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Analysis on the Crystal Structure of the Piezoelectric Nanocrystal Ceramic of Pr-doped Bi_{1/2}Na_{1/2}TiO₃ using Molten-Salt Synthesis

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Abstract

One of the future technologies in nuclear reactors is the ability of piezoelectric materials to monitor reactor cores as sensors. Particularly, Pb-free piezoelectric materials, such as $Bi_{1/2}Na_{1/2}TiO_3$, have been examined to improve the ability of their piezoelectric properties. In this study, we attempted to add Pr_6O_{11} dopant material with mole ratios of 0, 0.3, 0.5, and 0.7 mol%. The synthesis process used in this study is the molten-salt synthesis method with a NaCl and KCl salt mole ratio of 1:1. The crystal structure analysis using the refinement process of the Rietveld method of the HighScore software was performed. Accordingly, a rhombohedral crystal structure system with lattice parameters of 3.8809(2), 3.8831(2), 3.8834(7), and 3.8816(2) angstroms and variations in the content of Pr_6O_{11} was obtained. The optimal lattice parameter was discovered with the addition of 0.5 mol% of Pr_6O_{11} . The morphology of the synthesis product is still unclear for each addition of dopant material due to the large number of granular agglomerations.

Keywords: Goldschmidt's tolerance, molten-salt method, piezoelectric materials

Introduction

The unique properties of piezoelectric ceramic materials are useful for current and future applications. This material principle can convert mechanical stress or deformation into an electrical output, and if electricity is applied to the material, it will result in shape changes or deformations. Thus, it is widely applied in electronic and mechanical devices [1]. One of them that gives great hope is to be used as a transducer or sensor placed in the core of a nuclear reactor. Studies have been performed to monitor and improve the safety of modern reactors, as has been done by one of the research groups of D. A. Parks et al. [2]. Another application is energy harvesting to generate electricity, such as in the case of the wheels of a car pressing piezoelectric devices placed along highways, which generates mass power. This method has been applied on the highways of developed countries, such as Israel, Japan and Germany, to light up villages. Its development is also being intensively carried out in their study [3].

At present, the piezoelectric material of $PbZr_xTi_{(1-x)}O_3$ (PZT), which has high performance, has been widely applied, but it contains Pb, which is not environmentally friendly. Therefore, lead-free piezoelectric materials that are superior to replace PZT, such as BaTiO₃ (BT) and Bi_{1/2}Na_{1/2}TiO₃ (BNT), have been formulated. This

BNT has received more attention than BT due to its high Curie temperature and piezoelectric constant. BNT is a ferroelectric material that was first discovered by Smolenskii *et al.* [4]. It is considered an excellent leadfree material and has a rhombohedral perovskite structure at room temperature [5, 6]. Therefore, the study on environmentally friendly BNT materials needs to be intensively developed with the addition of a dopant. Such an addition will change the structure itself, thus affecting the amount of piezoelectric constant or the performance of the material.

The synthesis process technology for piezoelectric materials is an important part in improving the quality of ready-to-use materials. Accordingly, several researchers have used several synthesis methods, including dry method (solid-state reaction) [7], and wet methods, such as hydrothermal [8], sol-gel [9], and molten-salt reaction [10]. Each synthesis process tends to obtain products with different characteristics. The BNT piezoelectric material is an interesting thing to be developed with the addition of the Pr_6O_{11} dopant material (labeled as BNT-Pr hereinafter), especially in the synthesis process.

Several researchers have conducted research on BNT-Pr with various synthesis methods, including H. Sun *et al.* [7] and A. Paul Blesing *et al.* [11], using the solid-state

reaction synthesis method and Khairunnisa Abdul Razak *et al.* [12] using a gentle combustion technique. In this study, we applied the molten-salt method for the continuation of a new series of BNT-Pr synthesis processes. However, molten-salt synthesis is a relatively simple process, has low energy consumption, and can easily control the shape and size of crystals [13]. This study focuses on a BNT product synthesized by the molten-salt method and then analyzes the changes in the crystal structure with the addition of Pr_6O_{11} dopant variations using Rietveld analysis.

The Pr_6O_{11} dopant material with mole ratios of 0, 0.3, 0.5, and 0.7 mol% for each BNT sample have been applied in the molten-salt synthesis process with a sintering temperature of 875 °C. The HighScore Plus (PANalytical) software has also been used to support the analysis of crystal structures.

