Synthesis of $BaTiO_3$ Compound doped Ca and Gd Element Using Wet-Mixing Method

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Abstract: In this study, the wet-mixing method was used for synthesis $(Ba_{0.95}Ca_{0.05})TiO_3$ ceramic material, with Gd variations of 0.05, 0.10, 0.15, 0.20, 0.25. The study's goal is to develop a piezoelectric material that has a high crystalline concentration and density. As source materials, $BaCO_3$, TiO_2, $CaCO_3$, and Gd_2O_3 compounds were used. By weighing the raw material and dissolving it, the synthesis process can be completed. Calcine and sinter processes were carried out at the 600 °C for 3 hours and 900 °C for 5 hours, respectively. Ultraviolet-Visible (UV-Vs), Laser-induced Breakdown Spectroscopy (LIBS), and X-ray Diffraction (XRD) were used to characterize the samples. Absorption was detected at wavelengths of 251.00, 351.00, 429.00, 504.50, and 590.00 nm in the UV-Vis characterization. Crystallization was confirmed by the XRD characterization data, which revealed a smooth spectrum. The addition of the Gd element (from 0.05 to 0.25) result in the volume percentage of the $(Ba_{0.95}Ca_{0.05})(Ti_{1-x}Gd_x)O_3$ combination decreased (from 94% to 91%). It also shows that the a and c-axes parameters of the unit cells, as well as the density, are increasing. A volume fraction more than 90% and an increase in density in the sample indicate that the sample is suitable for use.

Keywords: ferroelectric, dielectric, piezoelectric, wet-mixing, crystalline

I. INTRODUCTION

Barium titanate ($BaTiO_3$) is a ferroelectric ceramic material having a Perovskite structure. This material has a lower Curie temperature, a higher dielectric constant, and a more stable chemistry than other dielectric materials. As a result, it's commonly employed in electronic applications. When the electric voltage is withdrawn, ferroelectric materials have the ability to sustain electrical polarization. When a dielectric material is impacted by an external electric field, a charge shift occurs. Electric dipoles will form as the charge shifts. Barium Titanate has a perovskite crystal structure with the formula ABO_3, where A is a monovalent, divalent, or trivalent metal, B is a trivalent, pentavalent, or tetravalent element, and O is an oxygen element. Several researchers have created various Barium Titanate uses [1, 2, 3]. The type of element, substitution position, and doping technique all affect the dielectric value of Barium Titanate. Dopants can take up octahedral coordinates in the Ti^{4+} position or dodecahedral coordinates in the Ba^{2+} position. At a Currie temperature 120 °C, $BaTiO_3$ experiences a ferroelectric phase shift to cubic polymorphism [4, 5, 6]. Ca doping was used to lower the Curie point, resulting in the formation of the barium calcium titanate complex $Ba_{1-x}Ca_xTiO_3$. The atomic polarizability of the element Ca in $Ba_{1-x}Ca_xTiO_3$ is higher, strengthening the interaction between Ti ions and lowering the Currie temperature. Electrical characteristics alter when allovalent cations are substituted in $BaTiO_3$ due to the acceptor and donor effects [7]. BCT [8] is the composition of the $Ba_{1-x}Ca_xTiO_3$.

