

Crystal Structure Analysis of the BaTiO₃ and ZrO₂-doped (Bi_{0.5}Na_{0.5})TiO₃ with X-ray Diffraction Techniques Using the Rietveld Method

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ABSTRACT

The compound of (Bi_{0.5}Na_{0.5})TiO₃ (BNT) doped with BaTiO₃ (BT) and ZrO₂ were synthesized and its crystal structure were analyzed. Three types of samples, namely (Bi_{0.5}Na_{0.5})_{0.93}Ba_{0.05}Zr_{0.02}TiO₃ (BNBZT1), (Bi_{0.5}Na_{0.5})_{0.90}Ba_{0.05}Zr_{0.05} (BNBZT2) and (Bi_{0.5}Na_{0.5})_{0.85}Ba_{0.05}Zr_{0.10}TiO₃ (BNBZT3) were prepared. The samples were synthesized by solid state reaction method using raw materials of Bi₂O₃, Na₂CO₃, BaCO₃, TiO₂ and ZrO₂ powders. The raw materials were mixed with agate mortar for 3 hours. Precursor was made into pellets with hydraulic press at 3,000 psi. Pellets were calcined at 300 °C for an hour, and then sintered at 1000 °C for 5 hours. The samples were characterized with X-ray diffraction techniques using the Rietveld method and Raman spectroscopy. The analysis results showed that BNT doped BT and ZrO₂ have tetragonal structure, space group I4/mcm, Volume I, No.140 with lattice parameters a = b = 5.519 (2) Å, c = 7.808 (4) Å (BNBZT1), a = b = 5.512 (1) Å, c = 7.798 (5) Å (BNBZT2) and a = b = 5.513 (1) Å, c = 7.800 (2) Å (BNBZT3). For these three samples, Ba²⁺ and Zr⁴⁺ cations entered into the BNT crystal system by partial substitution of cations (Bi,Na)²⁺. But there were also some of Ti³⁺ cations in the BNBZT3 replaced by Zr⁴⁺. Ionic configuration (compound) of BNBZT1, BNBZT2 and BNBZT3 are respectively (Bi_{0.45}Na_{0.48})_{0.93}Ba_{0.05}Zr_{0.01}TiO₃, (Bi_{0.41}Na_{0.49})_{0.90}Ba_{0.05}Zr_{0.03}TiO₃ and (Bi_{0.42}Na_{0.43})_{0.85}Ba_{0.05}Zr_{0.01}(Ti_{0.97}Zr_{0.03})O₃.

KEYWORDS: Crystal structure, BNT, BT, ZrO₂ doping, X-ray diffraction, Rietveld method, Raman spectroscopy

INTRODUCTION

Piezoelectric materials which are most widely used today are lead-based ceramics, such as PbTiO₃-PbZrO₃ (PZT). This is because these materials have very good piezoelectric properties. However, PZT pollute the environment as toxic. Therefore, many scientists all over the world then perform R & D activities on piezoelectric materials that are environmentally friendly to replace PZT [1].

Among the lead-free piezoelectric materials widely studied are (Bi_{0.5}Na_{0.5})TiO₃ (BNT), in which this material was first reported by Smolenskii et al [2]. BNT is projected as the replacement candidate of lead based piezoelectric materials which have been widely used in various industrial fields. BNT used as a replacement option of PZT, because it has a high remanent polarization and temperature phase transition, ie, respectively, Pr = 38 μC/cm² and Tc = 320 °C [3].

However BNT applications have been constrained due to this ceramic has a high coercive field, ie, Ec = 7.3 kV / mm, making it difficult to do a poll on this material [4]. To solve this problem, various types of compounds, such as CaTiO₃, NaNbO₃, ZrO₂, BaTiO₃ and others are doped into BNT with the hope of forming solid solutions with mechanical and electrical properties commensurate with PZT.

The chemical formula of BNT is (Bi_{0.5}Na_{0.5})TiO₃ and having a perovskite structure of ABO₃. Thus, site-A and site-B successively are occupied by cations (Bi_{0.5}Na_{0.5})²⁺ and Ti⁴⁺. Based on the fraction of atomic coordinates, ABO₃ perovskite can be classified into three categories. The first category, coordinate fraction (Bi_{0.5}Na_{0.5})²⁺: (0.0,0.0,0.0), Ti⁴⁺: (0.5,0.5,0.5) and O₂⁻: (0.5,0.0,0.0), (0.0,0.5,0.0), (0.0,0.0,0.5). The second category, coordinate fraction (Bi_{0.5}Na_{0.5})²⁺: (0.5,0.5,0.5), Ti⁴⁺: (0.0,0.0,0.0), and O₂⁻: (0.5,0.0,0.0), (0.0,0.5,0.0), (0.0,0.0,0.5) [5]. The third category, coordinate fraction (Bi_{0.5}Na_{0.5})²⁺: (0.0,0.5,0.25), Ti⁴⁺: (0.0,0.0,0.0) and O₂⁻: (0.0,0.0,0.25), (0.17,0.77,0.0) [6].

