Dielectric properties of BNT-xBT prepared by hydrothermal process

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The BNT ceramic sample might be a good replacement for PZT piezoelectric in industrial applications, especially in energy harvesting from crystal vibrations. In order to enhance the performance of BNT ceramic, the solid solution was chosen by substitution with Ba^{+2} at Morphotropic Phase Boundary (MPB). The BNT-xBT powders with $x = 1, 0.07, 0.06$ and 0 were prepared by the hydrothermal method with average particle size (65–150 nm) at ($90^\circ\text{C}/72\text{ h}$). The ceramic disc was sintered at ($1150^\circ\text{C}/4\text{ h}$) and showed excellent relative density of about 96%. The results of X-ray diffraction (XRD) confirmed the MPB for $x = 0.06$ and 0.07 , while the BNT had a rhombohedral structure and BT had a tetragonal structure. The dielectric measurements showed that BNT, BNT-7BT, BNT-6BT behave as the relaxator ferroelectric and showed a strong dependence on frequency, especially in the MPB region while BT behaves as a normal ferroelectric. Both the Curie temperature and depolarization temperature decrease at the MPB region and showed strong dependency on frequency.

Keywords: Ferroelectric behavior; piezoelectric behavior; energy harvesting; hydrothermal process.

1. Introduction

The bismuth sodium titanate, BNT-system, has chemical formula $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ with a complex A-site perovskite application. The BNT has a Rhombohedral perovskite structure with Na^{+1} and Bi^{+3} distributed sequentially in A-site.¹ Many studies focused on BNT as a ceramic, and focused on this compound as a lead-free piezoelectric or the replacement for PZT in industrial applications especially in energy harvesting from crystal vibrations. The BNT has several drawbacks in the alternative replacement for PZT such as the high value of the coercive electric field ($> 60\text{ kV/cm}$). This difficulty is making the limitation in the applications of BNT.^{2–4} The BNT is considered as the relaxator ferroelectric that has a high Curie temperature (320°C), and high depolarization temperature of about ($> 200^\circ\text{C}$) that is a second drawback of BNT. One of the possible solutions to overcome the drawbacks in BNT, is using a solid solution by substituting of either A or B sites or by creating an oxygen vacancy. The last will lead to a fast degradation of polarization. The substitution of A and B sites is suitable to solve the problem of high coercive electric field.^{4–6} To overcome the second drawback, one must be decreasing the value of depolarization temperature from 200°C to nearly room temperature in order to enhance the piezoelectric performance. In this research, the substitution of A-site in BNT with Ba^{+2} had been done, it had an ionic radius greater than (Bi,Na). The substitution of Ba^{+2} led to the creation of a solid solution between bismuth sodium titanate and barium titanate (BT) ($(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$). It had a direct effect on the

decreasing the depolarization temperature because the BT was ferroelectric with a Curie temperature of about 120°C .

2. Experimental Work

A hydrothermal method was used in the preparation of BNT-xBT powder with $x = 0, 0.06, 0.07$ and 1 . The preparation of the powder started by adding TiCl_4 gradually to propanol with a ratio of 1:10 under constant stirring to get a yellow gummy solution. The distilled water of 10 ml was added to this solution to get a transparent solution (Sol-1). The bismuth nitrate was added to 10 ml of concentrated hydrochloric acid, then the sodium acetate and/or barium nitrate were added with stoichiometric amounts to the resultant solution producing a transparent solution (Sol-2). The mixing of (Sol-1) and (Sol-2) with oxalic acid at stoichiometric ratio was done under warm conditions, and with stirring at $90^\circ\text{C}/15\text{ min}$. Then a gradual dropping of 10 M solution of sodium hydroxide was added to the oxalate solution with continuous stirring at $90^\circ\text{C}/72\text{ h}$.^{7–10} The resultant powder was washed and filtered for five times with distilled water, then characterized by X-ray diffraction XRD analysis. The steps for preparation of BNT via a hydrothermal process is shown in Fig. 1.

The resultant powder was pressed into a disc by 250 MPa then sintered at ($1150^\circ\text{C}/4\text{ h}$) for all samples. The prepared samples were analyzed by XRD that was carried out at room temperature using Panalytical diffractometer with $\text{Cu } k_{\alpha 1}$ wavelength ($\lambda = 1.54064\text{ \AA}$). The XRD computational analyses were performed using different software packages to

Fig. 1. Steps for preparation BNT-xBT via hydrothermal method.

determine the lattice constants, symmetry, and resolving the overlapping of MPB tetragonal and rhombohedral phases. The crystal impact match V3¹¹ and crystal impact diamond V4 software¹² were used for the phase identification by unit cell refinement and space group determination. A diffraction database was used for the specification of the produced powder PDF# 89-1428 for BaTiO₃,¹³ PDF# 05-0626 for BaTiO₃,¹⁴ International Center for Diffraction Data (ICDD),¹⁵ COD#1507756 for BaTiO₃,¹⁸ COD#2100858 for BaTiO₃,¹⁶ COD# 2103295 for Bi_{0.5}Na_{0.5}TiO₃,² COD#2102068 for Bi_{0.5}Na_{0.5}TiO₃,¹⁷ and COD#1532924 for Bi_{0.5}K_{0.5}TiO₃¹⁸ from Crystallography Open Database were used for the specifications of the produced powder.

