STUDY THE EFFECT OF SUBSTITUTION OF RARE EARTH ELEMENTS ON CRYSTALLIZATION AND MAGNETIZATION OF BCT

WG Suharta[1*], AAN Gunawan[2]

[1, 2] Faculty of Mathematics and Natural Sciences, Udayana University, Indonesia
*Corresponding Author

Abstract

Piezoelectric $BaTiO_3$ samples with substitution of Ca and RE (Y, Gd, Nd) elements have been successfully synthesized using a wet-mixing method. The final sample was obtained piezoelectric $(Ba_{0.90}Ca_{0.10})(Ti_{0.95}RE_{0.05})O_3$ in high crystallinity. The synthesis process used the wet-mixing method with nitric acid (HNO_3) as a solvent. The process of calcination was carried out at 600^oC for 3 hours and sintering at 900^oC for 5 hours. Fourier Transformed Infrared Spectroscopy (FTIR) characterization results showed M-O group absorption in the IR area of about 375-425 cm^{-1}, while the $BaCO_3$ group of the calcite type as impurities was detected in the area of around 1390-1435 cm^{-1}. X-ray diffraction (XRD) characterization showed phase dominance $(Ba_{0.90}Ca_{0.10})(Ti_{0.95}RE_{0.05})O_3$ with a purity greater than 90% and the impurity phase $BaNd_2Ti_4O_{12}$ and $BaCO_3$ with an intensity less than 10%. Substitution of Y, Gd, and Nd results in an increase in lattice constant values for a, b and c-axis sequentially. Vibrating Sample Magnetometer (VSM) characterization showed that the substitution of Y, Gd, and Nd results in an increase in the coercivity and remanence magnetization value as well as a decrease in the saturation magnetization values.

Keywords: piezoelectric, wet-mixing, magnetization, rare earth, barium titanium oxide

1. Introduction

Barium titanate is a compound with a Perovskite crystal structure that is a piezoelectric material. Piezoelectric materials have two unique properties: as a producer of voltage when given pressure and are able to hold current when given current. These two properties of piezoelectric materials are used in applications. The materials are used for electro-ceramic application as capacitors and memory because they have high dielectric constants and show spontaneous polarization properties [1, 2, 3].

At the Currie temperature of 120^oC, $BaTiO_3$ undergoes a ferroelectric phase transition to cubic polymorphism [4, 5, 6]. Various modifications have been made to increase the Currie point. The metal material that has been tried as a modification is the calcium that forms the compound barium calcium titanium oxide, $Ba_{1-x}Ca_xTiO_3$ (BCT) [7]. Ca doping on $BaTiO_3$ is stated as a candidate for electro-optical modulator and memory devices [8]. The doping element Ca^{2+} has smaller ion fingers than Ba^{2+} in the compound $Ba_{1-x}Ca_xTiO_3$, showing a single phase at x=0.3 [9]. The synthesis of $BaTiO_3$ by doping Ca, the compound $Ba_{0.8}Ca_{0.2}TiO_3$, has also been synthesized by Medeiros and colleagues with various variations of the early compounds [10]. The substitution of the alliovalent cation in $BaTiO_3$ results in changes in the electrical properties due to both the acceptor and the donor. Rare earth trivalent cations that have ion fingers between Ba^{2+} and Ti^{4+} ions have the ability to substitute positions A and B [12, 13].

Venkata Sreenivas Puli and colleagues have also carried out the synthesis of Ba-Sr-Ti (BST), Ba-Ca-Ti (BCT) and Ba-Zr-Ti (BZT) using the method of solid state reaction with a calcination temperature of $1250^{\circ}C$ for 10 hours and sintering at a temperature of $1500^{\circ}C$ for four hours [15]. Paul Praveen and his colleagues synthesized $BaTiO_3$ using the sol-gel method, with barium acetate, calcium nitrate tetrahydrate, titanium isopropoxide, and zirconium oxychloride as the raw material [16]. The synthesis process was followed by calcination and sintering at $1100^{\circ}C$ for four hours and $1550^{\circ}C$ for two hours respectively. Cai-Xia Li and colleagues also synthesized $BaTiO_3$ using a solid-state reaction with a calcination at a temperature of $1050^{\circ}C$ for two hours and sintering at a temperature of $1270\text{-}1400^{\circ}C$ for four hours [17]. In general, the synthesis process of $BaTiO_3$ has been carried out by previous researchers mostly using the solid-state reaction, followed by the processes of sinter at high temperature.

