The addition of bismuth (Bi) to the barium titanate (BaTiO$_3$) prepared by chemical solution deposition

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Abstract. The manufacture of BaTiO$_3$ thin films and Ba$_{1-x}$Bi$_x$TiO$_3$ have been conducted successfully on the quartz substrate using Chemical Solution Deposition method. The results of characterization using XRD showed that the crystals of BaTiO$_3$ and Ba$_{1-x}$Bi$_x$TiO$_3$ were perovskite. The diffraction angle shift between BaTiO$_3$ and Ba$_{1-x}$Bi$_x$TiO$_3$ shifts to the right as the mole concentration of Bi. The crystallinity of the Ba$_{1-x}$Bi$_x$TiO$_3$ sample increases along with the increase of Bi mole concentration. The higher the sample annealing temperature, the crystallinity decreases. The addition of Bi mole concentrations and the increase of annealing temperature in Ba$_{1-x}$Bi$_x$TiO$_3$ samples causes the crystal size of the thin film to increase. Lattice strain is greater with the addition of Bi concentration and the increase of annealing temperature. The result of UV-Vis showed that the transmittance of the thin film was relatively small. Therefore, the thin film made has a high ability to absorb light in the UV area. The greater the addition of Bi mole concentration, the greater the ability of light absorption. When the thin film was given an additional concentration of Bi mol, the refractive index value was greater. The addition of Bi mole concentrations in Ba$_{1-x}$Bi$_x$TiO$_3$ thin films leads to an increase in dispersion values.

1. Introduction
Nowadays, research on the ferroelectric material attracts the physicists as the ferroelectric material is very promising towards the development of science and technology, especially in the material field. Ferroelectric material has fabricated characteristic based on the needs. Moreover, it is easily integrated. Ferroelectricity is a great potential material as new solar cells, light drivers, and optical sensors because of the anomaly photovoltaic (APV) effect [1]. Some methods have been successfully conducted in making epitaxial and polycrystalline films including metal-organic chemical vapor deposition (MOCVD), pulse laser deposition (PLD), metal-organic decomposition (MOD) and sol-gel technique or chemical solution deposition (CSD) [2].

Barium Titanate (BaTiO$_3$) is the most well-known ferroelectric compound studied largely because of the simplicity of the crystal structure. Thus, it can accommodate various types of dopants [3]. BaTiO$_3$ has a high dielectric constant, ferroelectric activity, spontaneous polarization, and nonlinear optical coefficients [4, 5]. BaTiO$_3$ is a ferroelectric material that has a perovskite crystalline structure.
of ABO₃, where A is a cation with valence 1 and 2, B is a cation with valence 4 and 5, and O is oxygen [6]. Atom A is located in the corner of the cube. Atom B is located in the diagonal of the cube space and O atom is located in the diagonal plane of the cube [7]. Perovskite BaTiO₃ has five types of crystal structures such as hexagonal, cubic, tetragonal, orthorhombic, and rhombohedral, each of which depends on the temperature of the phase [4].

This research used ferroelectric material namely BaTiO₃ and Ba₁₋ₓBiₓTiO₃. This material is formed from Barium Titanate added with bismuth. The addition of bismuth (Bi³⁺) to Ba₁₋ₓBiₓTiO₃ thin films can cause changes in the characteristics of the material. Thus, it can be useful to improve the quality and function. Bismuth is a donor doping that donates excess valence electrons to the Ba²⁺ ion and the radius is almost the same as the radius of the Ba²⁺ ion. The Bi³⁺ doping ion radius is 1.03 Å [8], while the Ba²⁺ ion radius is 1.35 Å and the Ti⁴⁺ ion radius is 0.68 Å [9]. Doping is a common method for reducing the semiconductor band gap [1].

In this research, the growth of BaTiO₃ and Ba₁₋ₓBiₓTiO₃ thin film was conducted using Chemical Solution Deposition (CSD) method. Chemical Solution Deposition (CSD) is a way to make a thin film by deposition of chemical solutions on the substrate, then prepared by coating a spin coating at a certain rotational speed. This method is superior because stoichiometry is easily well-controlled [10]. BaTiO₃ and Ba₁₋ₓBiₓTiO₃ thin films are grown on quartz substrates with annealing temperature variations of 800°C, 850°C, and 900°C. The thin film that has been formed was then tested for microstructure using X-Ray Diffraction (XRD) and optical properties testing using a UV-Vis spectrophotometer. X-Ray Diffraction (XRD) examination aims to determine the microstructure of the sample. The optical properties test aims to determine the absorption spectrum of BaTiO₃ and Ba₁₋ₓBiₓTiO₃ thin films.