$BaTiO_3$ with Ca doping has been produced by Panigrahi et al. Many experiments have been carried out, such as those on the compound $Ba_{1-x}Ca_xTiO_3$ (for x=0.05 to 0.9), which has been thoroughly researched in terms of characteristics and relaxation. Because element Ca^{2+} has a smaller ionic radius than Ba^{2+}, it can dope element Ca into the location of element Ba [9]. Medeiros and coworkers have also synthesized $BaTiO_3$ with Ca doping, namely $Ba_{0.8}Ca_{0.2}TiO_3$ with various starting compounds [10]. Solid compounds of the $BaTiO_3$ perovskite system, such as barium zirconium titanate (BZT), barium calcium titanate (BCT), barium magnesium titanate (BMT), barium strontium titanate (BST), and others, have piqued researchers' interest. The experiment was carried out with different dopant concentrations and combinations. The solid state reaction approach has been used to make $BaTiO_3$ so far, but it has various limitations, including a very high sintering temperature of 1300 °C to 1600 °C. Abdul Moquim and colleagues used the traditional approach to making $BaTiO_3$ with Ca and Gd doping, namely the solid state reaction followed by calcining at 1280 °C for 4 hours and sintering at 1320 °C for 6 hours [1]. Venkata Sreenivas Puli and colleagues used the solid state reaction approach to make Ba-Sr-Ti (BST), Ba-Ca-Ti (BCT), and Ba-Zr-Ti (BZT) using a calcination temperature of 1250 °C for 10 hours and sintering at 1500 °C for 4 hours [11]. Cai-Xia Li and colleagues [12] used the solid state reaction technique to manufacture $BaTiO_3$ at a calcination temperature of 1050 °C for 2 hours and sintering at the 1270-1400 °C for 4 hours. In general, the solid state reaction approach is used in the $BaTiO_3$ synthesis process, which is followed by calcination and sintering at high temperatures, above 1000 °C and 1300 °C, respectively. $BaTiO_3$ was produced in this study by doping Gd with a wet-mixing technique. The effect of Gd doping on the density of $Ba_{0.95}Ca_{0.05}(Ti_{1-x}Gd_x)O_3$ is investigated in this work. What effect does the wet-mixing procedure have on the crystallinity of $Ba_{0.95}Ca_{0.05}$ and how may it be improved? $(Ti_{1-}$

$_xGd_x)O_3$. The goal of this study is to create a $Ba_{0.95}Ca_{0.05}(Ti_{1-x}Gd_x)O_3$ material with high crystallinity and density, as well as piezoelectric characteristics.

II. EXPERIMENT

2.1 Materials

$Ba_{0.95}Ca_{0.05}(Ti_{1-x}Gd_x)O_3$ was synthesized in this work with the addition of Ca and variations in the addition of Gd components in 0.05, 0.10, 0.15, 0.20, and 0.25, giving the compound the chemical formula $Ba_{0.95}Ca_{0.05}(Ti_{0.95}Gd_{0.05})$ O_3. The wet-mixing method is used in the material synthesis process. $BaCO_3$, TiO_2, $CaCO_3$, and Gd_2O_3 compounds were used as starting materials in this study.

2.2 Fabrication of $Ba_{0.95}Ca_{0.05}(Ti_{1-x}Gd_x)O_3$ Compounds

The steps in the synthesis process are as follows, (a) The starting material was weighed to ensure that the molar composition of $Ba_{0.95}Ca_{0.05}(Ti_{1-x}Gd_x)O_3$, with x values of 0.05, 0.10, 0.15, 0.20, and 0.25, (b) HNO_3 was used to dissolve each of the starting compounds until a homogeneous solution was formed, (c) Each homogeneous solution was combined, then stirred with a magnetic stirrer, (d) The uniform mixture was heated to 100 ºC until it stiffened, (e) The final product, in the form of crust, is calcined for 3 hours at 600 ºC, (f) Pellets are formed from the calcined results, (g) The pellets were then sintered for 5 hours at 900 °C, (h) For each composition x, steps a-g are carried out.

2.3 Characterization

The following methods are used to characterize the material, (a) Ultraviolet- Visible (UV-Vis) characterization, (b) Laser-induced Breakdown Spectroscopy (LIBS) characterization, and (c) X-ray Diffraction (XRD) characterization.

III. RESULTS AND DISCUSSION

The $Ba_{0.95}Ca_{0.05}(Ti_{1-x}Gd_x)O_3$ samples with variations of Gd elements has produced a pellet-shaped with a diameter of 1.5 cm and a thickness ranging from 3-5 mm. The results of the pellet-shaped sample are shown in Figure 1.