Generally, the size of the particles obtained by using this method is on the micro-meter scale. The size of the piezoelectric material particle will affect the pressure strength and the traction strength of the material. The smaller the particle size, the less empty space or holes contained in the material and the stronger the bonds that occur between ions and between atoms. Therefore, the synthesis process in this study was carried out using the wet-mixing method to produce size on a nano-meter scale.

2. Research Method

In this study, the piezoelectric $(Ba_{0.90}Ca_{0.10})(Ti_{0.95}RE_{0.05})O_3$ was synthesized using a wet-mixing method, while the rare earth elements (RE) used were yttrium (Y), gadolinium (Gd), and neodymium (Nd). The synthesis steps began with the weighting of the initial material according to the molar composition $(Ba_{0.90}Ca_{0.10})(Ti_{0.95}RE_{0.05})O_3$. These compounds are $(Ba_{0.90}Ca_{0.10})(Ti_{0.95}Y_{0.05})O_3$, $(Ba_{0.90}Ca_{0.10})(Ti_{0.95}Gd_{0.05})O_3$, and $(Ba_{0.90}Ca_{0.10})(Ti_{0.95}Nd_{0.05})O_3$, that abbreviated as BCTY, BCTG, and BCTN, respectively. Then the initial weighted material was mixed using a magnetic stirrer with a nitric acid medium (HNO_3). The solution was heated at $100^{\circ}C$ until it germinated. The resulting crust was calcinated at a temperature of $600^{\circ}C$ for three hours. The resulting calcination was diluted and smoothed in mortal, then pressed into pellets. The pellets were sintered at $900^{\circ}C$ for five hours. Characterization was done with FTIR, XRD, and VSM.

3. Results and Discussion
3.1. FTIR Characterization Results

FTIR is an instrument for material analysis using an infrared spectroscope. Infrared spectroscopy is a method that observes the interaction of molecules with electromagnetic radiation that is at the wavelength of 0.75-1000 μm or at the values of 13000-10 cm^{-1}. From the division of the electromagnetic spectrum regions above, the wavelength area used by infrared spectroscopy is in the middle infrared area, i.e. at the wavelength of 2.5-50 μm or at the values of 4000-200 cm^{-1} wave area, often referred to as the fingerprint region.

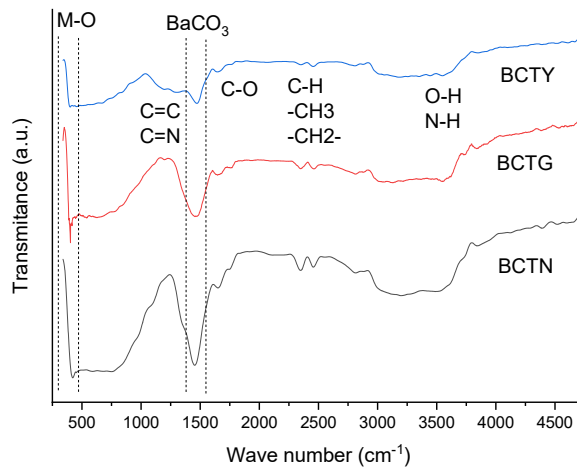The FTIR spectrum of BCTY, BCTG, and BCTN samples are shown in Figure 1.

Figure 1. FTIR spectrum of BCTY, BCTG, and BCTN samples

Figure 1 depicts a measured IR vibration mode for compound groups with an area of around 375-425 cm^{-1} and an area of around 1390-1435 cm^{-1}. The IR area around 375-425 cm^{-1} was the formation area of the M-O group, while the area around 1390-1435 cm^{-1} is the rich area of Ba, which is the $BaCO_3$ type calcite group, as described by Vladislav and colleagues [18].