The dielectric measurement was performed using TEGAM-3550 LCR meter at 1 V. The disc was placed in a suitable testing quartz cell under vacuum.¹⁹ The ceramic disc was polished and sandwiched between two gold electrodes coated on the surface by sputtering. The dielectric measurement had been performed by changing the temperature from room temperature to 500°C at different frequencies 1 kHz, 10 kHz, 100 kHz, 1 MHz, 3 MHz and 5 MHz. The ferroelectric relaxation behavior with phase diffusion transition was deduced according to the modified Curie-Wise relation equation⁹

$$\frac{1}{\varepsilon'} - \frac{1}{\varepsilon'_{\max}} = C^{-\gamma}(T - T_{\max})^{\gamma},$$

where ε' is the dielectric constant, $\varepsilon'_{\max}$ is the maximum value of the dielectric constant, C is the Curie constant, $T_{\max}$ is the temperature at $\varepsilon'_{\max}$ and γ is the diffusion coefficient of the phase transition.

3. Results and Discussion

The substitution with barium (Ba⁺²), had an equivalent valence number of Ba⁺² and (Bi_{0.5}⁺³Na_{0.5}⁺¹)⁺². The net valence of

(Bi, Na) is (+2), so Ba⁺² is suitable for the replacement of both Bi and Na together by the following equation. The BaTiO₃ (BT) has a tetragonal phase while BNT has a rhombohedral, so MPB could be easily obtained. The compound BT has a high value of dielectric constant which makes the substitution of Ba⁺² suitable for energy harvesting applications.^{20–22}

where $y = 1, 0.07, 0.06$ and 0 for BNT, BNT-7BT, BNT-6BT and BT, respectively. The XRD analysis showed that BNT had a rhombohedral phase, while BT had a tetragonal phase. Both phases BNT-6BT and BNT-7BT had MPB, they had both a tetragonal and rhombohedral phase. The XRD patterns for BNT-xBT samples are shown in Fig. 2, the MPB recognized by the appearance of (111) regarding to the tetragonal phase. It was overlapped with the dual peaks of rhombohedral (02 $\bar{2}$)(006), around $2\theta = 40$. The rhombohedral single peak (024) was overlapped with a tetragonal dual peak (020)(002) that appears around ($2\theta = 46$), the deconvolution of these overlapping is shown in Fig. 3.

The BNT-6BT had MPB with a rhombohedral lattice ($a = b = 5.4955 \text{ \AA}$, $c = 13.387 \text{ \AA}$, $\alpha = \beta = 90$ and $\gamma = 120$) and a tetragonal lattice with ($a = b = 3.8871 \text{ \AA}$, $c = 3.8971 \text{ \AA}$ and $\alpha = \beta = \gamma = 90$). The BNT-7BT had MPB with the same lattice constants of BNT-6BT tetragonal lattice, but there was a slight difference in the c -axis of the rhombohedral lattice ($c = 13.5276$) as shown in Table 1. The relative density of the sintered disc was (96%, 94%, 94%, and 70%) for BNT, BNT-7BT, BNT6BT and BT, respectively. The high density of the ceramic discs was due to the successful sintering process. The output of SEM showed the particle size of the prepared powder in the range (60–150 nm), while the grain size was about 1, 0.8, 0.7, 1 for BNT, BNT-7BT, BNT6BT and BT, respectively. The particle

Fig. 2. XRD patterns for BNT, BNT6BT, BNT-7BT and BT.

Fig. 3. De-convolution of the overlapping of tetragonal and rhombohedral peaks.

and grain size for BNT-*x*BT powder and ceramics were shown in Fig. 4.

The dielectric constant and loss factor as a function of temperature was a good indication to show the relaxator

behavior of ferroelectrics.²³ The samples BNT, BNT-6BT, BNT-7BT showed the relaxator behavior of ferroelectrics. The results of dielectric measurements for BNT ceramic showed the depolarization temperature above 200°C. The

Table 1. The XRD results for BNT-*x*BT.