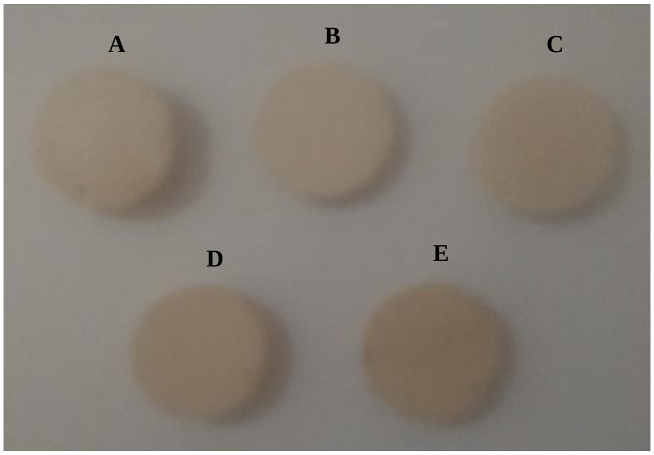

Fig. 1 The results of the synthesis of $Ba_{0.95}Ca_{0.05}(Ti_{1-x}Gd_x)O_3$ samples in the form of pellets with variation of Gd element from: A) 0.05, B) 0.10, C) 0.15, D) 0.20, E) 0.25

3.1 UV-Vis Characterization

UV-Vis spectroscopy has been used to characterize samples in the ultraviolet (200-350 nm) and visible (350-800 nm) regions. In this study, the UV-Vis characterization of all samples used a UV-1800 series spectrophotometer, the measurement mode was absorbance, the slit width was 1.0 nm. Measurement was carried out in the wavelength range from 200 to 800 nm, the scan speed was medium, the enumeration interval was 0.5. To obtain accurate information about the absorption produced by the sample, the UV-Vis characterization was carried out in two stages, namely the first stage using variations in solvent concentration since 10, 50, 100, 500, and 1000 ppm, the second stage using variations in Gd element.

The UV-Vis results of $Ba_{0.95}Ca_{0.05}(Ti_{0.95}Gd_{0.05})O_3$ samples with variation in solvent concentration showed in `Figure 2. That shows some absorption values of compounds at certain wavelengths (251, 351, 429, 504, 590 nm) with differences of intensity. It can be seen that the addition of solvent concentration resulted in a higher absorption value at almost the same wavelength. In this study, the solvent 1000 ppm produces the greatest absorption intensity. Therefore, further for the characterization of UV-Vis with a variation of Gd elements, the compound dissolution process was carried out using a concentration of 1000 ppm.

The second stage uses variations of Gd elements with solvent 1000 ppm. The UV-Vis results of the samples are shown in Figure 3.

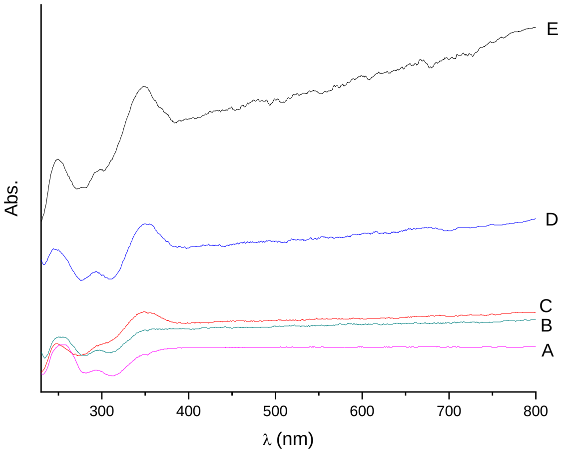

Fig. 2 The UV-Vis results of $Ba_{0.95}Ca_{0.05}(Ti_{0.95}Gd_{0.05})O_3$ samples with various solvent concentrations from: A) 10 ppm, B) 50 ppm, C) 100 ppm, D) 500 ppm, E) 1000 ppm

These results show absorption with almost the same pattern and intensity for all samples.