Experimental Method

The BNT-Pr synthesis procedure using the molten-salt method begins by weighing the base materials, such as Bi_2O_3 (ABCR; 99.99% purity), Na_2CO_3 (Merck; 99.9% purity), TiO₂ (Merck; 99.9% purity), and Pr_6O_{11} (ABCR; 99.9% purity), through stoichiometry and then mixing and crushing them for 4 hours. With the balance in stoichiometry, the equation for the reaction that occurs in the BNT synthesis process is as follows:

$$Bi_2O_3 + Na_2CO_3 + 4 TiO_2 \rightarrow 4 Bi_{0.5}Na_{0.5}TiO_3 + CO_2 (1)$$

The Pr-doped BNT powder was signed according to the formula of $(Bi_{1/2}Na_{1/2})_{(1-x)}Pr_xTiO_3$ (where 0.3% < x < 0.7%) was synthesized using the molten-salt method [7].

The salt used was a mixture of eutectic NaCl and KCl with a mole ratio of 1:1. A mixture of salt and a base material with a weight ratio of 1:1 was crushed for 2 hours to get smaller and more homogeneous particles [10, 14]. The synthesis process was continued by sintering at 875 °C for 4 hours. The sintering temperature was below the melting point of the base material, while the mixture of NaCl and KCl salts were melted. The reaction mechanism among the base materials took place through a diffusion process in liquid salts and formed new compounds [11]. Then, the salt content in the sample as a synthesized product was removed by washing it with boiling aquabides (100 °C) and filtering it repeatedly. The absence of salt was tested with drops of colorless AgNO₃ solution into the liquid after filtering the sample. Finally, the BNT products obtained were dried at 100 °C. The laboratory steps in the synthesis process using the molten salt method are presented in Figure 1.



Figure 1. Schema of the Synthesis Procedure using the Molten-Salt Method [15]

The BNT samples with the addition of Pr_6O_{11} dopants were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results of the XRD pattern were analyzed using the Rietveld method with the HighScore Plus (PANalytical) software to determine the crystal structure system.

Results and Discussion

A perovskite crystal structure system, as shown in the piezoelectric material, is defined as an ABO₃ compound with a network of B-O octahedral sharing angles that surround the large cation site A (ionic radii of $r_A > r_B$). To predict the stability of the perovskite structure based on the ABO₃ (non-experimental) chemical formula, the Goldschmidt's tolerance factor (*t*) involving the ionic radius of each ion (A, B, and O) was used [16]:

$$t = (r_A + r_O)/2^{\frac{1}{2}}(r_B + r_O)$$
(2)

As mentioned above, the BNT-Pr formula is $(Bi_{1/2}Na_{1/2})_{(1-x)}Pr_xTiO_3$. It has a perovskite structure system, such that site A is occupied by $(Bi_{1/2}Na_{1/2})_{(1-x)}Pr_x$ and site B is occupied by Ti. In this modified BNT, the Pr^{3+} -doped ion radius is smaller than the average A-site ion radius of the undoped BNT. In other words, the occupation of site A by Pr^{3+} ions causes lattice shrinkage due to the formation of cation vacancies at site A and with Pr^{3+} ion size smaller than Bi^{3+} and Na^+ sizes (ionic radii: 0.139, 0.140, and 0.126 nm for Bi^{3+} , Na^+ [17], and Pr^{3+} , respectively). The *t* value of BNT-Pr was obtained in the range of 0.98745–0.98786, as shown in Figure 2.

The reduction of the tolerance factor is still assumed to be in a stable region because it is mathematically related to a small A-site substitution. In general, the stability of perovskite structures is estimated to occur in the range



Figure 2. Goldschmidt's Tolerance Factor for the Addition of Dopant Pr6O11 Represented by X in the Percentage of Moles

of 0.880 < t < 1.090 [18]. Therefore, the value of *t* also gives an indication of how far the atom can move from its ideal packing position and is still "tolerated" in the perovskite structure. However, a high symmetry can generally occur at *t* values closer to 1 (as a cubic structure, the piezoelectricity is very weak). The addition of a dopant material reflects structure modifications, such as rotation, distortion, and octahedral tilt. Thus, changes in structural factors can affect the piezoelectric properties.

Crystal structure analysis. The variations in the addition of the Pr_6O_{11} dopant into each sample were 0, 0.3, 0.5, and 0.7 mol% (BNT for no addition and BNT-Pr for the addition of Pr), as shown in Figure 3. A change in color was observed for each sample, as shown before and after the synthesis. The results indicate a reaction among the base materials to form new compounds. Accordingly, these new compounds were identified using the XRD profile.

