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CHARACTERIZATION OF ENERGY BAND GAP THIN FILM BATIO$_3$ - BAZR$_{0.5}$TI$_{0.5}$O$_3$ USING DIFUSION REFLECTANCE SPECTROSCOPY (DRS) METHOD

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ABSTRACT

Ferroelectric material is a dielectric material that has a high dielectric constant value so that it can be made in the form of thin films. Its application is based on electro-optical properties, one of which is the infrared thermal switch. This paper aims to determine the bandgap energy (Eg) of a 0.3BaTiO$_3$ - 0.7BaZr$_{0.5}$Ti$_{0.5}$O$_3$ thin film. The 0.3BaTiO$_3$ - 0.7BaZr$_{0.5}$Ti$_{0.5}$O$_3$ thin film is a semiconductor material with the valence band and conduction band separated by an energy bandgap (Eg). Thin films of 0.3BaTiO$_3$ - 0.7BaZr$_{0.5}$Ti$_{0.5}$O$_3$ were grown on FTO substrates using the sol-gel method. The films of 0.3BaTiO$_3$ - 0.7BaZr$_{0.5}$Ti$_{0.5}$O$_3$ were annealed at different temperatures of 700°C, 750°C and 800°C within 1 hour. Characterization was carried out using Ultra Violet Visible (UV-Vis) spectroscopy to determine Eg using the Diffusion Reflectance Spectroscopy (DRS) method. The DRS method was found to be better for solid materials considering the scattering component. The UV-Vis characterization results show that an increase in annealing temperature causes a decrease in Eg. For example the values at 700°C, 750°C and 800°C are 3.5 ± 0.01 eV; 3.3±0.01 eV and 3.2 ± 0.01 eV. The decrease in Eg is related to the diffusion of Barium Titanate (BaTiO$_3$) ions into the Barium Zirconium Titanate (BZT) lattice forming a new sub-gap which in turn gives BT-BZT the ability to absorb lower light. Lower light absorption means more capable optics for multilayer systems.

Keywords: ferroelectric material, thin film, sol-gel method, diffusion reflectance spectroscopy (DRS)

INTRODUCTION

In recent years, many ferroelectric film applications use the special dielectric, pyroelectric, and electro-optic properties of ferroelectric materials. The use for fabrication in the form of a thin film is very wide because the properties of ferroelectric materials can be fabricated according to needs and are easily integrated into the form of devices. Furthermore, ferroelectric has electro-optic properties, hence it can be applied to infrared thermal switches [1]. Many of the materials in the structure of lead-based perovskite can be harmful to the environment. For this, the laws have restricted the use of lead-containing materials [2]. Recently, the lead-free materials have been widely used, two of them are Barium Titanate (BT) and zirconium oxide (ZrO_2).

Ferroelectric material Barium titanate (BT) is the most practical and important ferroelectric, where the perovskite BT structure and vibration modes play a role in light absorption. Also, zirconium oxide (ZrO_2) thin film has received considerable attention in recent decades. This is because it can be used for various applications such as laser mirrors, broadband interference filters, and ionic conductors. ZrO_2 is an important material with attractive properties such as good resistance to oxidation, high melting point (2.715°C), excellent thermal stability, and ionic conductivity in the Y-stable cubic phase. For example, ZrO_2 thin film is a promising candidate to replace silicon dioxide as a gate dielectric in complementary metal oxide semiconductor technologies [3]. Furthermore, ZrO_2 is an insulator with an energy band gap of 5 eV and has the potential as an alternative material for in-memory storage capacitors. Besides its attractive electrical properties, ZrO_2 thin film has attractive optical properties such as low light absorption, high refractive index, high transparency over a wide spectral range, and high threshold of field breakdown making it very good for laser optics [4-13].