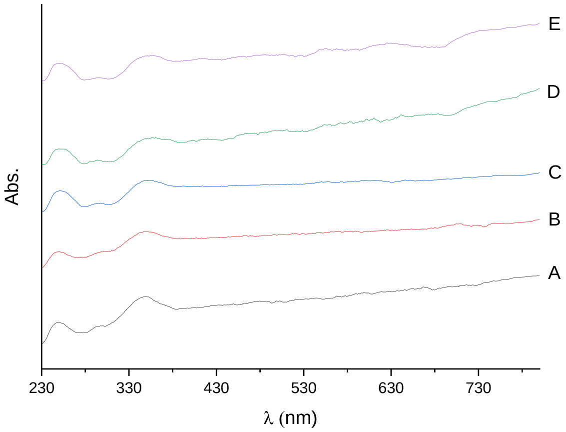

Fig. 3 The results of the synthesis of $Ba_{0.95}Ca_{0.05}(Ti_{0.95}Gd_{0.05})O_3$ samples in the form of pellets with variation of the Gd element from: A) 0.05, B) 0.10, C) 0.15, D) 0.20, E) 0.25

3.2. XRD Characterization

The results of the XRD characterization of the $Ba_{0.95}Ca_{0.05}(Ti_{0.95}Gd_{0.05})O_3$ samples with Gd variations (from 0.05 to 0.25) and Ti variations (from 0.95 to 0.75) are shown in Figure 4. In general, all XRD characterization results show almost the same spectrum pattern at every 2θ angle, but detected intensity is different. The spectrum has shown fine and sharp peaks, which indicate that the crystallization process has occurred completely. The results of XRD characterization also showed a decrease in peak intensity with the addition of Gd elements, especially at the peak with an angle of 2θ about 31°. The decrease in peak intensity was followed by an increase in peak intensity at an angle of 2θ about 29.5°.

Rietveld refinement was carried out using the Rietica software. The results of the refinement of $Ba_{0.95}Ca_{0.05}(Ti_{0.95}Gd_{0.05})O_3$ samples are shown in Figure 5. The curve explains that the res peaks are sourced from the reference data, the black peaks are sourced from the sample characterization data, while the green curve is the difference between the reference peak and the characterization peak.

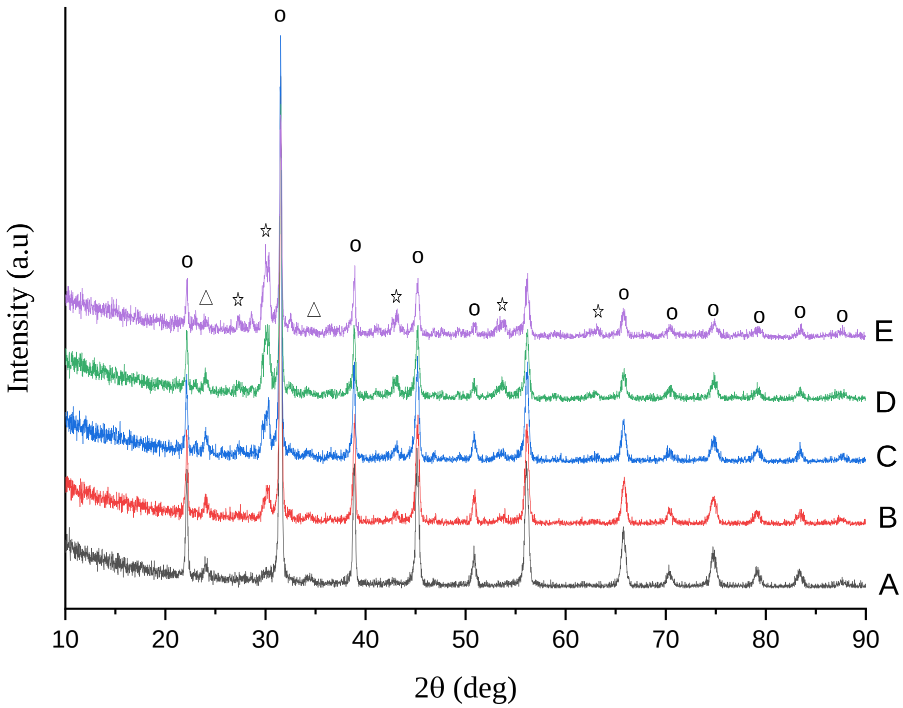

Fig. 4 The results of the synthesis of $Ba_{0.95}Ca_{0.05}(Ti_{0.95}Gd_{0.05})O_3$ samples in the form of pellets with variation of Gd element from: A) 0.05,) 0.10, C) 0.15, D) 0.20, E) 0.25