Sample	<i>x</i>	Chemical composition	Space group	Lattice parameter (Å)/Angle		Space group	Lattice parameter (Å)
BNT	1	Bi _{0.5} Na _{0.5} TiO ₃	R 3 c (161) Rhombohedral	A = 5.490 B = 5.490 C = 13.387	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$		
BNT-7BT	0.07	Bi _{0.465} Na _{0.465} Ba _{0.07} TiO ₃	R 3 c (161) Rhombohedral	A = 5.4955 B = 5.4955 C = 13.5276	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	P 4 mm (99) Tetragonal	A = 3.8871 B = 3.8871 C = 3.8971
BNT-6BT	0.06	Bi _{0.47} Na _{0.47} Ba _{0.06} TiO ₃	R 3 c (161) Rhombohedral	A = 5.4955 B = 5.4955 C = 13.387	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	P 4 mm (99) Tetragonal	A = 3.8871 B = 3.8871 C = 3.8971
BT	0	BaTiO ₃				P 4 mm (99) Tetragonal	A = 3.99 B = 3.99 C = 4.07

Fig. 4. SEM image (a) BNT powder, (b) BNT ceramic, (c) BNT-6BT ceramic, (d) BNT-7BT ceramic, (e) BT ceramic.

Fig. 5. Dielectric constant and loss factor as a function of temperature for (a) BNT, (b) BNT-6BT, (c) BNT-7BT, (d) BT.

value of Curie temperature had a maximum temperature for BNT around 300°C depending on the frequency as shown in Fig. 5(a). While BNT-6BT had a Curie temperature in the range (300–350°C), and decreased as frequency increased. The depolarization temperature was about (80°C) depending on the frequency as shown in Fig. 5(b). The Curie temperature for BNT-7BT was close to 300°C and varied with frequency. While the depolarization temperature was about 120°C and varied with frequency as shown in Fig. 5(c). The dielectric measurement of the BT-sample exhibited the presence of normal ferroelectrics. The Curie temperature of the BT was about 100°C. There was another transition temperature that appeared at about 5°C that was related to the transition from orthorhombic (Amm2) to the tetragonal (P4mm) as shown in Fig. 5(d).

The diffusion coefficient of transition (γ) had the value in the range (1–2), if $\gamma = 1$ means the normal ferroelectrics, whereas $\gamma = 2$ means the ideal relaxator ferroelectrics.^{24,25} The diffusion coefficient of BNT was in the range (1.2–1.6) and varied with frequency. The frequency increases led to increase in the value of the diffusion coefficient i.e., increasing

the frequency led towards ideal relaxator ferroelectrics as shown in Fig. 6(a). The diffusion coefficient for BT was about the one that means the behavior was normal ferroelectrics and frequency independent, as shown in Fig. 6(d). The diffusion coefficient for BNT-6BT and BNT-7BT was in the range (1.4–1.95). It was greater than BNT and strongly depends on frequency, as shown in Figs. 6(b)–6(c). The MPB region for BNT-6BT and BNT-7BT showed a strong dependence on the diffusion coefficient of transition. Increasing the frequency was tending to increase γ while BNT showed a little dependence on frequency. The BT sample had a fixed value of diffusion coefficient and was frequency-independent, and the behavior was similar to normal ferroelectrics, as shown in Fig. 7(a). The Curie temperature for BNT-xBT was frequency dependent, especially in the BNT-7BT sample, while in the BT sample the Curie temperature was frequency independent as shown in Fig. 7(b). The depolarization temperature for the dielectric constant curve was T_{d1} , and the second depolarization temperature in the loss factor curve was (T_{d2}).

There was no significant value of T_{d1} and T_{d2} for BT sample, while for BNT the T_{d1} decreased with frequency

Fig. 6. The diffusion coefficient of transition (γ) for (a) BNT, (b) BNT-6BT, (c) BNT-7BT, (d) BT.

Fig. 7. Dielectric measurement results for BNT-xBT system.

Fig. 7. (Continued)

increase, while the value of T_{d2} appeared at higher frequency only. Both the BNT-6BT and BNT-7BT samples showed depolarization values lower than BNT and decreased with frequency increase, as shown in Figs. 7(c) and 7(d).

4. Conclusion

The BNT-xBT ceramic samples were prepared by hydrothermal processes with spherical particle shape in the range of 60–150 nm, at $x = 1, 0.07, 0.06$ and 0. Both BNT-7BT and BNT-6BT samples showed MPB phase, so it had a high piezoelectric performance. The dielectric measurements showed that the BNT, BNT-7BT, BNT-6BT samples indicated as a relaxator behavior of ferroelectrics while the BT sample showed the normal ferroelectric behavior. The depolarization temperature in MPB region was decreased to about 80°C and became strongly dependent on frequency. The diffusion coefficient of transition at MPB region also strongly depended on frequency. When the frequency increased the diffusion coefficient also increased and the depolarization temperature decreased.

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