{1/2})TiO_3$  were prepared using high-temperature solid-state reaction method at  $1050^\circ C$  and subsequent sintering at  $1090^\circ C$  in air atmosphere. Rietveld analyses of XRD data indicated the formation of a single-phase hexagonal structure with  $R3c$  symmetry. Dielectric studies revealed the relaxor behaviour. The addition of  $ZrO_2$  to  $(Na_{1/2}Bi_{1/2})TiO_3$  shifted phase transition temperature as well as depolarization temperature to higher side which is desirable for piezoelectric applications. The frequency dependence of the temperature of the permittivity maximum was modeled using Vogel-Fulcher relation. The dielectric relaxation in the system is found to be analogous to the magnetic relaxation in spin-glass system.

Keywords: Lead free compound; Perovskite; Dielectric properties; Relaxor.

## I. INTRODUCTION

Perovskite  $ABO_3$ -type oxides exhibit interesting properties providing potential applications in piezoelectric transducers, pyroelectric detectors, electrostrictive actuators, MEMs, etc. The materials used for these applications are mainly lead bearing compounds e.g.  $PbTiO_3$ ,  $Pb(Zr,Ti)O_3$ ,  $Pb(Mg_{1/3}Nb_{2/3})O_3$ , etc. However, volatilization of toxic  $PbO$  during high-temperature sintering not only causes environmental pollution but also generate instability of composition and electrical properties of the products. Also, products containing  $Pb$ -based gadgets are not recyclable. Taking these aspects into consideration, search of eco-friendly lead-free compounds having either comparable or superior electrical properties for such applications are the main trends of research nowadays [1].

Sodium bismuth titanate,  $(Na_{1/2}Bi_{1/2})TiO_3$  (NBT) is considered to be an excellent candidate as a key material of lead-free piezoelectric ceramic, which shows strong ferroelectric properties having a phase transition temperature at  $320^\circ C$  with relaxor behaviour [2-6]. Further, the electronic structure of different components of  $(Na_{1/2}Bi_{1/2})TiO_3$  and  $Pb(Zr,Ti)O_3$  are:  $Na(Z = 11)$   $[(Ne)3s^1]$ ;  $Bi(Z = 83)$   $[(Xe)6s^2 4f^{14} 5d^{10} 6p^3]$ ;  $Ti(Z = 22)$   $[(Ar)4s^2 3d^2]$ ;  $O(Z = 8)$   $[(He)2s^2 2p^4]$ ;  $Pb(Z = 82)$   $[(Xe)6s^2 4f^{14} 5d^{10} 6p^2]$  and  $Zr(Z = 40)$   $[(Kr)5s^2 4d^2]$ . The covalency between unoccupied states of the A-site ion in the perovskite structure, such as  $Pb$  6d-states and  $Bi$  6d-states, and  $O$  p-states favoured ferroelectric ground states [7, 10]. Also  $Bi^{3+}$  ions are iso-electronic with  $Pb^{2+}$ , both showing a lone pair effect, encouraged further studies of NBT as alternative to PZT ceramics. In addition, NBT exhibits an anomaly in its dielectric properties as a result of low temperature phase transition from the ferroelectric to the anti-ferroelectric phase at

about  $200^\circ C$ , which is termed as depolarization temperature  $T_d$ . This  $T_d$  is an important factor for NBT and NBT-based ceramics in view of their practical uses, because the piezoelectric response disappears above  $T_d$ . It has been reported that the additives like  $MnCO_3$  [11],  $La_2O_3$  [12, 13],  $CeO_2$  [13],  $Bi_2O_3 - Sc_2O_3$  [14],  $LiTaO_3$  [15],  $NaNbO_3$  [16], etc. showed improvement in the electrical properties of NBT while the  $T_d$  was greatly reduced. Recently, it has been observed that  $WO_3$  added NBT system showed relaxor behaviour and both  $T_d$  ( $\sim 300^\circ C$  at 1 kHz) as well as  $T_m$  ( $= 438^\circ C$  at 1 kHz) shifted towards higher temperature side [1, 17]. In view of these, in the present work, structural, microstructural and dielectric studies of  $(1-x)NBT - xZrO_2$ ; ( $0 \leq x \leq 0.1$ ) (abbreviated hereafter NBT –  $ZrO_2$ ) ceramics are reported.