3.2. XRD Characterization Results

The synthesis samples were characterized with XRD for phase identification and to find out the level of crystallinity of the sample. The XRD characterization result of all samples at a 2θ angle from 10 to 90° is shown in Figure 2.
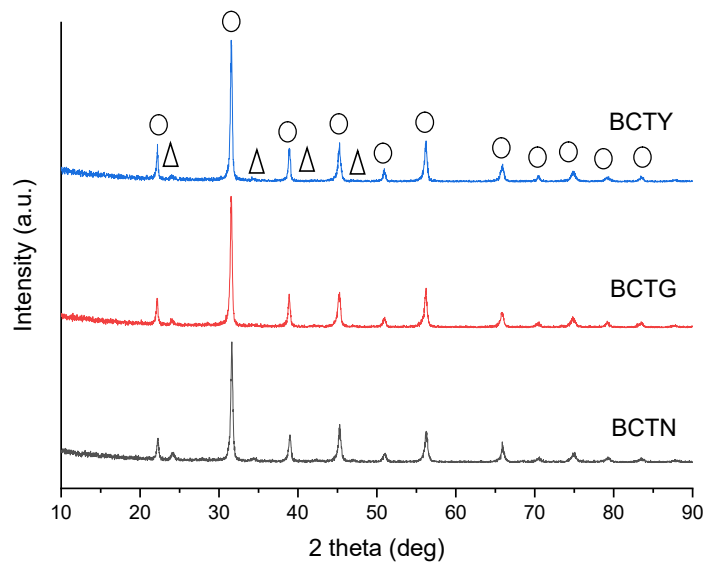

Figure 2. XRD spectrum of BCTY, BCTG, and BCTN samples. The symbol: o is $(Ba_{0.90}Ca_{0.10})(Ti_{0.95}RE_{0.05})O_3$ and Δ is an impurity

In general, the XRD results showed a smooth and sharp spectrum (peak) indicating that crystallization has gone well. The spectrum showed almost the same pattern for each sample, only differentiated by the intensity level of each spectrum. The XRD results showed several spectra, namely at angles of 22.23°, 31.63°, 38.99°, 45.29°, 51.05°, 56.29°, 65.89°, 70.59°, 74.87°, 79.27° and 83.55°, with the highest peak being at the angle of 31.63°. The spectrum (top) for the phase $(Ba_{0.95}Ca_{0.05})(Ti_{1-x}RE_x)O_3$ is marked by the circle symbol and the spectrum for the impurity phase is marked with the triangle symbol. The image shows that the spectrum is dominated by the appearance of a phase $(Ba_{0.95}Ca_{0.05})(Ti_{1-x}RE_x)O_3$ and also detects the presence of an impurity phase with a much smaller intensity than the intensity of the phase. This indicates that the method used in the synthesis process in this study has successfully grown $(Ba_{0.95}Ca_{0.05})(Ti_{1-x}RE_x)O_3$ phase well.

3.3. Phase Identification

Phase identification aims to determine the content of the compounds present in the sample. The identification was done by matching the data spectrum with the reference spectrum. The peak that does not match the reference peak is called the impurity phase. The phase identification was done using the Match program, referring to several corresponding references. The results showed the existence of the compound $BaTiO_3$ (Barium Titanium Oxide) with reference to the database form PDF (Powder Diffraction File) number 00-00500626 and the composite $BaNd_2Ti_4O_{12}$ (Barium Neodymium Titanium Oxide) referencing the database format PDF number 00-044-0061. The phase identification applied to all samples, indicated the presence or occurrence of phase-dominated compounds such as $BaTiO_3$, plus the occurrence of compounds such as $BaNd_2Ti_4O_{12}$ as impurity phases.

The crystallinity of the sample was determined by calculating the volume fraction, i.e., by comparing the amount of intensity of a compound $BaTiO_3$ with the sum of the intensities of the entire phase that appears ($BaTiO_3$-phase plus impurity-phase) or by using the formula:

$$FV = \frac{\sum I_{BaTiO_3}}{\sum I_{BaTiO_3} + \sum I_{imp}}$$

information: FV is the volume fraction
 I_{BaTiO_3} is the intensity of the $BaTiO_3$ compound
 I_{imp} is the intensity of the impurity compound

The volume fraction of the sample is shown in Table 1. The addition of RE doping (Y, Gd, and Nd) to the compound $(Ba_{0.95}Ca_{0.05})(Ti_{1-x}RE_x)O_3$ has a volume fraction value greater than 90% and varies.