Ferroelectric material Barium Titanate-Barium Zirconium Titanate (BT-BZT) is a semiconductor material with valence and conduction bands separated by an energy band gap (Eg). Also, Eg value is an important characteristic of the electronic structure. Like other physical and chemical properties, this value can be influenced by the synthesis route or processing method. Therefore, precise determination of its value is very important in materials science and engineering. The optical characterization technique using the Tauc method is the most widely used procedure to determine the Eg of the support material [14]. The method is based on the relationship between Eg and the absorption coefficient α, according to EQUATION 1.

$$\alpha h v = A\,(hv - E_g) \qquad (1)$$

where α is the absorption coefficient, h is Planck's constant (J.s), A is the absorption constant, v is the frequency of light (s^{-1}), and Eg is the band gap energy (eV). The exponent n in EQUATION 1 is connected to the types of possible electronic transitions and the values are 2 for indirect permitted, 3 for indirect forbidden, 1/2 for direct allowed, and 3/2 for directly forbidden transitions [14].

To determine Eg, two methods can be used, namely by measuring the absorbance using EQUATION 1. The second method is calculating the coefficient n from the original reflectance data [15], leading to higher precision. Also, for solid samples, the scattering component cannot be neglected, hence optical absorption spectroscopy is not an appropriate technique to determine Eg. Instead, diffusion reflectance spectroscopy (DRS) is a better option [16]. Using DRS, an analog Tauc plot can be obtained by calculating the Kubelka-Munk or remission function, F(R), according to EQUATION 2.

$$F(R) = \left(\frac{(1-R)^2}{2R} = \frac{\alpha}{S} \right) \quad (2)$$

where F(R), is the Kubelka-Munk function, R is the Reflectance, α is the absorption coefficient, and s is the scattering coefficient. Also, Eg is determined through the relationship of the Kubelka-Munk function with energy. The calculation is plotted $y = (F(R)\ hv)^{1/2}$ with x = hv. The value of Eg is determined when y = 0 [17].

This paper aims to determine Eg of $0.3BaTiO_3 – 0.7BaZr_{0.5}Ti_{0.5}O_3$ thin films with different annealing temperatures of 700°C, 750°C and 800°C respectively, using UV-Vis spectroscopy characterization.

METHOD

In this research, $0.3BaTiO_3 – 0.7BaZr_{0.5}Ti_{0.5}O_3$ thin film was made using the sol-gel method which was placed on an FTO substrate using a spin coater and annealed at temperatures of 700°C, 750°C, and 800°C for 1 hour. The characterization used UV-Vis Spectroscopy. Furthermore, basic materials such as 99% purity Barium Carbonate ($BaCO_3$) powder, 99% purity Zirconium Carbon dioxide ($ZrCO_2$), and titanium dioxide (TiO_2) powder were used.

The first solution was made using $BaCO_3$ powder with a composition of 0.3, dissolved with 80% Acetic acid and 20% dionez water, and added as much as 10 ml, then stirred using a magnetic stirrer on a hotplate until it was clear. TiO_2 solution with composition x=0.3 was dissolved with 96% ethanol. Meanwhile, 0.6 ml and 0.4 ml of 10% Ethylene Glycol were added and then covered with aluminum foil and stirred on a hotplate for the dissolving process for 25 hours until clear. The Ba solution was subsequently added to the Ti solution and stirred until it was completely mixed.

The second solution of $ZrCO_2$ and TiO_2 powder with a composition of 0.5 was placed in a 40 ml glass bottle and stirred using a magnetic stirrer on a hotplate. Furthermore, the Ba powder was added to a 10 ml solution of $ZrCO_2$ and TiO_2 and then stirred on a hotplate until it was clear. After that, the first solution was mixed with the second and 3 drops of Acetyl Acetone were added into the solution while continuously stirring on the hotplate until it was clear yellowish color (±1 hour). The addition of acetylacetone drops aimed to stabilize the reaction and the concentration of the previously mixed solutions (thicken). In other words, it changes the nature of the sol phase into a gel.

The mixed BT-BZT solution was homogeneous and was dripped on the substrate at 3 (three) drops of FTO substrate. Subsequently, it was rotated with a spin coater at a speed of 3500 rpm for 2 x 30 seconds and heated in an oven at 150°C and 300°C for 15 minutes. The coating was repeated three times and then annealed at 700°C, 750°C, and 800°C for 1 hour. The thin film structure can be seen in FIGURE 1. Flow chart making of thin film BT-BZT can be seen in FIGURE 2.