## II. EXPERIMENTAL PROCEDURE

A high temperature solid-state reaction method was used to prepare  $ZrO_2$  added  $(Na_{1/2}Bi_{1/2})TiO_3$  ceramics using AR-grade (99.9%+ pure) chemicals  $Na_2CO_3$ ,  $Bi_2O_3$ ,  $TiO_2$  and  $ZrO_2$ . The calcination temperature was kept at  $1050^\circ C$  for 4h. Circular disc shaped pellets were made by applying uniaxial stress of 650 MPa. The pellets were then subsequently heated at  $1090^\circ C$  for 3h in air atmosphere followed by furnace cooling. Completion of the reaction and the formation of the desired compound were checked by X-ray diffraction method. The weights of the samples were monitored before and after heat treatments. The maximum difference was about 1.12 mg for the total of 10 g for all the compounds. Therefore, the compositions of the samples were considered to be the same as the initial one. The XRD data were collected on calcined powder with a X-ray diffractometer (Rikagu miniflex, Japan) at room temperature, using  $CuK\alpha$  radiation ( $\lambda = 0.15418$  nm), over a wide range of Bragg angles ( $20^\circ \leq 2\theta \leq 80^\circ$ ) with a scanning speed of  $2^\circ \text{ min}^{-1}$ . Rietveld analyses [18] were carried on the samples to estimate the unit cell parameters, their crystal struc-

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ture, profile matching, *etc.* The refinements were carried out using the program FULLPROF 2000 [19] under Windows XP together with WinPLOTR. The microstructure of the sintered  $NBT - ZrO_2$  samples were taken on the fractured surface using a computer controlled scanning electron microscope (JEOL-JSM840A). The temperature dependence of dielectric constant ( $\epsilon$ ), phase angle ( $\theta$ ) and loss tangent ( $\tan\delta$ ) were measured at different frequencies using a computer-interfaced LCR Hi-Tester (HIOKI 3532-50), Japan on a symmetrical cell of type Ag|ceramic|Ag, where Ag is a conductive paint coated on both the flat faces of pellets.

### III. RESULTS AND DISCUSSION

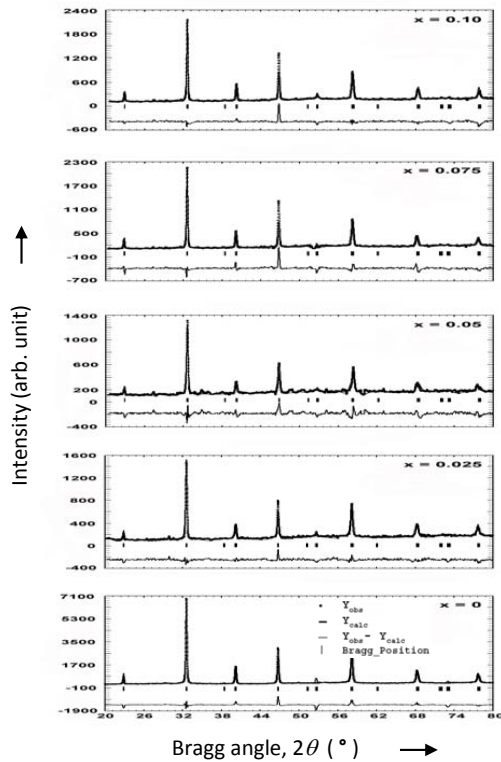


FIG. 1: Rietveld refined patterns of  $(1-x)(Na_{1/2}Bi_{1/2})TiO_3 - xZrO_2$ ;  $x = 0, 0.025, 0.05, 0.075$  and  $0.10$  systems in the space group  $R3c$ . Symbols represent the observed data points and the solid lines their Rietveld fit.