Doping is designed for partial substitution of ions in site-A, because the partial substitution at site-B, it just makes the piezoelectric properties of materials increased slightly [7]. By choosing the right type of cations at site-A, the properties of piezoelectric ceramics BNT could be better [8].

In previous studies, Kumari et al. [9] added ZrO₂ on the BNT. The results of the analysis with the Rietveld method of X-ray diffraction data indicate that the sample is a single crystal with a hexagonal structure, R3c space group, and the lattice parameters, a = 5.4812 Å and c = 13.4832 Å. The addition of ZrO₂ causes phase transition temperature, T_m and depolarization temperature, T_d of BNT increased. In this study, Kumari did not explain whether Zr⁴⁺ cations entered into the site-A or-B site. Rao et al. [10] investigated the effects of substitution of Ba²⁺ and Zr⁴⁺ in site-A and site-B from BNT, respectively. The results of the analysis of x-ray diffraction data showed that BNT has a rhombohedral structure with its lattice parameters, a =

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$b = c = 3.87 \text{ \AA}$. Park et al [11] examined the doping effect of Zr^{4+} on depolarization temperature and piezoelectric properties of $(Bi_{0.5}Na_{0.5})TiO_3$ - $BaTiO_3$ (BNT-BT). From the data of x-ray diffraction patterns revealed there are two phases in the synthesized samples, namely rhombohedral phase and tetragonal phase. As a result of the substitution of Zr^{4+} on site-B, causing depolarization temperature, T_d decreases.

The three samples mention above, each synthesized by solid state reaction method. It appears that, the structure identity of BNT after being doped with Ba^{2+} and Zr^{4+} cations in previous studies differs from each other. This issue is interesting to be studied in more depth, because the given structure of crystalline materials is closely related to the electrical properties, and mechanical properties of the materials. In the current study the synthesis of BNT samples was conducted, where some cations in site-A simultaneously replaced by cations Ba^{2+} and Zr^{4+} . Both types of cations Ba^{2+} and Zr^{4+} come from $BaTiO_3$ and ZrO_2 oxides, respectively. The purpose of the research is to conduct qualitative and quantitative phase analysis of the BNT after being doped by $BaTiO_3$ and ZrO_2 .

MATERIALS AND EXPERIMENTAL

The raw materials for synthesizing BNT doped by $BaTiO_3$ and ZrO_2 were Bi_2O_3 (99.999%, Strem Chemicals), Na_2CO_3 (99.9%, Merck), TiO_2 (99.9%, Strem Chemicals), $BaCO_3$ (99%, Merck), and ZrO_2 (99.9%, Merck) in the form of powder. The five types of raw materials are weighed with the appropriate mole ratio. In this study, we prepared three types of samples, as shown in Table 1. The raw materials were then mixed by stirring using agate mortar for 3 hours. Precursor powder is pressed into pellets by using hydraulic press machine at 3,000 psi. Pellets were calcined at $300 \text{ }^\circ\text{C}$ for 1 h (heating rate of $6.7 \text{ }^\circ\text{C}/\text{min}$), followed by sintering at $1,000 \text{ }^\circ\text{C}$ for 5 h (heating rate of $5.8 \text{ }^\circ\text{C}/\text{min}$), then cooled to room temperature (cooling rate of $5.4 \text{ }^\circ\text{C}/\text{min}$).

Table 1. Sample chemical composition

No.	Sample	Chemical composition
1.	BNBZT1	$(Bi_{0.5}Na_{0.5})_{0.93}Ba_{0.05}Zr_{0.02}TiO_3$
2.	BNBZT2	$(Bi_{0.5}Na_{0.5})_{0.90}Ba_{0.05}Zr_{0.05}TiO_3$
3.	BNBZT3	$(Bi_{0.5}Na_{0.5})_{0.85}Ba_{0.05}Zr_{0.10}TiO_3$

Sintered pellets were characterized by x-ray diffraction techniques. Characterization is intended to determine the quality and quantity of BNT phase in the preview phase. This study used X-ray Diffractometer (XRD), brand: Philips, Type: PW1710, $CuK\alpha$ radiation, wavelength, $\lambda = 1.5406 \text{ \AA}$, mode: continuous-scan, step size: 0.02° , and time per step: 0.5 seconds. Profile of x-ray diffraction patterns were analyzed using the Rietan software (Rietveld Analysis) [12]. To confirm the ionic configuration of site-A and site-B in the BNT crystals doped BT and ZrO_2 , the characterization was performed by using Raman Microscope-Spectrometer, brand: Bruker, type: Senterra R200-785.