2. Experiment
The materials used in this research were Barium Acetate [Ba(CH₃COO)₂] 99.00%, Bismuth Acetate [Bi(CH₃COO)₃] 99.9%, Acetic Acid [(CH₃COOH)] 100%, Titanium Isopropoxide [Ti(OC₃H₇)₄] 97%, and Ethylene Glycol [(HOCH₂CH₂OH)] 100%. The substrates used for the deposition of BaTiO₃ and Ba₁₋ₓBiₓTiO₃ films were quartz substrates. The manufacture of BaTiO₃ and Ba₁₋ₓBiₓTiO₃ thin films used the Chemical Solution Deposition method with three main stages: namely the making/manufacturing of a solution, the process of spin coating, and the annealing process. Ba₁₋ₓBiₓTiO₃ thin films were prepared using a ratio of bismuth mole compositions of 0.10 and 0.15. The process of making the solution was mixed using a magnetic stirrer until all the ingredients were homogeneously mixed. The layer was deposited using a spin coater with a speed of 5000 rpm. After obtaining the desired number of films, it was then annealed using a furnace with annealing temperature variation of 800°C, 850°C, and 900°C with a holding time of one hour. The sample was then characterized using X-Ray Diffraction (XRD) to determine the microstructure of the sample and using a UV-Vis spectrophotometer to determine the optical properties of the thin film.

3. Result and Discussion
The crystal structure of thin films of BaTiO₃ and Ba₁₋ₓBiₓTiO₃ was characterized using XRD. Samples of BaTiO₃ and Ba₁₋ₓBiₓTiO₃ varies with the concentration of mol Bi with an annealing temperature of 800°C, 850°C, and 900°C. Figure 1 shows the diffraction patterns of BaTiO₃ and Ba₁₋ₓBiₓTiO₃ thin films with variations in the concentration of mol Bi annealed at temperatures of 800°C, 850°C, and 900°C. Diffraction peaks resulted from XRD characterization had different plane orientations. The diffraction pattern was matched with the ICDD database to identify the angular shift that occurred between the theory and this research.
Based on Figure 1, it shows that the sample still had other phases. The existence of other phases showed that Ba, Bi, Ti, and O atoms had not been able to diffuse completely. Other phases identified in the sample are phases of BaTi$_2$O$_5$. In the XRD diffraction pattern, the other phases are marked with $\oplus$. Figure 1 shows that the addition of Bi mole concentration causes a diffraction angle shift ($\theta$). The diffraction angle shift between BaTiO$_3$ and Ba$_{1-x}$Bi$_x$TiO$_3$ shifted to the right as the mole concentration of Bi was given. This result is under the research conducted by Alkathy and Raju [8]. The angular shift that occurred was not significant because the concentration of mol Bi added was very small. This angular shift was caused because the radius of the Bi atom was smaller than the radius of the Ba atom. The addition of Bi atoms to Ba$_{1-x}$Bi$_x$TiO$_3$ samples acts as a substitute for Ba atoms in the perovskite structure of BaTiO$_3$. Bi atoms can replace Ba atoms because they have nearly the same atomic radius.

The intensity of the diffraction pattern affected crystallinity values from BaTiO$_3$ and Ba$_{1-x}$Bi$_x$TiO$_3$ samples. The addition of mol Bi concentration in the sample caused the intensity of the diffraction pattern to increase. These results are under the research of Iriani et al., they state that with the addition of doping mole concentrations in the BaTiO$_3$ thin film, the intensity value formed increases [9]. The higher the intensity, the greater the crystallinity of the sample. The crystallinity of the Ba$_{1-x}$Bi$_x$TiO$_3$ sample increased with increasing mol Bi concentration. Besides, crystallinity samples were also affected by the sample annealing temperature. The higher the sample annealing temperature, the crystallinity decreased. This decrease in crystallinity was affected by the vibrations of the atoms scattered in each film. This is consistent with the results shown in Table 1. This crystallinity shows the level of regularity of a crystal. The crystallinity of BaTiO$_3$ and Ba$_{1-x}$Bi$_x$TiO$_3$ thin films can be

**Figure 1.** XRD patterns of BaTiO$_3$ and Ba$_{1-x}$Bi$_x$TiO$_3$ using annealing temperature variations (a) 800$^\circ$C, (b) 850$^\circ$C, and (c) 900$^\circ$C
calculated based on the ratio of the highest peak intensity in a specific field orientation with the highest number of intensities and the lowest intensity in a specific field orientation. The crystallinity of the thin film is determined by the equation as follow [11]:

\[
\% \text{ Crystallinity} = \frac{I_{\text{max}}}{I_{\text{max}} + I_{\text{min}}} \times 100
\]