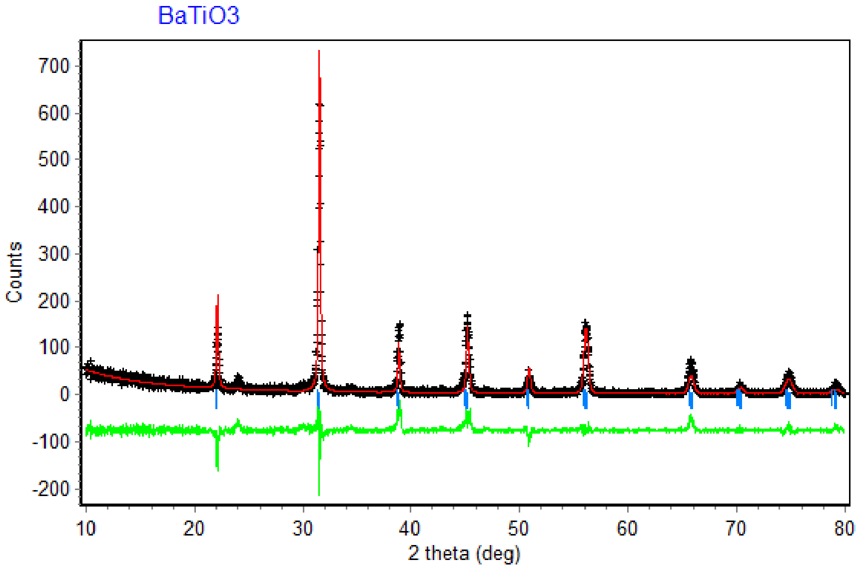

Fig. 5 The results of refinement $Ba_{0.95}Ca_{0.05}(Ti_{1-x}Gd_x)O_3$ samples by Rietica software

The value of the lattice constant in the direction of the a-axis, the c-axis and the value of goodness-of-fit (GoF) or χ^2 showed in Table 1. The relationship of the lattice constant with x at $Ba_{0.95}Ca_{0.05}(Ti_{1-x}Gd_x)O_3$ is showing in Figure 6. From Table 1 and Figure 6, it can be seen that the addition of Gd element from 0.05 to 0.25 resulted in an increase in the value of lattice constant towards the a-axis and c-axis. This is due to the differences in the ionic radii of Ti and Gd elements, where the Gd ionic radius is larger than the Ti ion radius.

Table 1. The value of the lattice constant in the direction of the a-axis, the c-axis and the value of χ^2

Sample	Lattice constant	χ^2

	a-axis (Å)	c-axis (Å)	
$Ba_{0.95}Ca_{0.05}(Ti_{0.95}Gd_{0.05})O_3$	4.010404(9)	4.016649(6)	1.74
$Ba_{0.95}Ca_{0.05}(Ti_{0.90}Gd_{0.10})O_3$	4.011714(6)	4.017413(5)	1.86
$Ba_{0.95}Ca_{0.05}(Ti_{0.85}Gd_{0.15})O_3$	4.012275(1)	4.020380(9)	2.24
$Ba_{0.95}Ca_{0.05}(Ti_{0.80}Gd_{0.20})O_3$	4.013228(1)	4.022643(4)	2.42
$Ba_{0.95}Ca_{0.05}(Ti_{0.75}Gd_{0.25})O_3$	4.016376(6)	4.022951(2)	2.67