RESULTS AND DISCUSSION

In the first step of x-ray diffraction data refinement of the three types of samples BNBZT1, BNBZT2 and BNBZT3 it was assumed that the samples have a single phase. The crystal structure of samples was assumed to satisfy the third category, namely the tetragonal structure, with space group of $I4/mcm$, Volume I, Number 140 with the atomic coordinate fraction as illustrated in Table 2 [6,13].

Table 2. Atomic coordinate fraction (x_j, y_j, z_j) and atomic occupation factor (g_j) in BNT-BT unit cell, lattice parameter : $a = b = 5.48 \text{ \AA}$, $c = 7.75 \text{ \AA}$.

Atom	g_i	x_i	y_i	z_i
Bi	0.5	0.0	0.5	0.25
Na	0.5	0.0	0.5	0.25
Ti	1.0	0.0	0.0	0.0
O(1)	1.0	0.0	0.0	0.25
O(2)	1.0	0.17	0.77	0.0

X-ray diffraction patterns of the BNBZT1, BNBZT2 and BNBZT3 samples which were analyzed by using Rietveld method are shown in Figure 1. The observed profile are indicated by the dots and the calculated profiles are described by solid lines; vertical short lines indicate the position of Bragg peaks. Under the vertical short lines are the deviation profile between the observed and calculated intensities.

The refinement results of lattice parameters, temperature factors, lattice strain, crystallite size, crystal density, the volume of the crystal, the atomic occupation factors and reliability index of BNBZT1, BNBZT2, and BNBZT3 are shown in Table 3. Numbers in brackets are the accuracy imposed on the last digit after the decimal point.

It is shown in Figure 1 that almost all of the calculated diffraction profile coincide with the observed diffraction pattern. Figure1 shows a single peak observed, namely at $2\theta \approx 30^\circ$ (peak •), is not fitted yet. This means that the peak does not belong to the BNT-BT phase. The position of the angle and intensity of the peaks originating from the foreign phases is shown in Table4 in detail.

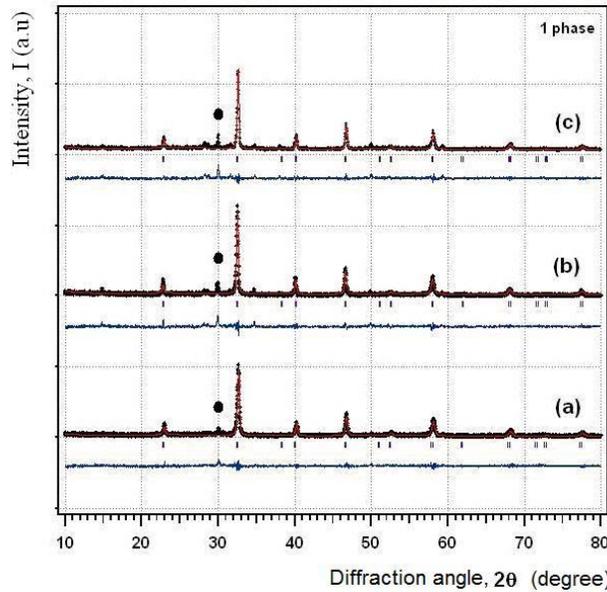


Figure 1. The Rietveld refinement results based on X-ray diffraction patterns of (a) BNBZT1, (b)BNBZT2and(c) BNBZT3samples.

Table 3. Lattice parameter (*a*, *b*, *c*), temperature factor (*Q*),crystal density (ρ), crystal volume (*V*), atomicoccupation factor (*g_j*) and*R*and*S*factor for BNBZT1, BNBZT2, and BNBZT3.

Structure parameter	BNBZT1	BNBZT2	BNBZT3
<i>a</i> = <i>b</i> (Å)	5.519(2)	5.511(1)	5.513(1)
<i>c</i> (Å)	7.807(4)	7.799(3)	7.800(3)
<i>Q</i> (Å ²)	2.4(9)	2(1)	2(1)
Bi ³⁺ : <i>g_i</i>	0.43(5)	0.39(6)	0.38(7)
Na ⁺ : <i>g_i</i>	0.50(5)	0.51(6)	0.47(7)
Ba ²⁺ : <i>g_i</i>	0.05	0.05	0.05
Zr ⁴⁺ : <i>g_i</i>	0.02	0.05	0.10
Ti ³⁺ : <i>g_i</i>	1.0	1.0	1.0
O(2) ²⁻ : <i>g_i</i>	0.9(2)	0.8(2)	0.8(3)
<i>x_i</i>	0.29(2)	0.28(3)	0.21(5)
<i>y_i</i>	0.79(2)	0.7(1)	0.6(1)
<i>V</i> (Å ³)	237.880	236.903	237.136
ρ (gr/cm ³)	5.762	5.495	5.492
<i>R</i> _{wp}	26.63	27.70	29.38
<i>R</i> _p	19.65	20.39	21.47
<i>S</i>	1.186	1.272	1.331