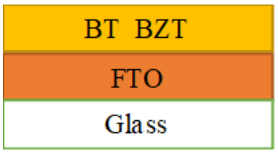

FIGURE 1. BT-BZT Thin Film Structure

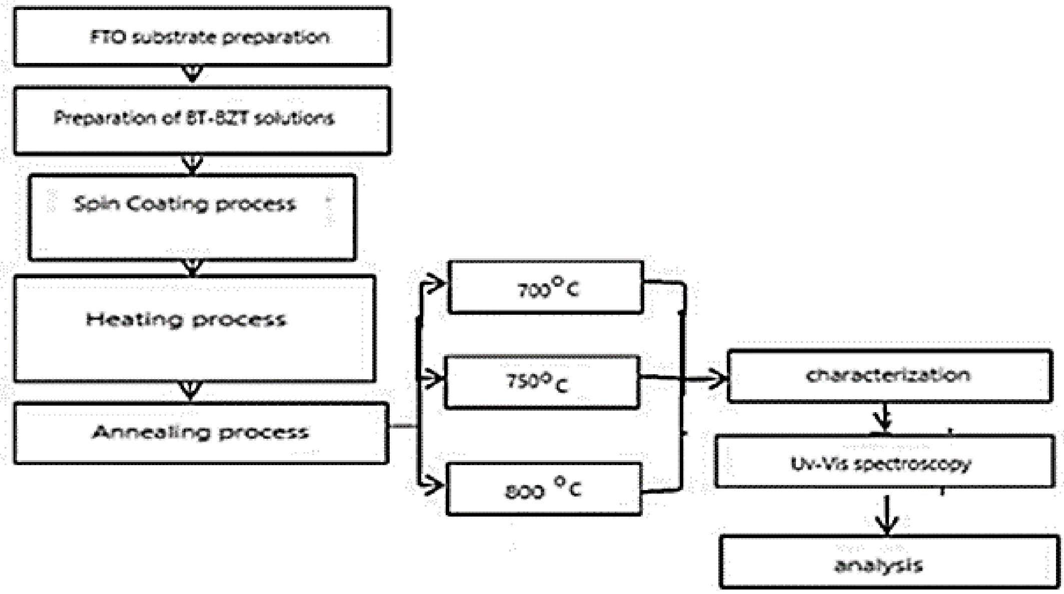

FIGURE 2 : Flow chart making of thin film BT-BZT.

RESULT AND DISCUSSION

DRS measurements were carried out to determine the absorption character in the UV-Vis wavelength region, namely 200 to 600 nm, and to determine the Eg produced by the $0.3BaTiO_3 - 0.7BaZr_{0.5}Ti_{0.5}O_3$ thin film. FIGURE 3 shows the DRS measurement curve and the UV-Vis reflectance curve of the $0.3BaTiO_3 - 0.7BaZr_{0.5}Ti_{0.5}O_3$ thin film structure annealed at 700°C, 750°C, and 800°C. Also, the reflectance spectrum shows that the higher the annealing temperature, the lower the spectrum. The reflectance occurs from the wavelength of 300 to 600 nm.