Table 2. The value of Lorenz, density and cell volume

Sample	Lorenz	Density (gr/cm^2)	Cell volume (Å^3)
$Ba_{0.95}Ca_{0.05}(Ti_{0.95}Gd_{0.05})O_3$	0.120950(1)	42.096	64.601132(8)
$Ba_{0.95}Ca_{0.05}(Ti_{0.90}Gd_{0.10})O_3$	0.128955(2)	42.107	64.655639(1)
$Ba_{0.95}Ca_{0.05}(Ti_{0.85}Gd_{0.15})O_3$	0.146028(9)	42.122	64.721487(2)
$Ba_{0.95}Ca_{0.05}(Ti_{0.80}Gd_{0.20})O_3$	0.150888(1)	42.176	64.788636(6)
$Ba_{0.95}Ca_{0.05}(Ti_{0.75}Gd_{0.25})O_3$	0.180077(4)	42.213	64.895334(5)

The goodness-of-fit (GoF) for each sample varies from 1.74 to 2.67. The greater the addition of Gd elements, the higher the goodness-of-fit value. This indicates that the match between the reference spectrum and the characterization spectrum is decreasing. The results are in accordance with the results of the search match analysis, where the addition of Gd element produces greater impurities.

The value of Lorenz, density and unit cell volume are shown in Table 2. The Lorenz value is related to the particle size.

From the data in Table 2, it can be seen that the addition of the Gd element results in an increasing Lorenz value, which indicates that the particle size is also getting bigger. Likewise, the unit cell volume value increases with the addition of the Gd element, in accordance with the addition of the lattice constant. The addition of the Gd element also resulted in an increase in the density value from 42.096 to 42.213 gr/cm^2, as shown in Table 2 and Figure 7. The increase in density is caused by the occupancy of empty spaces (holes) scattered in the sample by of the Gd element, thereby reducing the existing empty space and at the same time increasing the density of the sample.

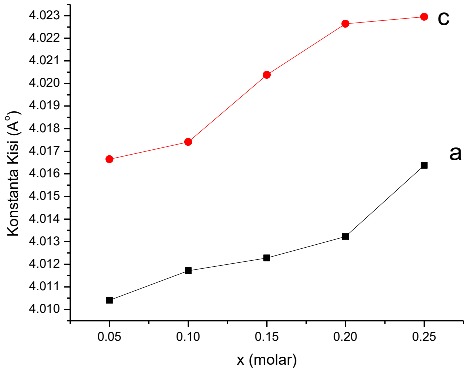

Fig. 6 The relationship of the lattice constant with x at $Ba_{0.95}Ca_{0.05}(Ti_{1-x}Gd_{x})O_3$

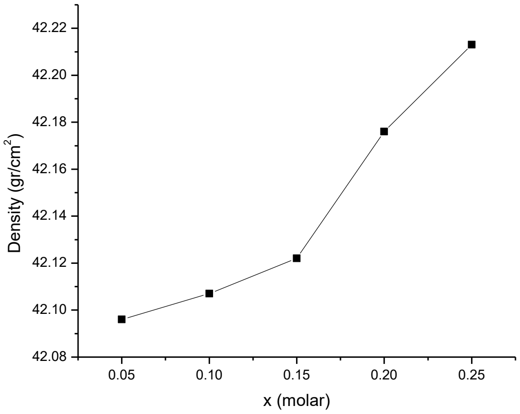

Fig. 7 The results of the synthesis of $Ba_{0.95}Ca_{0.05}(Ti_{0.95}Gd_{0.05})O_3$ samples in the form of pellets with variation of Gd element from 0.05 to 0.25

IV. CONCLUSION

From the results of the study, several conclusions were obtained, namely the addition of the element Gd from 0.05 to 0.25 to the compound $Ba_{0.95}Ca_{0.05}(Ti_{0.95}Gd_{0.05})O_3$ resulted in :

- The value of the lattice parameters in the a-axis and c-axis increases
- The value of density increases
- The unit cell volume value increases
- The particle size increases

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