Fig. 1 depicts the observed, calculated and difference profiles for each compositions of  $NBT - ZrO_2$  after final cycle of refinement. Rietveld refinements were done on  $NBT - ZrO_2$  system, selecting the space group  $R3c$  in Glazers notation [20, 21]. The fractional coordinates for the hexagonal setting of rhombohedral perovskites with space group  $R3c$  in terms of independent refinable parameters used for the analyses were originally developed by Megaw and Darlington [22]. It can be seen that the profiles for observed and calculated one are perfectly matching. The value of  $\chi^2$  comes out to be of the order of 3, which is considered to be very good for estimations. The profile fitting procedure adopted was minimizing the  $\chi^2$  function [18]. Also, XRD analyses

indicated that  $ZrO_2$  added NBT system do not change their basic structure *i.e.* rhombohedral symmetry:  $a = 3.890(6)$  Å and  $\alpha = 89.71^\circ$  [6]; however, some shifting in the peak positions and changes in intensities of the peaks could be observed. All the compounds were found to have single-phase hexagonal crystal structure. The refined structural parameters for the all the compositions along with their unit cell volume are illustrated in Fig. 2. It is observed that the value of  $a$  increases (from 5.4812 Å for  $x = 0$  to 5.4897 Å for  $x = 0.10$ ) while that of  $c$  decreases (from 13.4832 Å for  $x = 0$  to 13.4774 Å for  $x = 0.10$ ) with the increasing  $ZrO_2$  content. Also an increase in the unit cell volume has been observed with the increment in additive percentage. Further, it can be seen that the changes in unit cell edges are at the third place of decimal (the overall volume increase was less than 0.3%). The average crystallite size of  $NBT - ZrO_2$  system was estimated from some strong reflections of low  $2\theta$  values of X-ray profile using Scherrer's equation:  $L_{hkl} = 0.89\lambda/\beta_{1/2}\cos\theta$ , where  $\beta_{1/2}$  is the full width at half maximum. The average particle size was estimated to be of the order of 50 nm.

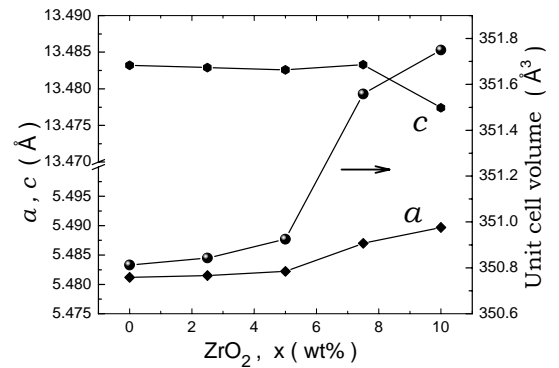


FIG. 2: Variation of lattice parameters and unit cell volume with  $ZrO_2$  content at room temperature for  $(1-x)(Na_{1/2}Bi_{1/2})TiO_3 - xZrO_2$  ( $x = 0, 0.025, 0.050, 0.075$  and  $0.10$ ).

Fig. 3 shows the SEM-micrographs of  $NBT - ZrO_2$  at  $1\mu m$  magnification. Grain shapes are clearly visible, indicates the existence of polycrystalline microstructure. The grain of unequal sizes ( $\sim 1 - 5\mu m$ ) appears to be distributed throughout the sample. The ratio of the average crystallite size to the grain size of  $NBT - ZrO_2$  is found to be of the order of  $10^{-2}$ .