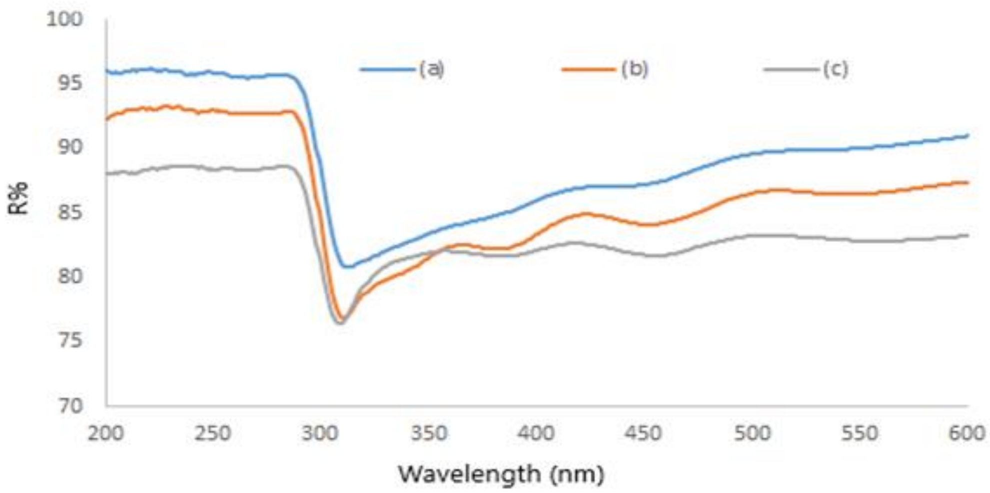

FIGURE 3. UV-Vis reflectance curve of $0.3BaTiO_3$ - $0.7BaZr_{0.5}Ti_{0.5}O_3$ thin film annealed at (a) 700°C, (b) 750°C and (c) 800°C.

The reflectance spectrum was then converted to F(R) using EQUATION 2. The Eg value for each sample was calculated by plotting $y = (F(R)hv)^{1/2}$ with x=hv. The higher the annealing temperature, the smaller the Eg. Also, the decrease in Eg was due to the diffusion of BT ions into the BZT lattice, forming a new sub-slit which will give the ability of BT-BZT to absorb lower light as shown in FIGURE 4. The Figure below shows the absorbance spectrum concerning wavelength with annealing temperatures of 700°C, 750°C, and 800°C stages of the experiment (preliminary process), the melting point of the material was very important to be performed. These melting point information were used to estimate the temperature range of the process.

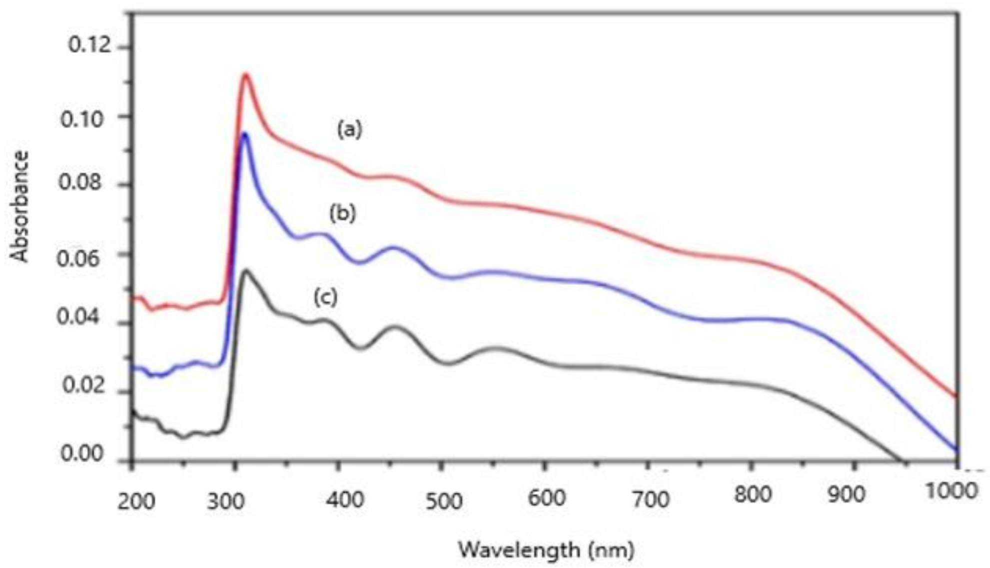

FIGURE 4. Spectrum of the $0.3BaTiO_3$ – $0.7BaZr_{0.5}Ti_{0.5}O_3$ thin film with (a) at 700°C, (b) at 750°C and (c) at 800°C

FIGURE 5 and TABLE 1 show the Eg value in each sample. These Eg values are obtained using EQUATION 2. The results obtained show that the higher the annealing temperature, the lower the Eg. This is because an increase in temperature can increase the distance between atoms. As Eg decreases, the energy required for the electron excitation from the valence to the conduction band decreases, or a larger wavelength is needed. This lower light absorption provides better optical film quality for use in multilayer capacitors. The results are the same as those reported by other studies [18-23]. This Eg value indicates that $0.3BaTiO_3$-$0.7BaZr_{0.5}Ti_{0.5}O_3$ thin film is a semiconductor material that can be applied to infrared thermal switches.