Qualitative analysis of a foreign phase was conducted by the Hanawalt method as follows: (1)In the Hanawalt table, we looked for compounds that have a *d* value at about 2.90to3.00Å. (2)It was found that *d*₁-*d*₂-*d*₃values corresponding to the intensity of the strongest diffraction peak of the first, second, third, respectively. The data are shown in Table5.It is shown in the table that the compound which has a *d* value at about 2.90 to 3.00Å is ZrO₂.

Table 4.2θ, *d* (Å) and*I* (counts/s) data from foreign peaks.

sample	2θ	<i>d</i> (Å)	<i>I</i> (c/s)
BNBZT1	30,04	2,975	66
BNBZT2	29,94	2,984	98
BNBZT3	30,04	2,975	104

From the elucidation above it can be concluded that all of the three samples show diffraction peaks of ZrO_2 . This means that some of the added ZrO_2 does not enter into the BNT-BT system, but instead form a composite with BNT-BT.

Table 5. Searching result data from the Hanawalt Table.

Compound	d (Å)	ID number
ZrO_2	3.00-2.64-1.82	42-1164
ZrO_2	2.96-1.82-1.83	37-1413
ZrO_2	3.00-2.59-1.84	37-0031
ZrO_2	3.00-1.84-1.56	24-1164
ZrO_2	2.96-1.83-1.55	17-0923
ZrO_2	2.95-1.80-1.54	14-0534

Therefore, refinement of x-ray diffraction data of the three types of samples BNBZT1, BNBZT2 and BNBZT3 was performed again by entering parameters of ZrO_2 phase. From the literature [14], it is known that ZrO_2 has a tetragonal structure, space group $P4_2/nmc$, Vol. I, No. 137. The atomic coordinate fractions are shown in Table 6. By performing two-phase calculations simultaneously (BNT-BT and ZrO_2 phase), it is expected to know what a mole fraction of the solid-dissolved ZrO_2 in BNT-BT crystalline system is.

Table 6. Atomic coordinate fraction (x_j , y_j , z_j) and atomic occupation factor (g_j) in ZrO_2 unit cell, lattice parameter : $a = b = 3.64$ Å, $c = 5.27$ Å.

Atom	g_i	x_i	y_i	z_i
Zr	1.0	0.0	0.0	0.0
O	1.0	0.0	0.5	0.185

The calculations were carried out step by step as follows: Iteration-1, refinement on the background counts parameters (b_0 , b_1 , ..., b_9) and scale factor (s) were carried out. Iteration-2, refinement on the FWHM parameter (U , V , W), and Lorentzian factor (X , Y) were done. Iteration-3, refinement on the lattice parameters (a , b , c) was performed. Iteration-4, scale factor (s) and preferred orientation factor (p) were refined. Iteration-5, the atomic occupation factor parameters (g_j), the atomic coordinate fraction (x_j , y_j , z_j) and temperature parameters (Q_j) were refined. Iteration-6, 7, 8, and so do the smoothing for all parameters simultaneously.

Table 7. Boundary condition of atomic occupation factor (g_j) in BNBZT1, BNBZT2 and BNBZT3 sample.

Sample	Boundary condition
BNBZT1	$g(Na) = 0.93 - g(Bi)$ $g(Ba) = 0.05$ $g(Zr) = 0.020, 0.015, 0.010, 0.005$.
BNBZT2	$g(Na) = 0.90 - g(Bi)$ $g(Ba) = 0.05$ $g(Zr) = 0.050, 0.040, 0.030, 0.020, 0.015, 0.010, 0.005$.
BNBZT3	$g(Na) = 0.85 - g(Bi)$ $g(Ba) = 0.05$ $g(Zr) = 0.100, 0.090, 0.080, 0.070, 0.060, 0.050, 0.040, 0.030, 0.020, 0.015, 0.010, 0.005$.

After all of the refinements were done, it is shown apparently that the atomic occupation factor of Ti is greater than 1.0. Therefore, the parameter is fixed, $g(Ti) = 1.0$. While the values of $g(Ba)$ and $g(Zr)$ after being refined they are each smaller than zero. To resolve this case the following steps were done: (1) Parameter $g(Ba) = 0.05$ is maintained at all three samples according to the experimental design. Because based on the diffraction data in Figure 1, there were no foreign peaks from Ba compounds. This means that the Ba element as much as 5 mol% is entirely soluble in crystalline solid of the BNT-BT system that goes for all three types of samples. (2) $g(Zr)$ parameter was varied manually, because based on the diffraction data in Figure 1, it was found the peak derived from Zr compounds. This means that not all elements of Zr dissolved in the crystalline solid of BNT-BT system. Thus, the mole fraction of Zr which enter into the BNT-BT crystalline system on BNBZT1, BNBZT2 and BNBZT3 samples is less than 2, 5, and 10 mol% respectively.