Table 1. Volume fraction calculation results of $(Ba_{1-x}Ca_x)(Ti_{1-x}RE_x)O_3$ samples

No	Sample	Volume Fraction (%)
1	BCTY	91.90
2	BCTG	92.30
3	BCTN	91.54

3.4. Refinement (Rietveld Analysis)

Rietveld analysis is a method of non-linier matching a calculated diffraction curve pattern (model) with a measured diffraction pattern based on data of crystalline structures using the smallest square method (least-squares). The Rietveld analysis was first published by Rietveld Hugo. Rietveld's analysis describes the relationship between the characteristics of the diffraction peak and the parameters in the model of diffraction intensity. These parameters are:

1. Peak position: where the influential crystal parameters are parameters, asymmetry, and sample displacement.
2. Peak height: influenced by scale factors, asymmetry, thermal parameters, preferred orientation, and extinction.
3. The width and shape of the tip are influenced by the tip shape parameters U, V, W, and asymmetry.

The Rietveld analysis (refinement) in this study employed the Rietica program , to find out the level of matching of the spectrum produced with the spectrum from the reference, determine the lattice constant values, determine goodness-of-feet (GoF), and determine the reliability. The results of the refinements are shown in Figure 3a to 3c. In figure, a black spectrum is the spectrum of the sample that has been synthesized in this study. The red spectrum represents the reference used, and the green spectrum constitutes the difference between the intensity of the referential spectrum and the spectral spectrum used. For good samples, there should be no difference between the intensity of the reference and the sample spectrums. In the results obtained in this study, almost all samples still showed differences between reference and sample spectrums, but with small differences.
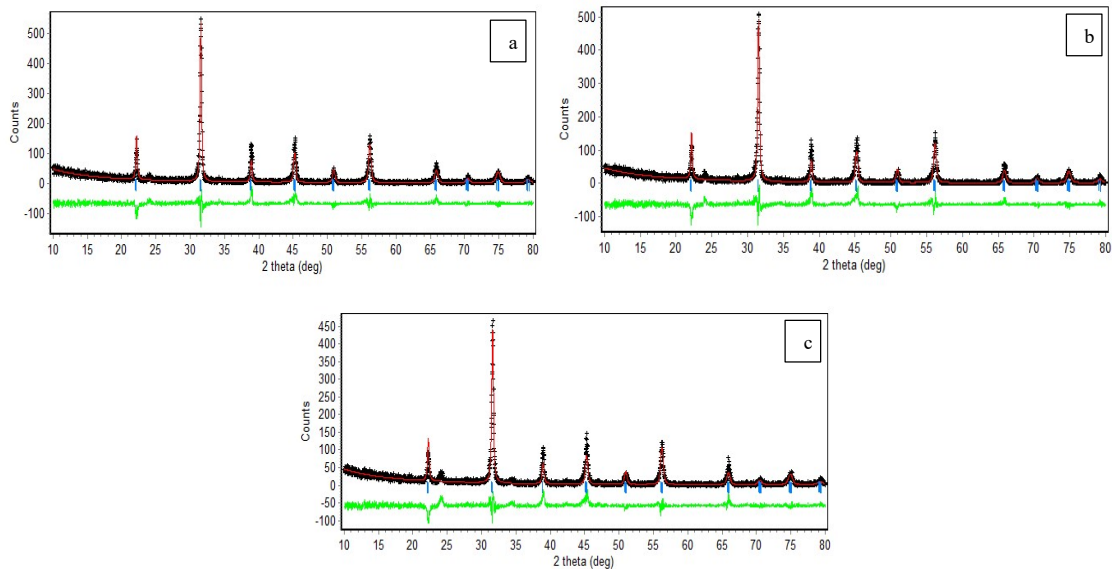

