Analysis of Ferroelectric Thin Film BaZr$_{0.6}$Ti$_{0.4}$O$_3$ with Annealing Temperature Increase Variations Using x-ray Diffraction

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Abstract. Ferroelectric is a dielectric material which has spontaneous polarization and has the ability to change its internal polarization using a suitable electric field. The aim of this research is to decrease the FWHM value and increase the crystal size so that the dielectric constant increases for capacitor applications. Thin film ferroelectric material of Barium Zirconium Titanate (BZT) with the composition BaZr$_{0.6}$Ti$_{0.4}$O$_3$ was prepared using the sol-gel method. The substrate used was FTO glass which has been treated etching and coated with BZT and in annealing at 800°C with annealing temperature increase of 5°C and 10°C. Samples were characterized using XRD with an angle interval of 2θ between 20° to 60°. The results of XRD characterization show that there were peaks indicating that there was a crystal structure. The resulting crystal structure was in a plane 100 at an angle of 2θ = 22.55°, a plane 110 at an angle of 2θ = 32.00°, a plane 111 at an angle of 2θ = 38.54°, and a plane 200 at an angle of 2θ = 47.64°. The resulting structure in this study was tetragonal where a = b = 3.955 and c = 4.266. The rate at which temperature rose had an effect on the peak of X-Ray diffraction. The FWHM value for 5°C was less than 10°C. This implies a greater density when annealing at 5°C. The crystal size values obtained with an increase in temperature of 5°C and 10°C in the 100 plane were 3.22 and 2.954, respectively. The crystal size was inversely proportional to the FWHM value where the small speed of the annealing temperature increase caused the crystal size to enlarge.

Keyword: BaZrTiO$_3$, Thin Film, Annealing Temperature Rise Speed, Sol-gel Method, X-Ray Diffraction (XRD).

1. Introduction
The increasing population every day in the world has an effect on the increasing energy needs and the depletion of reserves of non-renewable fuel. One of the most needed energy is electrical energy. This is due to the large number of electrical energy needs in everyday life as a source of lighting and other electronic devices. Along with the times, scientists are aggressively researching a device which is able to store energy. One of the energy stores is a capacitor.

Capacitors are electronic components which are able to store charge and energy. The capacitor has a capacity which can be increased by applying a dielectric to the capacitor. Researchers have conducted many experiments by making dielectric materials to increase the capacitance value in the capacitor.

Ferroelectric is one of the materials used as a dielectric such as BaTiO$_3$, PbTiO$_3$ and SrTiO$_3$. Some of the ferroelectric materials are pure and some are doped, so that they change their electrical properties. The pure ferroelectrics that are often used, namely: lead Titanate (PbTiO$_3$) and Barium...
Titanate (BaTiO_3) where the pure ferroelectric is independent of frequency, the doped ferroelectric is like Barium Strontium Titanate (BST), Lead Zirconium Titanate (PZT) and Barium Zirconium Titanate (BZT) which is called a ferroelectric relaxor has a frequency dependence effect disorder of diffusion at each site [1]. The ferroelectric relaxor is able to increase the dielectric constant and reduce dielectric loss at low frequencies [2]. Barium titanate BaTiO_3 is a perovskite structure (ABO_3) and has the properties of high dielectric constant, low dielectric loss and good dielectric efficiency [3]. Dielectrics are made in various forms, one of which is a thin film. The easiest and simplest method of making thin films is the sol gel method.

The researchers conducted a study using the Pb material as a dielectric to increase the dielectric constant as has been reported by [4] which explains that the Zr pending on PbTiO_3 causes a dependence on frequency to increase the value of the dielectric constant. However, Pb is capable of causing environmental pollution, while PZT is able to make high dielectric constant values due to temperature variations [5]. The rate of temperature rise has an impact on the granular arrangement of the PZT material. The rapid increase in calcination temperature causes the granules to quickly change to the crystal phase before the granules move to cover the empty space, so that it will leave porosity [6]. Referring to the aforementioned researches, this study used Barium material to be more environmentally friendly. Zr doping in BaTiO_3 varies the temperature velocity, namely 5°C/min and 10°C/min with annealing temperature of 800°C for 2 hours, then it is characterized using XRD. The aim of this research is to decrease the FWHM value and increase the crystal size so that the dielectric constant increases for capacitor applications.