Therefore the calculation is done by applying some boundary conditions for the parameter of atomic occupation factor, g_j . The boundary condition for the g_j parameter of BNBZT1, BNBZT2 and BNBZT3 samples are shown in Table 7. By entering the values of the parameters in Table 7, then the best fitting quality of the diffraction pattern profile was chosen. Thus, the mole fraction of ZrO_2 that solid soluble in the crystalline BNT-BT system could be obtained. The best fitting qualities were determined by searching the smallest reliability index R_{WP} , R_P and S .

Table 8. Mol fraction of Zr that solid soluble in BNT-BT crystal system of BNBZT1, BNBZT2 and BNBZT3 sample.

Sample	g(Zr)	Reliability Index		
		R_{WP}	R_p	S
BNBZT1	0.020	25.31	18.77	1.128
	0.015	25.30	18.77	1.127
	0.010	25.25	18.72	1.125
	0.005	25.27	18.73	1.126
BNBZT2	0.050	26.39	20.15	1.212
	0.040	26.43	20.26	1.214
	0.030	26.33	19.97	1.209
	0.020	26.36	20.07	1.211
	0.015	26.38	20.12	1.212
	0.010	26.40	20.16	1.213
	0.005	26.41	20.21	1.213
BNBZT3	0.100	27.05	20.03	1.226
	0.090	27.03	19.98	1.225
	0.080	27.03	19.99	1.226
	0.070	27.03	19.98	1.225
	0.060	27.03	19.99	1.226
	0.050	27.03	19.98	1.225
	0.040	27.03	19.97	1.225
	0.030	27.03	19.98	1.225
	0.020	27.03	19.99	1.226
	0.015	27.03	19.99	1.226
	0.010	27.03	19.98	1.226
	0.005	27.03	19.98	1.225

X-ray diffraction patterns of the BNBZT1, BNBZT2 and BNBZT3 sample of analytical results are shown in Figure2. The picture is the best fitting results of the diffraction pattern profiles derived by applying the boundary conditions in Table7. It is shown in Figure 2 that no wall the calculated results of diffraction pattern profile coincide with the observed profile. Zr mole fraction that solid soluble in the BNT-BT crystal system of BNBZT1, BNBZT2 and BNBZT3 samples are 1, 3, and 4mol% respectively(Table 8). While smoothing results of the lattice parameters, temperature factors, the density of the crystal, the crystal volume, occupation factors of atoms, crystallite size and reliability index in BNBZT1, BNBZT2, andBNBZT3 are shown in Table9. Numbers in brackets are the accuracy imposed on the last digit after the decimal point.

Crystallite size, D is calculated by Scherrer formula[15], $D=(K\lambda)/(B.\cos\theta)$, where K is the Scherrer constant or dimensionless shape factor which has a typical value of about 0.98, but varies with the actual shape of the crystallite, $\lambda=1.5406\text{\AA}$ is the wavelength of X-rays, B is the line broadening at full width at half maximum (FWHM) intensity in radians, and θ is the Bragg angle.In Table 9 appears that the size of crystallites, D increases with increasing of ZrO_2 dopingfractionfrom 2to 5mol %,but then D slightly decrease in the addition of 10mol % doping.

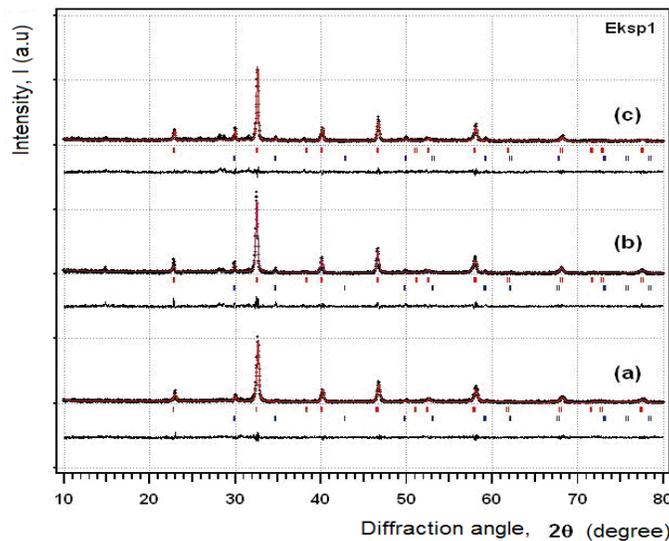


Figure 2. The best fitting results of the Rietveld refinement based on X-ray diffraction patterns by applying boundary conditions of (a)BNBZT1, (b) BNBZT2and (c)BNBZT3sample.