Figure 4 shows the XRD pattern of the BNT synthesis product without dopants and the base material of the Pr₆O₁₁ dopant. The presence of the three highest peaks for BNT at 20 diffraction angles, i.e., 32.57°, 46.66°, and 58.12°, can be identified as the Bi_{1/2}Na_{1/2}TiO₃ (BNT) pattern. This condition was also investigated by S. Dargham with synthesis using the sol-gel method [9]. Meanwhile, Pr₆O₁₁ peaks were not found in the BNT pattern itself. The formation of a single-phase BNT with a perovskite structure occurred during the synthesis process. The identification of this BNT pattern corresponds to the file on the Joint Committee on Powder Diffraction Standard No. 36-340 with a perovskite rhombohedral crystal system. In other words, the XRD profile indicates that a single phase of BNT was obtained due to the absence of other foreign peaks in the synthesis product. Therefore, the diffusion and reaction processes among the base materials in the BNT synthesis with the molten-salt method were successfully conducted to form new compounds.



Figure 3. Samples with Variations in the Addition of Pr₆O₁₁ Dopants (0, 0.3, 0.5, and 0.7 mol%) before the Sintering Process (a) and after the Sintering Process (b). A Color Change Occurred Very Clearly after Sintering



Figure 4. XRD Profile for the Synthesis Product without Dopants (BNT) and the Dopant Base Material of Pr₆O₁₁

However, in the XRD profile, particularly the rhombohedral structure, it is rather difficult to distinguish because of the overlapping peaks, such that the lattice parameters are close to cubic. The lattice angle parameters are also very close for certain piezoelectric materials. Due to the small degree of distortion in the rhombohedral structure for BNT or BNT-Pr crystals, the peak lines of the diffraction plane were indexed based on the pseudocubic crystal system. [19, 20]. The ionic Bi radius is close to Na in its cell unit, which causes a slight lattice distortion. Doping with Pr with an ionic radius of 1.26 Å in BNT causes local lattice contractions and then distorts the lattice. However, the very close ionic radius causes unclear lattice distortion level changes. Moreover, the Ti ion radius is 0.605 Å [20], which is quite far from that of the Pr ion. Therefore, the occupation of the Pr ion in the A-site position will be very possible.

As already mentioned, in the absence of Pr_6O_{11} peaks, the occurrence of praseodymium ion substitution in the perovskite lattice is possible. Moreover, the close ionic radii of the three elements prepares the substitution of Pr^{3+} ions for Bi^{3+} ions or Na^+ ions into the perovskite lattice, because Pr ions with a charge of 2+ or 3+ can replace the A site in the BNT perovskite structure with an ABO₃ group.

The diffraction pattern of BNT and BNT-Pr syntheses at various additions of the Pr_6O_{11} dopant content is presented in Figure 5 (black dots represent the data). Intensity data as a function of diffraction angle were refined using the HighScore Plus software by entering the parameters of the starting point shift, background, space group, and unit cell. The success of a refinement process can be seen from the statistical errors indicated in the values of the profile factor (R_p) and weighted profile factor (R_{wp}). According to Kniess and Tamer, the success of a refinement process of a refinement process occurs when the value of R_p and R_{wp} is below 10% [21–23]. In this case, for samples added with Pr_6O_{11} (0, 0.3, 0.5, and 0.7 mol%), the values of R_p and R_{wp} were obtained, as shown in Table 1.

The results of the sample analysis with the values of R_p and R_{wp} below 10% indicate a refinement process with good agreement, as shown in Figure 5. The results of the refinement process as a diffraction pattern performed on the BNT and BNT-Pr samples can be displayed with close calculation data (red) and experimental data (black), where the difference (green) is very low.

The rhombohedral perovskite crystal system on BNT with the addition of Pr_6O_{11} dopant has also been demonstrated as has been investigated by Dargham *et al.* for addition of other dopant to BNT [9, 22, 24–26]. In the HighScore Plus software, there is no direct rhombohedral crystal system available. Therefore, to

perform Rietveld analysis, we used a hexagonal system as an input parameter, with space group R3c, and then converted it to a rhombohedral crystal system with Inorganic Crystal Structure Database number 98-028-0983.

In this study, the lattice shift and its doping effect on R3c (space group) were refined on the hexagonal axis and then linked to pseudocubic/rhombohedral cells. The best agreement between the observed (obs) and calculated (cal) interplanar distances at the Bragg angle was found for a rhombohedral crystal structure (space group R3c) with a hexagonal axis.