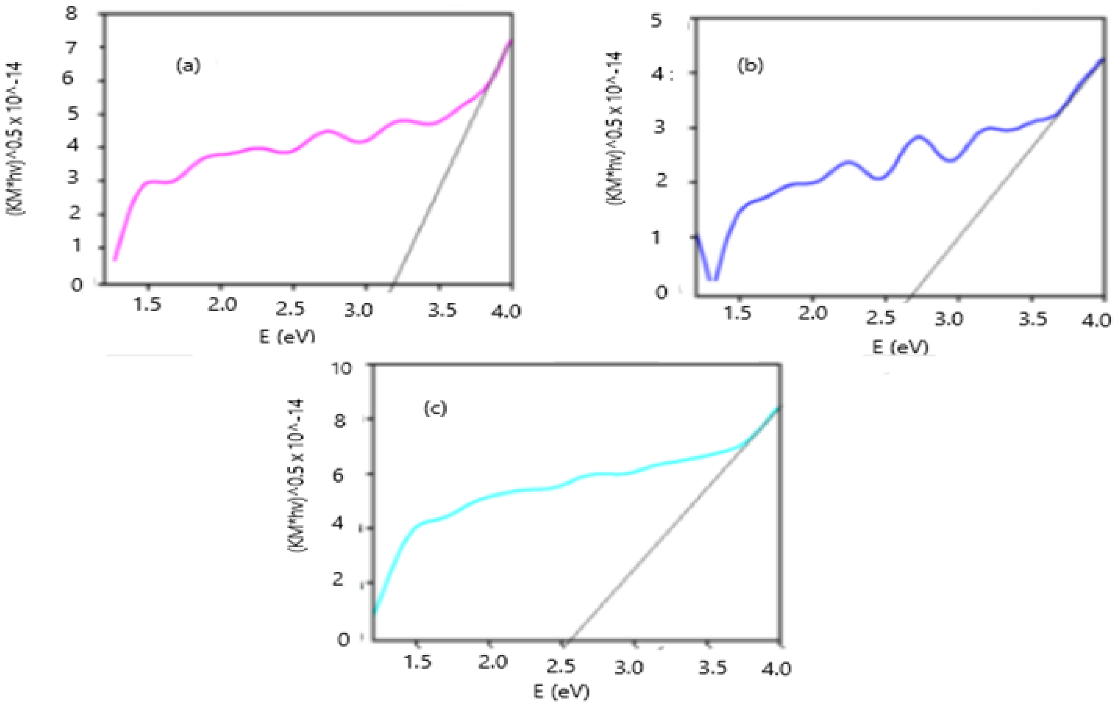

FIGURE 5. Determination of Eg Value from the relationship $(F(R)\ h\nu)^{\frac{1}{2}}$ and hv Energy (eV), (a) at 700°C, (b) at 750°C and (c) at 800°C

TABLE 1. Eg values from FIGURE 5 a, b and c

Annealing temperature (°C)	Eg (eV)
700	3.1
750	2.6
800	2.5

CONCLUSION

This research on the ferroelectric thin films $0.3BaTiO_3$-$0.7BaZr_{0.5}Ti_{0.5}O_3$ has been successfully prepared using the sol-gel method. The thin film was annealed at 700°C, 750°C, and 800°C for 1 hour, and showed that the absorption, reflectance, and Eg values decreased with increasing annealing temperature. The Eg values at 700°C, 750°C, and 800°C were 3.1 eV, 2.6 eV and 2.5 eV, respectively. Furthermore, the decrease in the Eg value was due to the diffusion of BT ions into the BZT lattice forming a new sub-slit that will give the ability to absorb lower light. This thin film is a semiconductor material that can be applied to multilayer capacitors as infrared thermal switches.

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