The entry of Zr into the BNT-BT crystalline system can be seen indirectly, i.e. by observing the value of the lattice parameter and/or the volume of the unit cell. If the lattice parameter and/or unit cell volume shrink, then more Zr^{4+} cations enter into the unit cell, i.e. by partial substitution of Bi^{3+} cations. This is possible because the size of Zr^{4+} cations ($r_{Zr^{4+}} = 0.72 \text{ \AA}$) is smaller than the size of Bi^{3+} cations ($r_{Bi^{3+}} = 1.36 \text{ \AA}$) and/or Na^+ ($r_{Na^+} = 1.39 \text{ \AA}$). This fits with the data in Table 9 for BNBZT1 and BNBZT2. However, the lattice parameter (volume) of the BNT-BT unit cell in BNBZT3, which has a 4 mole % of Zr, even a little larger than the lattice parameter (volume) of the BNT-BT unit cell in BNBZT2, which has a 3 mole % of Zr. This means there are some Zr^{4+} cations that replace Ti^{3+} cations, where the size of this cation, $r_{Ti^{3+}} = 0.61 \text{ \AA}$ is smaller than the size of Zr^{4+} cations.

Table 9. Lattice parameter (a, b, c), temperature factor (Q), crystal density (ρ), crystal volume (V), atomic occupation factor (g_j), crystalline size (D) and Rands factors in BNBZT1, BNBZT2, and BNBZT3 sample.

Structure parameter	BNBZT1	BNBZT2	BNBZT3
$a = b$ (Å)	5.519(2)	5.512(1)	5.513(1)
c (Å)	7.808(4)	7.798(5)	7.800(2)
Q (Å ²)	2.4(5)	2.7(6)	2.7(7)
$Bi^{3+} : g_j$	0.45(3)	0.41(3)	0.42(4)
$Na^+ : g_j$	0.48(3)	0.49(3)	0.43(4)
$Ba^{2+} : g_j$	0.05	0.05	0.05
$Zr^{4+} : g_j$	0.01	0.03	0.04
$Ti^{3+} : g_j$	1.0	1.0	1.0
$O(2)^{2-} : g_j$	1.0	1.0	1.0
x_j	0.20(1)	0.21(1)	0.20(1)
y_j	0.71(5)	0.73(6)	0.68(6)
V (Å ³)	237.900	236.970	237.118
ρ (gr/cm ³)	5.806	5.686	5.718
R_{wp}	25.25	26.33	27.03
R_p	18.72	19.97	19.97
S	1.125	1.209	1.225
D (nm)	31	41	38

Table 10. Boundary condition of atomic occupation factor (g_j) in BNBZT3 sample.

Sample	Boundary condition
BNBZT3	$g(Na) = 0.85 - g(Bi)$ $g(Ba) = 0.05$ $g(Zr1) = 0.03, 0.020, 0.010.$ $g(Zr2) = 1.0 - g(Ti)$

To test the truth of this postulate, then we did a recalculation by applying boundary conditions as shown in Table 10. Where the Zr1 and Zr2 are Zr^{4+} cations which enter into the lattice site of $(Bi, Na)^{2+}$ and Ti^{3+} cation, respectively. The results of the analysis are shown in Table 11. It is shown in Table 11 that the chemical composition BNBZT3 that produces the smallest reliability index is a composition with $g(Zr1) = 0.01$ and $g(Zr2) = 0.03$. Thus, the chemical composition of the three types of samples are shown in Table 12.

Table 11. Zr^{4+} mol fraction, i.e. $g(Zr1)$ and $g(Zr2)$ which solid soluble in BNT-BT crystal system of BNBZT3 sample.

$g(Zr1)$	$g(Zr2)$	Reliability Index		
		R_{wp}	R_p	S
0.03	0.01	27.04	19.98	1.226
0.02	0.02	27.03	19.97	1.225
0.01	0.03	27.02	19.96	1.225

It is depicted in Table 12 that the B-site ionic configurations at BNBZT3 are different with the B-site ionic configurations at BNBZT1 and BNBZT2. Where B-site on BNBZT3 occupied jointly by Ti^{3+} and Zr^{4+} , whereas B-site on BNBZT1 and/or BNBZT2 occupied by Ti^{3+} only. However, the crystallites size are not related with the crystal structure, where the size of crystallites in BNBZT1 ($D_1 = 31$ nm), BNBZT2 ($D_2 = 41$ nm) and BNBZT3 ($D_3 = 38$ nm) does not have an interdependent relationship.

Table 12. Chemical composition of the sample.