Figure 3. The refinement results used the Rietica program of: a) BCTY, b) BCTG, c) BCTN samples

The lattice constant values of a, b and c-axis as a result of Rietveld's analysis using the Rietica program are shown in Table 2. The results showing the sequence of lattice constant values of a, b and c-axis from the largest to the smallest is the sample BCTN, BCTG, and

BCTY. The change in the lattice constant value is caused by the values of the ionic radius of each dopant. It is known that the ion radius of the Ti^{4+} element is 74.5 pm, Y element is 104 pm, Gd element is 107 pm, and the Nd^{3+} element is 112.3 pm. The increase of lattice constant values of a, b, and c-axis is consistent with an increase in the ionic radius values of Y, Gd, and Nd.

The values of R_p, R_{wp}, R_{exp}, and GoF are shown in Table 3. The GoF value of all samples varies from 1.56 to 1.73. This study corresponds to the value of the volume fraction of each sample, which states that the greater the volume fraction value, the smaller the GoF value.

Table 2. The values of the lattice constant for $(Ba_{0.95}Ca_{0.05})(Ti_{1-x}RE_{0.05})O_3$ samples

No	Sample	Lattice constant (a-axes) (Å)	Lattice constant (b-axes) (Å)	Lattice constant (c-axes) (Å)
1	BCTY	4.008128(4)	4.008128(4)	4.000003(6)
2	BCTG	4.012363(7)	4.012363(7)	4.021206(9)
3	BCTN	4.014194(5)	4.014194(5)	4.0246582(8)

Table 3. The values of R_p, R_{wp}, R_{exp} and GoF for the sample $(Ba_{0.95}Ca_{0.05})(Ti_{1-x}RE_{0.05})O_3$

No	Sample	Rp	Rwp	Rexp	GoF
1	BCTY	23.80	31.78	25.44	1.65
2	BCTG	23.72	31.54	24.58	1.73
3	BCTN	24.39	31.85	24.23	1.56

3.5. SEM Characterization Results

SEM characterization was carried out to determine the morphology of the sample, which covers the shape, size, and homogeneity of the sample. The morphology of the sample is shown in Figure 4a, 4b and 4c for BCTY, BCTG, and BCTN, respectively. The particle sizes that are obtained vary, ranging from 100 nm to 250 nm, which indicates less homogeneous particle size. All samples showed the average particle sizes above 100 nm, indicating the occurrence of agglomerations that resulted in low dispersibility of the obtained nanoparticles.
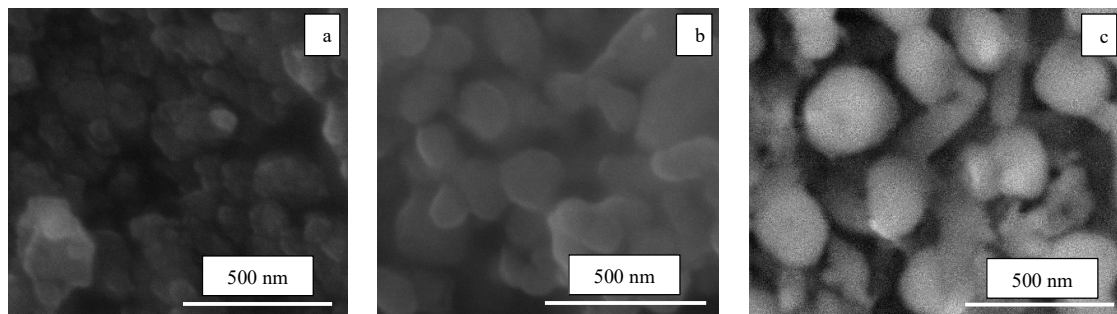