2. Theory

2.1. Perovskite structure
A ferroelectric material is a material that maintains its polarization when the electric field is removed so that there is a permanent residual dipole alignment. Not all materials with permanent dipoles exhibit ferroelectric behavior because the dipoles are random and aligned with the field; if removed, there is no polarization remains clean.

Perovskite structure is one of the structures that characterizes ferroelectric materials. Perovskite structure with ABO_3 formula is shown in Figure 1 where A is a monovalent and divalent metal, B is a tetra or pentavalent metal, and O is the element oxygen.

![Figure 1. Perovskite structure: (a) cubic phase, (b) tetragonal phase [7].](image)

2.2. Barium Zirconium Titanate (BZT)
Barium Titanate with the chemical formula BaTiO_3 is the most widely used ferroelectric material since sixty years after its discovery. This material is a multi-layered dielectric ceramic which is widely used [8]. Ba (Zr_xTi_{1-x}O_3) has superior electrostatic properties, because T_c of the BZT ceramic can be easily shifted to reduce the temperature at the composition variation from x = 0 to x = 1 as can be seen in Figure 2.
2.3. X-Ray Diffraction (XRD)
XRD is a tool used to characterize the crystal structure, the crystal size of a solid material. All materials containing certain crystals when analyzed using XRD will lead to specific peaks. The diffraction method is generally used to identify unknown compounds contained in a solid by comparing it with the diffraction data from the database issued by the International Center for Diffraction Data in the form of a Powder Diffraction File (PDF).

The X-ray diffraction method can also explain lattice parameters, structure types, different atomic arrangements in a crystal, crystal imperfections, grain and grain size. The interplanar distances of all parallel planes have the same notation (hkl). The general formula for the interplanar distance or d-distance in the cubic crystal equation 1 and the tetragonal crystal equation 2 is as follows:

\[ d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \]  
\[ d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} + \frac{c}{l} \]

where \( d_{hkl} \) is the distance between the planes, a and c are the lattice parameters, and hkl is the miller's index.

3. Methods
The method used in the manufacture of this BZT is the sol-gel method and the research flow diagram can be seen in Figure 3 below.
First, FTO substrate was firstly washed and etched in the center of the FTO so that its conductive properties were vanished. Preparation of BZT solution using the sol-gel method was conducted using the following chemical equation:

\[
\text{BaCO}_3 + \text{ZrCO}_2(0.6) + \text{Ti}(0.4)\text{O}_2 \rightarrow \text{BaZr}_{0.6}\text{Ti}_{0.4}\text{O}_3 + 2\text{CO}_2
\]  

The finished BZT was coated on top of the etching and spin coating FTO substrate at a speed of 3600 rpm for 3 times. The next stage was to process annealing. Sample was annealed with a temperature of 800°C for 2 hours with variations in the temperature rise of 5°C and 10°C and then the sample was characterized using X-Ray Diffraction.

4. Results and Discussion
In XRD characterization, the diffraction pattern of BZT was obtained with the counter angle (2θ) between 20° to 60° from the interval for each counter of 0.025, and the wavelength (λ) = 1.544 Å. The results of characterization obtained the XRD pattern can be seen in Figure 4 below:

Figure 3. BZT thin film research flow chart.
Figure 4. BaZr$_{0.6}$Ti$_{0.4}$O$_3$ Thin Film XRD Pattern.