Sample	Chemical composition
BNBZT1	$(Bi_{0.45}Na_{0.48})_{0.93}Ba_{0.05}Zr_{0.01}TiO_3 + ZrO_2$
BNBZT2	$(Bi_{0.41}Na_{0.49})_{0.90}Ba_{0.05}Zr_{0.03}TiO_3 + ZrO_2$
BNBZT3	$(Bi_{0.42}Na_{0.43})_{0.85}Ba_{0.05}Zr_{0.01}(Ti_{0.97}Zr_{0.03})O_3 + ZrO_2$

To confirm the existence of differences in the ionic configuration on A-site and B-site, the Raman spectroscopy measurements were done. It is possible, as Raman spectroscopy can be used to examine a very local ionic configurations that are not detected by XRD[16]. Thus, Raman spectroscopy and XRD are complementary, where Raman spectroscopy is superior to XRD for studying the structural configuration of a long-range order region. Raman spectroscopic data are shown in Figure 3.

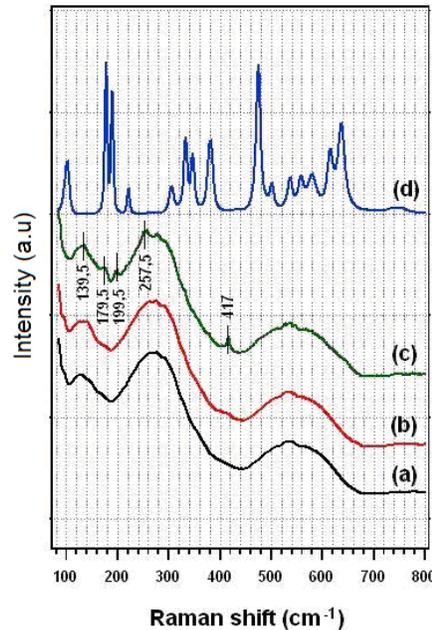


Figure 3. Raman spectrum of (a) BNBZT1, (b) BNBZT2, (c) BNBZT3, and (d) ZrO₂.

Figure 3 (a) and 3 (b) are in accordance with the Raman spectra of BNT-6% BT[16]. So the partial substitution of Zr⁴⁺ in A-site does not cause a non uniform distortion of the crystal lattice in the region of short-range order. However, it is shown in Figure 3 (c), due to the Zr⁴⁺ partial substitution at B-site occurs the Raman active in the band 179.5, 199.5, and 417 cm⁻¹ and there is an active Raman gain at 139.5 and 257.5 cm⁻¹. This data are evidence that the Zr⁴⁺ cations entered BNT lattice by partial substitution of cations in A-site and B-site. In Figure 3(a), 3(b) and 3(c) does not appear the Raman active from ZrO₂.

CONCLUSIONS

From this research, piezoelectric materials (Bi_{0.5}Na_{0.5})TiO₃(BNT) doped with 5 mol% BaTiO₃(BT) and 2, 5, and 10 mol % ZrO₂ could be synthesized successfully. Synthesis was conducted by using the solid state reaction method with powders of Bi₂O₃, Na₂CO₃, BaCO₃, TiO₂ and ZrO₂ as starting raw materials. Characterization results indicate that BT and BNT doped ZrO₂ have tetragonal structure, space group of I4/mcm, Volume I, No. 140 and the lattice parameter value depends on the mole percent of ZrO₂ doping. All Ba²⁺ cations entered into the BNT crystal system by replacing some (Bi, Na)²⁺ cations. By doping the 2, and 5 mol% ZrO₂, some of Zr⁴⁺ cations partially replace (Bi, Na)²⁺ and partly remains in the form of ZrO₂ compound. But in giving 10 mol% ZrO₂ doping, Zr⁴⁺ cations, in addition to replacing the cations (Bi, Na)²⁺ also Ti³⁺ and partly remains in the form of ZrO₂ compound.