(1)

**Table 1. Crystallinity with annealing temperature variations**

| Mole Concentration of Bi (x) | Annealing Temperature of 800°C | Annealing Temperature of 850°C | Annealing Temperature of 900°C |
|-----------------------------|-------------------------------|-------------------------------|-------------------------------|
| BaTiO₃                      | 66.73                         | 83.33                         | 69.57                         |
| 10%                         | 67.8                          | 71.56                         | 71.098                        |
| 15%                         | 69.61                         | 72.72                         | 71.76                         |

Based on the results of XRD characterization, it was obtained half the width of the diffraction peak or commonly known Full Width Half Maximum (FWHM). This FWHM value affected the size of the crystal. High diffraction peaks and sharp lines that resembled straight lines had a small FWHM value. It resulted in large crystal sizes, and vice versa, wide diffraction peaks that produced small crystal sizes. These results are in line with the research carried out by William et al., [12]. The crystal size of BaTiO₃ and Ba₁ₓBiₓTiO₃ thin films can be calculated using the following Scherrer equation:

\[
D = \frac{k \lambda}{\beta \cos \theta}
\]

(2)

Where, \( \beta \) value is FWHM value, \( \theta \) is the diffraction angle, \( k \) is the Scherrer constant of 0.9, and \( \lambda \) is the wavelength of the X-ray [1].

**Table 2. Crystal size with annealing temperature variations**

| Mole Concentration of Bi (x) | Annealing Temperature of 800°C | Annealing Temperature of 850°C | Annealing Temperature of 900°C |
|-----------------------------|-------------------------------|-------------------------------|-------------------------------|
| BaTiO₃                      | 12                            | 70                            | 27                            |
| 10%                         | 17                            | 11                            | 36                            |
| 15%                         | 20                            | 23                            | 71                            |

Table 2 shows the calculated crystal size values of the BaTiO₃ and Ba₁ₓBiₓTiO₃ samples toward the variation of the Bi mole concentration. It shows that the addition of mol Bi concentrations in Ba₁ₓBiₓTiO₃ samples caused the crystal size of the thin film to increase. Following the addition of mol Bi concentration that with the annealing temperature increase, the crystal size from the sample was also getting bigger. These results are consistent with the results observed by Alkathy et al., as the mole concentration of doping increases, the crystal size value of the sample increases [13]. Based on the results of a research that has been done by Rini et al., when the annealing temperature increases, the crystal size of the thin film will get bigger [14]. The increase size of the crystal happened because the film could diffuse from one another. Thus, the reaction was more perfect.
Table 3. Lattice strain with annealing temperature variations

| Mole Concentration of Bi (x) | Lattice Strain |
|-----------------------------|----------------|
|                             | Annealing Temperature of 800°C | Annealing Temperature of 850°C | Annealing Temperature of 900°C |
| BaTiO₃                      | 0.0295          | 0.3180          | 0.0080          |
| 10%                         | 0.0199          | 0.0324          | 0.0095          |
| 15%                         | 0.0423          | 0.0368          | 0.0030          |

Table 3 shows that the addition of mol Bi concentrations in Ba₁₋ₓBiₓTiO₃ samples caused the lattice strain from the thin film to increase. If the annealing temperature of the sample increased, the resulting lattice strain would be even greater. Based on the order of the ionic radius of Ti⁴⁺ < Bi³⁺ < Ba²⁺, it is possible that the lattice strain is getting bigger because bismuth undergoes substitution in barium [15].

Figure 2. Transmittance of BaTiO₃ and Ba₁₋ₓBiₓTiO₃ using annealing temperature variations (a) 800°C, (b) 850°C, and (c) 900°C

Samples that had been manufactured over the quartz substrate were examined using a UV-Vis spectrophotometer. This test aimed to determine the optical properties of Ba₁₋ₓBiₓTiO₃ samples in the wavelength range of 200 to 800 nm. The wavelength was the wavelength of UV light to be visible (visible light).

Based on the result of testing the optical properties, it was obtained the value of transmittance and absorbent of BaTiO₃ and Ba₁₋ₓBiₓTiO₃ thin films. Figure 2 shows the transmittance results of BaTiO₃.
and Ba$_{1-x}$Bi$_x$TiO$_3$ thin films. The transmittance results showed that as the mole concentration of Bi increased, the transmittance value of the Ba$_{1-x}$Bi$_x$TiO$_3$ thin film decreased. These results are consistent with the research conducted by Fu et al., they state that as the wavelength decreases, the transmittance value of the thin film also decreases [16]. This showed that the transmittance value of the thin film was relatively small. Thus, the thin film made had a high ability to absorb light in the UV region. The greater the addition of Bi mole concentration, the greater the ability of light absorption.