Fig. 4 shows the variation of dielectric constant ( $\epsilon$ ) and dielectric loss ( $\tan\delta$ ) with temperature at different frequencies for  $0.025 \leq x \leq 0.1$ . It can be seen that the temperature of maximum relative permittivity ( $T_m$ ) shifted to higher temperature and dielectric maximum ( $\epsilon_m$ ) decreases with the increase in frequency for all the compositions. Also, the plots show the diffuse phase transition (DPT) with strong frequency dispersion, which clearly indicates the relaxor behavior in  $NBT - ZrO_2$ . Besides, it is important to note that the addition of  $ZrO_2$  to NBT shifts  $T_m$  as well as  $T_d$  to higher temperature side which is desirable in case of NBT and NBT-based solid solutions for piezoelectric applications. Further, the value of  $\tan\delta$  in the working temperature region (from room temperature to  $150^\circ C$ ) was found to be of the order of  $10^{-2}$  for all the compounds. The low  $\tan\delta$  of this kind can

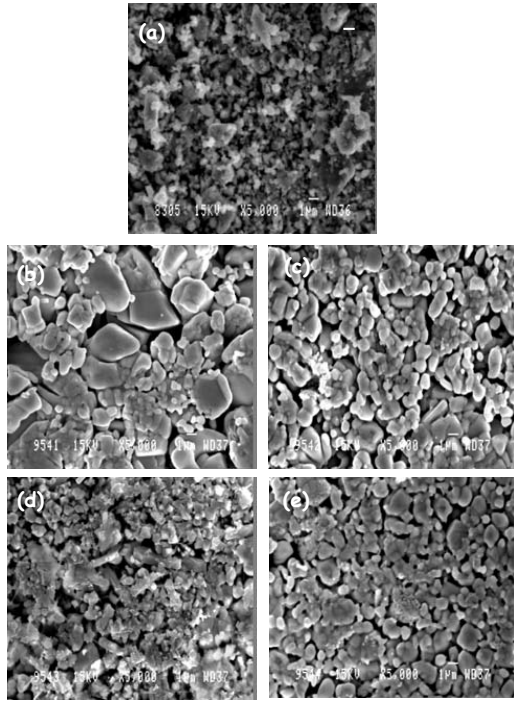


FIG. 3: SEM micrographs of  $(1-x)(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3-x\text{ZrO}_2$ ; (a)  $x = 0$ , (b)  $x = 0.025$ , (c)  $x = 0.05$ , (d)  $x = 0.075$  and (e)  $x = 0.10$ . The scale of the pictures is  $1 \mu\text{m}$ .

be advantageous when improved detectivity is required. The variation of  $\tan\delta$  with temperature follows similar as  $\epsilon$ - $T$  behaviour for all the compounds. Also, a decrease in the value  $\tan\delta$  at room temperature (from 0.097 for  $x = 0.025$  to 0.077 for  $x = 0.10$ ) has been observed with the increase in  $\text{ZrO}_2$  content ( $x$ ).

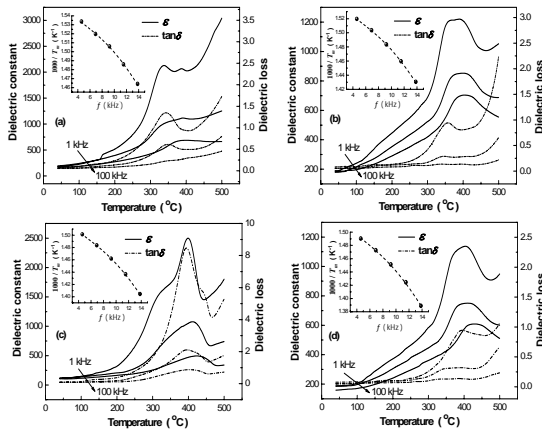


FIG. 4: Variation of dielectric constant (solid curves) and loss  $\tan\delta$  (dot-dashed curves) with temperature at different frequencies for  $(1-x)(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3-x\text{ZrO}_2$  ceramics (a)  $x = 0.025$ ; (b)  $x = 0.05$ ; (c)  $x = 0.075$  and (d)  $x = 0.10$ . Inset:  $1/T_m$  as a function of measuring frequency. The points correspond to the experimental data while the dotted line to fitting of Vogel-Fulcher relationship.