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REFERENCES

1. Shan-Tao Zhang, Feng Yan, and Bin Yang, Morphotropic Phase Boundary and Electrical Properties in $(1-x)\text{Bi}_0.5\text{Na}_0.5\text{TiO}_3\text{-}x\text{Bi}(\text{Zn}_0.5\text{Ti}_0.5)\text{O}_3$ Lead-Free Piezoceramics, *J. Appl. Phys.* 107, 114110-1 – 114110-2 (2010).
2. G. A. Smolenskii, V.A. Isupov, A.I. Agranovskaya, and N. N. Krainik, New Ferroelectrics of Complex Composition, *Sov. Phys. Solid State (Engl. Transl.)* 2, 2651-2654 (1961).
3. H. Lidjici, M. Rguiti, F. Hobar, C. Courtois, A. Leriche, Solid State Sintering Prepared $0.935(\text{Bi}_0.5\text{Na}_0.5)\text{TiO}_3 - 0.065\text{BaTiO}_3$ Lead-Free Ceramics: Effect of Sintering Temperature, *Ceramics-Silikáty* 54(3), 253-257 (2010).
4. Wei-Chih Lee, Chi-Yuen Huang, Liang-Kuo Tsao, Yu-Chun Wu, Chemical Composition and Tolerance Factor at The Morphotropic Phase Boundary in $(\text{Bi}_0.5\text{Na}_0.5)\text{TiO}_3$ -Based Piezoelectric Ceramics, *Journal Eur. Ceram. Soc.* (2008), doi: 10.1016 /j. jeurceramsoc. 2008.08.028.
5. Conor James Walsh, Bond Valence Structure Analysis of Doped Bismuth Sodium Titanate, A Thesis of Alfred University, New York, October 2004, p.1-2.
6. Yuan Li, Shan Qin, and Friedrich Seifert, Phase Transitions in A-site Substituted Perovskite Compounds: The $(\text{Ca}_{1-2x}\text{Na}_x\text{La}_x)\text{TiO}_3$ ($0 \leq x \leq 0.5$) Solid Solution, *J. Solid State Chem.* 180, 824-833 (2007).
7. Min Chen, Qing Xu, Bok Hee Kim, Byeong Kuk Ahn, Jung Hoon Ko, Woo Jin Kang, and O. Jeong Nam, Structure and Electrical Properties of $(\text{Na}_0.5\text{Bi}_0.5)_{1-x}\text{Ba}_x\text{TiO}_3$ Piezoelectric Ceramics, *J. Eur. Ceramic Soc.* 28, 843-849 (2008).
8. L. Noerochim, Effect of Rare Earth Oxides on Dielectric and Electro-mechanical Properties of BNKT Piezoelectric Ceramics, A Thesis of National Taiwan University of Science and Technology, Taiwan, July 2007, p. I-2.
9. K. Kumari, K. Prasad, K.L. Yadav, and S. Sen, Structural and Dielectric Properties of ZrO₂ Added $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ Ceramic, *Brazilian Journal of Physics* 39(2), 297-300 (2009).
10. K. S. Rao, B. Tilak, K. CH. V. Rajulu, P.M. Krishna, Relaxor Behavior of $(\text{Na}_0.5\text{Bi}_0.5)\text{TiO}_3$ Ceramic with Simultaneous Substitution of Ba²⁺ and Zr⁴⁺, *Optoelectronics and Advanced Materials-Rapid Communications* 4(5), 671-680 (2010).
11. J.S. Park, S.C. Lee, M.H. Lee, D.J. Kim, Y.S. Sung, M.H. Kim, T.K. Song, J.H. Cho, B.C. Choi and S.S. Kim, Effect of Zr Doping on the Depolarization Temperature and the Piezoelectric Properties in $(\text{Bi}_0.5\text{Na}_0.5)\text{-BaTiO}_3$ Lead-free Ceramics, *J. Korean Phys. Soc.* 57(6), 1905-1908 (2010).
12. F. Izumi, A Rietveld-Refinement Program RIETAN-94 for Angle-Dispersive X-Ray and Neutron Powder Diffraction, National Institute for Research in Inorganic Materials, Ibaraki, Japan, 1994, P1-P21.
13. Engkir Sukirman dan Syahfandi Ahda, Analisis Kualitatif dan Kuantitatif Fasa $(\text{Na}_0.5\text{Bi}_0.5)\text{TiO}_3$ dengan Teknik Difraksi Sinar-X Menggunakan Metode Rietveld, *Jurnal Sains Materi Indonesia* 13(1), 69-74 (2011).
14. G. Dercz, K. Prusik, L. Pajak, Structure Investigations of Commercial Zirconia Ceramic Powder, *Journal of Achievements in Materials and Manufacturing Engineering* 18(1-2), 259-262 (2006).
15. K. Sambasiva Rao, B. Tilak, K.CH. Varada Rajulu, P. Murali Krishna, Relaxor behavior of $(\text{Na}_0.5\text{Bi}_0.5)\text{TiO}_3$ ceramic with simultaneous substitution of Ba²⁺ and Zr⁴⁺, *Optoelectronics and Advanced Materials - Rapid Communications* 4(5), 671-680 (2010).
16. Dragan Damjanovic, Naama Klein, Li Jin, Viktor Porokhonskyy, Ben Wylie-van Eerd, Joe Trodahl, The Structural Complexity of $(\text{Bi}_0.5\text{Na}_0.5)\text{TiO}_3\text{-BaTiO}_3$ Revealed by Raman Spectroscopy, <http://arxiv.org/vc/arxiv/papers/1003/1003.066v1.pdf>, July, 2012.