![Refractive index of BaTiO$_3$ and Ba$_{1-x}$Bi$_x$TiO$_3$ using annealing temperature variations](Figure_3.png)

**Figure 3.** Refractive index of BaTiO$_3$ and Ba$_{1-x}$Bi$_x$TiO$_3$ using annealing temperature variations (a) 800°C, (b) 850°C, and (c) 900°C

The refractive index value of the thin film of BaTiO$_3$ and Ba$_{1-x}$Bi$_x$TiO$_3$ was calculated using the Swanepoel method. The following is an equation from the Swanepoel method [17]:

$$n = \left[ N_1 + \left( N_1^2 - s^2 \right)^{1/2} \right]^{1/2}$$

(3)

In which, $N$ and $s$ are defined as:

$$N_1 = \frac{2s}{T_m} + \frac{s^2 + 1}{2}$$

(4)

$$s = \frac{1}{T_s} + \frac{1}{\sqrt{T_s^2}} - 1$$

(5)
In which $s$ is the substrate transmission spectrum, $N_1$ is the area of transparent spectral, $T_S$ is the transmittance of the quartz substrate, $n_1$ is the refractive index, and $T_m$ is the transmittance of the sample.

Figure 3 shows the relationship between wavelength and refractive index of BaTiO$_3$ and Ba$_{1-x}$Bi$_x$TiO$_3$ thin films. The value of the refractive index produced by the Ba$_{1-x}$Bi$_x$TiO$_3$ thin film was inversely proportional to the transmittance value. When the thin film was given the addition of mol Bi concentrations, the refractive index value was greater. This result is in line with Tian et al., in which the addition of doping mole concentration causes the refractive index value of the thin film to increase [18]. The addition of doping mole concentration caused the density of atoms in the film to increase. Thus, the refractive index value increased.

![Graph 1](image1.png)

**Figure 4.** $1/(n^2-1)$ Vs E$^2$ of BaTiO$_3$ and Ba$_{1-x}$Bi$_x$TiO$_3$ using annealing temperature variations (a) 800°C, (b) 850°C, and (c) 900°C

The amount of light dispersion from BaTiO$_3$ and Ba$_{1-x}$Bi$_x$TiO$_3$ thin films is calculated using the following Equation [17]:

$$n^2 = 1 + \frac{E_d}{E_0^2 - E^2}$$

(6)

In which, $E_0$ is single oscillator energy, $E_d$ is dispersion energy, $E^2$ is photon energy, $\lambda = 1.9865 \times 10^{-25}$ kg m$^2$/s$^2$ and 1 joule = $6,242 \times 10^{18}$ eV.

The results of BaTiO$_3$ and Ba$_{1-x}$Bi$_x$TiO$_3$ thin-film dispersion calculations were displayed in the form of a relationship between $1/(n^2-1)$ Vs E$^2$. Based on the graph in Figure 4, it can be seen that the addition of mol Bi concentrations in the Ba$_{1-x}$Bi$_x$TiO$_3$ thin film causes an increase in the dispersion
value. It is supported by Mohamed et al., who state that light dispersion from thin films increases with the addition of doping mole concentrations [19]. Increasing the dispersion value in the film was caused by the density of atoms attached to the substrate.

4. Conclusions
Based on the results of the analysis, it was found that with the addition of Bi moles in the sample, there were still other phases. The existence of other phases showed that the atoms of Ba, Bi, Ti, and O have not been able to diffuse completely. The diffraction angle shift between BaTiO$_3$ and Ba$_{1-x}$Bi$_x$TiO$_3$ shifts to the right as the mole concentration of Bi. The crystallinity of the Ba$_{1-x}$Bi$_x$TiO$_3$ sample increases along with the increase of Bi mole concentration. The higher the sample annealing temperature, the crystallinity decreases. The addition of Bi mole concentrations and the increase of annealing temperature in Ba$_{1-x}$Bi$_x$TiO$_3$ samples causes the crystal size of the thin film to increase. Lattice strain is greater with the addition of Bi concentration and annealing temperature. Therefore, the thin film made has a high ability to absorb light in the UV area. The greater the addition of Bi mole concentration, the greater the ability of light absorption. When the thin film was given an additional concentration of Bi mol, the refractive index value was greater. The addition of Bi mole concentrations in Ba$_{1-x}$Bi$_x$TiO$_3$ thin films leads to an increase in dispersion values.

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