Figure 4. The morphology of: a) BCTY, b) BCTG, c) BCTN samples

3.6. VSM Characterization Results

Piezoelectric magnetic properties of $BaTiO_3$ can be determined based on VSM results. The VSM characterization results of the samples are shown in Figure 5. The value of coercivity (Ec), remanence magnetization (Dr) and saturation magnetization (Ds) of all samples are shown in Table 4. These results show coercivity values of 0.02, 0.20, and 0.32 kOe, with substitution of Y, Gd and Nd elements, respectively. The remanence magnetization values were 0.005×10^{-2}, 0.25×10^{-2}, 0.45×10^{-2} emu/g, for the addition of Y, Gd and Nd doping, respectively. Meanwhile, the saturation magnetization values were 14.00×10^{-2}, 2.90×10^{-2}, 1.55×10^{-2} emu/g, respectively of Y, Gd and Nd substitution. The data shows an increase in coercivity and remanence magnetization values with Y, Gd and Nd element substitutions respectively. Meanwhile, the saturation magnetization value decreases.
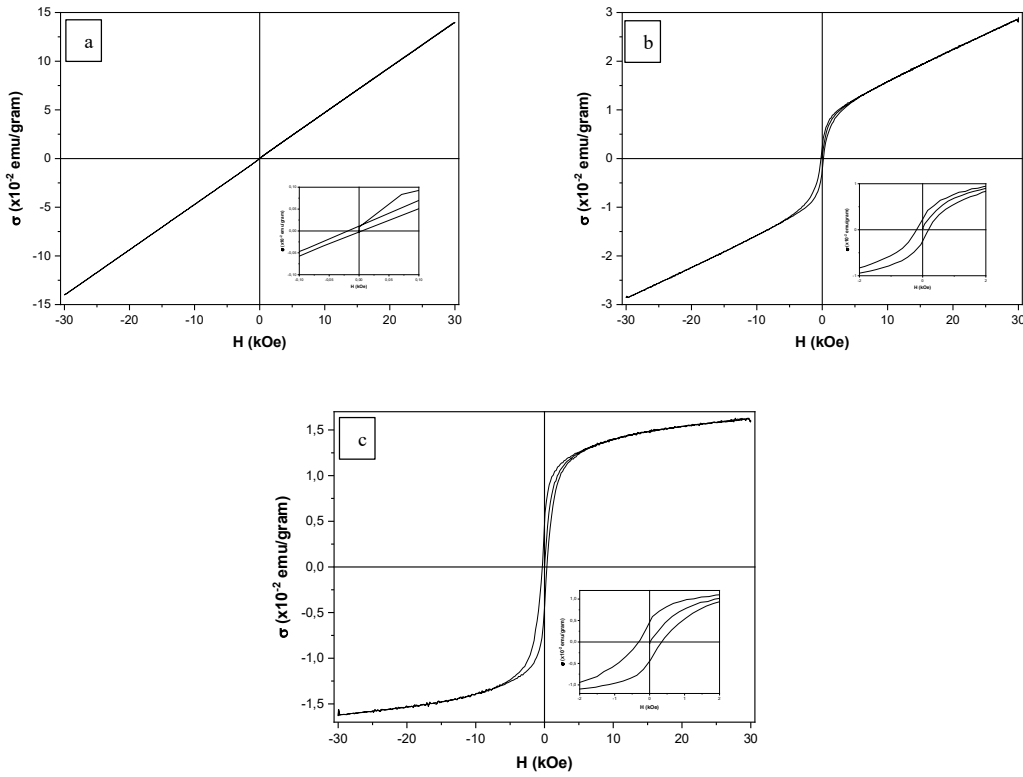
Figure 5. The results of characterization of: a) BCTY, b) BCTG, c) BCTN samples

Table 4. The value of Ec, Dr and Ds of all samples

Sample	Ec (kOe)	Dr (emu/g)	Ds (emu/g)
BCTY	0.02	0.005×10^{-2}	14.00×10^{-2}
BCTG	0.20	0.250×10^{-2}	2.90×10^{-2}
BCTN	0.32	0.450×10^{-2}	1.55×10^{-2}

4. Conclusion

Piezoelectric synthesis of barium titanate with rare earth element substitutions using the wet mixing method with purity above 90 % has been successfully carried out. Substitution of

Y, Gd, and Nd results in an increase in lattice constant values for a, b and c-axis sequentially. The substitution also results in an increase in the coercivity and remanence magnetization value as well as a decrease in the saturation magnetization value.

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