Hexagonal lattice parameters as the output of the refinement process are indicated by a_h and c_h . The transformation from the hexagonal axis to rhombohedral axis was performed using Equations 3–4, as described by Moreau, J. M *et al.* [27] and Paul Blessington Selvadurai *et al.* [11]. First, the conversion to a primitive rhombohedral unit cell was conducted by calculating the a_{pr} and α_{pr} parameters through the following equation:

$$a_{pr} = \sqrt{\frac{a_h^2}{3} + \frac{c_h^2}{9}} \text{ and } \sin \frac{\alpha_{pr}}{2} = \left(2\sqrt{\frac{1}{3} + \frac{c_h^2}{/a_h^2}} \right)$$
(3)

Table 1. Output Data from the Refinement Process with a Statistical Error of the Profile Factor (R_p) and Weight Profile Factor (R_{wp})

Sample	\mathbf{R}_{p}	R _{wp}
0% Pr ₆ O ₁₁	4.6291	6.0538
0.3% Pr ₆ O ₁₁	4.8945	6.4188
0.5% Pr ₆ O ₁₁	4.8709	6.3020
0.7% Pr ₆ O ₁₁	4.5148	6.0858



Figure 5. BNT Diffraction Patterns with Variations in the Addition of the Pr₆O₁₁ Dopants (0, 0.1, 0.3, and 0.7 mol%)

Sample	Hexagonal				Rhombohedral			
	а ь [Å]	c h [Å]	$\alpha_{\rm h} = \beta_{\rm h}[^\circ]$	γh [°]	volume [Å ³]	arh [Å]	α rh [°]	volume [Å ³]
0% Pr ₆ O ₁₁	5.4836(3)	13.466	90	120	350.595	3.8809(2)	89.905	58.451(3)
0.3% Pr ₆ O ₁₁	5.4891(3)	13.460	90	120	351.206	3.8831(2)	89.960	58.547(3)
0.5% Pr ₆ O ₁₁	5.490(1)	13.459	90	120	351.308	3.8834(7)	89.970	58.565(10)
0.7% Pr ₆ O ₁₁	5.481(3)	13.484	90	120	350.807	3.8816(2)	89.835	58.483(3)

Table 2.Calculation Results of the Lattice Parameters for BNT with the Addition of Pr₆O₁₁ Dopants at 0, 0.3, 0.5, and 0.7
mol%

After the calculation of the primitive unit cell, it is then converted into unit cell parameters (a_{fc} and α_{fc}) for rhombohedral center-face cells (Z = 8), which are determined by the following equations.

$$a_{fc} = \frac{1}{2} a_{pr} \sqrt{3 - 2\cos\alpha_{pr}}$$
 and $\cos\alpha_{fc} = \frac{2\cos\alpha_{pr}-1}{3-2\cos\alpha_{pr}}$ (4)

The length of the rhombohedral (pseudocubic) unit cell a_{rh} was obtained from $a_{fc}/2$ and $\alpha_{rh} = \alpha fc$. The calculated results are listed in Table 2. Meanwhile, the change in lattice parameters for BNT with the addition of Pr_6O_{11} dopants was calculated, as shown in Table 2.

The effect of the addition of dopants can be seen from the results of the refinement process in Figure 6, which shows the clear change in the intensity between the data (black dots) and their calculation (red lines) at diffraction angles with ranges of 32°-33° and 46.2°-47°. Systematically, the reflection plane peak shift to the left from the BNT peak ($x = 0 \mod \%$) with the addition of x = 0.3 mol% and 0.5 mol% of Pr₆O₁₁ dopants resulted in a large lattice plane distance (d) or increased lattice parameters (Table 2). Conversely, with the addition of x = 0.7 mol%, the peak shifts back to the right. Thus, the plane distance (d) becomes smaller or the lattice parameter decreases (Table 2). The optimal lattice parameter for the rhombohedral structure is a =3.8834 Å and the alpha angle = 89.970° obtained in the addition of dopant x = 0.5 mol%, while it is almost close to the cubic structure. The diffraction pattern shift is presented in Figure 5.

The high/low of a peak that affects the broad/narrow of the peak can be represented as a full width at half maximum (FWHM). Accordingly, the crystallite size of each sample can be interpreted. The Williamson-Hall (W-H) method as a function of FWHM and peak position 2θ can be applied in determining the size of crystallites and strain [28].

Using this approach, the W-H plot can be formulated as a straight-line function using the equation $\beta \cos \theta = k\lambda/d + 4 \epsilon (\sin \theta)$. The results of the refinement process in this study are illustrated in Figures 6, where *d* is the size

Makara J. Sci.