Here the region around the dielectric peak is broadened, which is one of the important characteristics of disordered perovskite type structure with DPT and does not follow the Curie-Weiss law, exhibiting the following type of temperature dependence:

$$1/\epsilon - 1/\epsilon_m = A(T - T_m)^\gamma \quad (1)$$

where  $\gamma$  is a critical exponent which lies in the range  $1 < \gamma \leq 2$ .  $\gamma = 1$  represents ideal Curie-Weiss behaviour while between 1 and 2 indicate diffuse behaviour [23, 24]. The value of exponent  $\gamma$  was estimated using linear least square fitting of experimental data to expression (1) [25]. We find  $\gamma > 1$  for all the cases. The value of  $\gamma > 1$  imply diffuse phase transition which may be due to compositional fluctuations where the local curie points of different microregions are statistically distributed around the mean Curie temperature.

It is known that the frequency dependence of  $T_m$  in relaxor ferroelectrics cannot be described by simple Arrhenius law, which is to be expected for Debye-type relaxation process, but instead this dependence obeys the Vogel-Fulcher law [1]. In order to analyse relaxation features of  $\text{NBT} - \text{ZrO}_2$  ceramics, the experimental data of  $\ln f$  vs.  $1/T_m$  were modeled using the Vogel-Fulcher relationship:

$$f = f_0 \exp[-E_a/k_B(T_m - T_f)] \quad (2)$$

where  $f$  is the operating frequency,  $f_0$  is the attempt frequency,  $E_a$  is the activation energy,  $T_f$  is the static freezing temperature and  $k_B$  is Boltzmann constant. Insets of Fig.4 shows the variation of  $\ln f$  with inverse of temperature  $T_m$  where the solid circles represent the experimental data. It can be observed from this figure that the frequency derivative of  $1/T_m$  is smaller at lower frequencies. This illustrates that as  $f \rightarrow 0$ , a static freezing temperature is approached. Further, the relaxation time ( $\tau = 1/f$ ) is distributed over a certain temperature region. As the temperature is lowered,  $\tau$  increases and at a critical value  $T_m = T_f$ ,  $\tau$  becomes extremely large and consequently the stable polarization is frozen to the glassy state [26]. This phenomenon has been observed in spin-glass system [27]. Excellent fitting of Vogel-Fulcher relation with experimental data suggests that this mechanism can also be employed to explain relaxor behavior in such ceramics. The fitting parameters:  $E_a$ ,  $f_0$  and  $T_f$  are depicted in Table 1, which are consistent with the earlier reports on similar system [1, 26, 28]. The value of  $f_0$  is found to be in the optical frequency range of lattice vibrations in all the cases. We speculate that the addition of oxides have caused nanoscale heterogeneity within the material leading to relaxor behaviour.

TABLE I: Vogel-Fulcher parameters for  $(1-x)\text{NBT} - x\text{ZrO}_2$ ;  $x = 0, 0.025, 0.05, 0.075$  and  $0.10$  ceramics.

Fitting parameters	$x = 0$	$x = 0.025$	$x = 0.05$	$x = 0.075$	$x = 0.10$
$f_0(\text{Hz})$	$9.020 \times 10^{11}$	$1.052 \times 10^{12}$	$1.230 \times 10^{12}$	$1.640 \times 10^{12}$	$1.980 \times 10^{12}$
$E_a(\text{eV})$	0.109	0.093	0.125	0.145	0.157
$T_f(^{\circ}\text{C})$	258.71	332.77	322.65	321.88	320.62
$R^2$	0.9999	0.9985	0.9997	0.9998	0.9997

#### IV. SUMMARY

Polycrystalline samples of  $\text{NBT} - \text{ZrO}_2$ , prepared through a high-temperature solid-state reaction technique, were found to have single-phase perovskite type hexagonal structure showed the relaxor behavior. The addition of  $\text{ZrO}_2$  to NBT shifts  $T_m$  as well as  $T_d$  to higher temperature side and

decreases the dielectric loss which is desirable for piezoelectric applications. Modeling of frequency dependent dielectric data using Vogel-Fulcher relationship gives a strong evidence for the static freezing temperature of thermally activated polarization fluctuations in the system. Therefore, the dielectric relaxation in the system may be considered analogous to the magnetic relaxation in spin-glass system.

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