Figure 4 shows the X-Ray Diffraction pattern of the BZT thin film sample after being annealed at a temperature of 800°C for 2 hours with a variation of the speed of temperature rise, namely 5°C/min and 10°C/min. X-ray diffraction peaks in the plane 100 angle 2θ = 22.55°, plane 110 angle 2θ = 32.00°, plane 111 angle 2θ = 38.54°, plane 200 angle 2θ = 47.64°. This peak shows that the annealed BZT sample has a crystalline structure which means that it has an orderly arrangement of particles [10]. The results of research conducted by [11] and [12] found a match for the 4 peaks shown in Figure 4 above where the peaks indicate that this BZT sample has a tetragonal structure. The lattice parameters of the tetragonal structure were a = b = 3.955 and c = 4.266.

The rate at which temperature rose also affected the peak of the X-Ray Diffraction. Table 1 shows that the FWHM value for 5°C/min was smaller than 10°C/min. This means that there was a greater density when annealing at a speed of 5°C/min than at 10°C/min. The results of this study are in line with [6]. The rate of temperature rose had an impact on the granular arrangement of the PZT material. The rapid increase in calcination temperature caused the granules to quickly change to the crystal phase before the granules moved to cover the empty space, so that it left porosity [6]. When the annealing temperature increased, there were 2 properties that prevailed, namely evaporation and hardening. Large temperature velocity resulted in rapid evaporation and rapid hardening. Slow temperature speed caused slow evaporation and slow hardening, therefore the granules had time to expand and occupy an empty place so as to minimize the porosity of the sample. Samples that had a large crystal size showed a small FWHM value. The results of this study are in line with [13] stating that the lowest FWHM value was around 0.28 with the BaZrO$_3$ sample modification (K, Na) NbO$_3$ annealed at 850°C with a temperature rise rate of 3°C/min.

| 2θ  | θ   | hkl | $h^2 + k^2 + l^2$ | a (nm) | c (nm) | d$_{hkl}$ (nm) | FWHM 5°C/min | FWHM 10°C/min | D (nm) 5°C/min | D (nm) 10°C/min |
|-----|-----|-----|-------------------|-------|-------|----------------|--------------|---------------|----------------|----------------|
| 22.55 | 11.27 | 100 | 1                | 3.955 | 4.266 | 3.955          | 0.440        | 0.480         | 3.222          | 2.954          |
| 32.00 | 16   | 110 | 2                | 3.955 | 4.266 | 2.797          | 0.440        | 0.480         | 3.285          | 3.012          |
| 38.54 | 19.27 | 111 | 3                | 3.955 | 4.266 | 2.342          | 0.520        | 0.560         | 2.832          | 2.629          |
| 47.64 | 23.82 | 200 | 4                | 3.955 | 4.266 | 1.977          | 0.480        | 0.520         | 3.165          | 2.924          |
Table 1 shows the crystal size is inversely proportional to the FWHM value where a small temperature rise causes the crystal size to enlarge. At an angle of 2θ = 22.55°, the FWHM value for 5°C/min was 0.440 and the crystal size value was 3.222; while for 10°C/min, the FWHM value was 0.480 and the crystal size was 2.954. When a small increase in annealing temperature was treated, the particles adjusted to occupy the empty space, so that it caused a larger level of crystallinity. This is why the crystal size increased with the smaller the rate at which temperature increased. Increased temperature annealing caused an increase in the X-ray diffraction peak value. [14] The results of this study were also reported by [15] and [16] stating the particle size increased as the temperature of annealing increased [15] and [16].

5. Conclusion
Thin film BaZr_{0.6}Ti_{0.4}O_{3} was annealed at 800°C for 2 hours with a speed increase of 5°C/min and 10°C/min. Characterization using XRD got the peak with plane 100 at 2θ = 22.55°, plane 110 at 2θ = 32.00°, plane 111 at 2θ = 38.54°, plane 200 at 2θ = 47.64° and had a crystal structure that was tetragonal with lattice parameters a = b = 3.955 and c = 4.266. At an angle of 2θ = 22.55° the FWHM value for 5°C/min was 0.440 and the crystal size value was 3.222, while for 10°C/min, the FWHM value was 0.480 and the crystal size was 2.954. The crystal size was inversely proportional to the FWHM value where the small speed of the annealing temperature increase caused the crystal size to enlarge.

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