Figure 6. Peak Shift Pattern of the BNT Diffraction Due to the Addition of Pr6O11 Dopants (a) at an Angle of 20 32° - 33° and (b) 46.2° - 47°

of the crystallite, ε is the elastic strain, β is the FWHM, and *K* is the Scherrer constant (or an arbitrary value that falls in the range of 0.87–1.0). We usually assume k = 1. The determination of the FWHM on the XRD intensity profile was first corrected with standard silicon samples, as was performed by Engkir S [29]. Thus, the size of the crystallite was obtained through an extrapolation of the above equation.

Figure 7 shows a linear statistical regression with equations that can be interpreted into the W-H equation. A statistical coefficient (*R*) above 90% indicates a very good agreement with the regression quality, as it is also supported by the results of good refinement. Intercepts to the Y-axis can be calculated to obtain the crystallite size as a function of adding a dopant material. Finally, the size of the crystallites obtained for x = 0.3, 0.5, and 0.7 mol% were 61.62, 51.69, and 42.79 nm, respectively.

BNT morphological analysis with the addition of Pr_6O_{11} dopants. BNT and BNT-Pr images were taken using the JEOL JSM-6510LA SEM tool to examine the grain morphology formed from the synthesis results with a magnification of 10,000 times, as shown in Figure 8. The shape and size of the grain BNT and BNT-Pr showed an unclear and formed agglomeration. Visually, the addition of a dopant material forms small grain sizes, so it fits with the XRD data analysis ranging from 40 to 65 nm.



Figure 7. Williamson-Hall (W-H) Plot of the Refinement Process Results for the BNT Phase with the Addition of Pr₆O₁₁ Dopants (x = 0.3, 0.5, and 0.7mol%, Respectively), where $\beta \cos(\theta) = Y$ and sin (θ) = X



Figure 8. Morphology of BNT-Pr Crystals from the Reaction Results in the Molten-Salt Method: (a) 0%, (b) 0.3%, (c) 0.5%, and (d) 0.7% mol Pr₆O₁₁

Sample -	% Atom					
	Bi	Na	Ti	Pr	0	
0% Pr ₆ O ₁₁	14.70	11.34	27.75	0.00	46.21	
0.3% Pr ₆ O ₁₁	16.69	10.99	32.22	0.20	39.91	
0.5% Pr ₆ O ₁₁	14.30	9.94	27.58	0.32	47.86	
0.7% Pr ₆ O ₁₁	15.27	7.37	30.97	1.69	44.70	

Table 3. Percentage of Atoms in the BNT and BNT-Pr Product Compounds with the Addition of Pr6O11 Dopant Materials

In this study, a semi-quantitative analysis with energydispersive spectroscopy (EDS) was successfully performed to identify the presence of basic materials of Bi, Na, Ti atoms, and Pr dopant atoms in certain scan areas. (In addition, it is important to identify other contaminants.) Moreover, EDS can qualitatively show the tendency of the content of the constituent atoms in the compound, as shown in Table 3.

In the EDS analysis of BNT and BNT-Pr compounds, the synthesis products showed an increase in the percentage of Pr atoms and a decrease in Na atoms, as shown in Table 3. However, the percentage of Bi atoms did not show a tendency to decrease, and Ti atoms were not yet stable because the EDS tool used for identification is semi-quantitative.

Conclusion

The Goldschmidt's tolerance model indicates that the addition of a Pr₆O₁₁ variation in the Bi_{1/2}Na_{1/2}TiO₃₋ synthesis is sufficient to obtain the characteristics of a piezoelectric material. The synthesis of Bi_{1/2}Na_{1/2}TiO₃ and addition of 0%-0.7 mol% using the molten-salt method was successfully performed at 875 °C for 4 hours. The XRD pattern analysis results show that the compound formed is a crystal structure with a rhombohedral perovskite system. The addition of 0.3 and 0.6 mol% Pr₆O₁₁ dopants shows a shift in the XRD peak to the left, which consequently causes an increased distance change between the reflection planes (d) and a larger lattice parameter. Meanwhile, the addition of 0.7 mol% Pr₆O₁₁ dopant shifts to the right, so the lattice parameter becomes smaller. The maximum lattice parameters obtained were a = 3.8834 Å and $\alpha = 89.970^{\circ}$ for the addition of the dopant with x = 0.5 mol%. The W-H plot identified a decrease in the crystal sizes of 61.62, 51.69, and 42.79 nm, with the dopant material of 0.3, 0.5, and 0.7 mol%, respectively. The morphological differences using the SEM technique with a magnification of 10,000 for the synthesis product showed unclear images.

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