

Analysis of Energy Gap and The Refractive Index of Barium Strontium Titanate ($\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$) Films doped of Chlorophyll from Green Leafy Vegetables

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Abstract. Ferroelectric films has superior optoelectronic properties and widely applied as a base of electronic components such as light sensors. Improvement the performance of the light sensor can be obtained by adding dopant materials to thin film. In recent years, organic materials as a dopant materials have been extensively used, one of them is chlorophyll. $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ without (0%) and with a (2.5%) dopant cassava, mustard greens, papaya, and spinach leaves chlorophyll extracts prepared on silicon substrate (100). The $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ film growth process using chemical solution deposition method with spin coating technique of 8,000 rpm for 30 seconds in solubility 0.2 M. The Barium Strontium Titanate film was annealing at 850°C for 8 hours with an increase of 1.7°C/ min. The results of the reflectance data processing from the UV-Vis spectrophotometer characterization showed that the $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ without chlorophyll has energy gap 3.25 eV at wavelength 580 nm with refractive index 1.46. Energy gap of $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ with dopant of cassava, mustard greens, papaya, and spinach in a row are 3.24 eV, 3.22 eV, 3.00 eV, and 3.22 eV at the wavelength are 570 nm, 565 nm, 640 nm, and 570 nm with refractive index 1.3, 1.27, 1.34, and 1.24. It can be concluded that $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ without chlorophyll is sensitive to the orange color spectrum, $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ with the cassava and mustard green chlorophyll are sensitive to the green spectrum, and $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ with papaya chlorophyll is sensitive to the red spectrum.

1. Introduction

In Indonesia, the development of biomass as a source of energy has been widely practised. Examples of biomass include plants, trees, grasses, agricultural wastes, forest waste, and feaces. Vegetable plants are available very much in various places in Indonesia and also chlorophyll because chlorophyll is a pigment which found in almost all green leafy plants and green algae. Chlorophyll has an important task in photosynthesis. Chlorophyll absorbs sunlight and carbon dioxide (CO_2) from the surrounding air and reduces CO to produce carbohydrates [1]. The efficiency of photosynthesis in the leaves depends on the distribution of quanta absorbed [2]. According to research done by (Vogelmann *et al* 1993), leaf anatomy is well designed to capture light and maximize absorption [3]. In a study done by (Takahashi *et al* 1994), it was found that gradients in light absorbed in the leaves were measured by visualizing the chlorophyll fluorescence profile, which allowed for more direct examination of the quanta distribution



absorbed in the leaves. [4]. The absorbance of the chlorophyll extracted from green leaves indicates that green light is absorbed only slightly [5].

Extraction of chlorophyll from green plants can be used as medicine, cosmetics and food. In materials science, chlorophyll usually used as energy storage and detector materials. For example in 2013, Khairul et al from Universiti Malaysia Trengganu used chlorophyll as a dopant material for Thiourea as an active potential photovoltaic cell [6]. In 2016, Dewi Suriyani et al from University Malaysia Perlis done synthesis of thin film of chlorophyll from noni leaves for application of Chlorophyll Photovoltaic Cell [1]. In the same year, Aep Setiawan was analyzed the optical and electrical properties of the BST thin film using Niobium and guava leaves chlorophyll as a dopant [7]. Two years later BB Panda et al from Indira Gandhi Institute of technology used chlorophyll as a dopant material for the Zinc Sulphide (ZnS) thin film in a Dye-Sensitized Solar Cell application [8]. After that Frias et al from University of Aveiro Portugal also used chlorophyll in his research for sustainable luminescent of solar concentrators [9].

In this study, the chlorophyll was extracted from spinach, mustard greens, cassava and papaya leaves. This chlorophyll extract was applied to organic dopant material on Barium Strontium Titanate film because of its ability to absorb light very efficiently.

Barium Strontium Titanate (BST) is one of the most applied ferroelectric materials in the production of Non-Volatile Random Access Memory (NVFRAM) Dynamic Random Access Memory (DRAM), infrared sensor, light sensor, temperature sensor, gas sensor and electronic equipment other commonly used in everyday life [7-13]. There are two methods to create BST films that are Physical Solution Deposition (PSD) and Chemical Solution Deposition (CSD) but often used is CSD method. The CSD method consists of several techniques such as Pulsed Laser Deposition (PLD), Metal Organic Solution Deposition (MOSD), Sol-Gel, dip coating, and spin coating [14]. In this study, the technique used is spin coating because this method is easy, relatively cheap, and produce good results. BST film were characterized using UV-Vis spectroscopy. Film reflectance data processing is done to get the energy gap value. The results are analyzed to determine which films have high absorption rates in red light. With the addition of chlorophyll material in BST solution is expected to improve the performance of red light absorption in the light sensor [14].

2. Experimental method

2.1. Chlorophyll extraction

In this step, remove the leaf bone on spinach, mustard greens, cassava and papaya leaves and weighed 500 grams. After that the leaves are washed using running water to remove dirt. Add the leaves to the blender by adding a 1000 ml aquadest solvent. The fine leaf was filtered, squeezed, and the solution was heated at 37°C for 20 minutes. Usually will form a lump. These clumps are filtered, squeezed and rinsed with aquadest. Then dry the extract using a digital oven at 50°C for 1 hour. After that, the chlorophyll was mashed using mortar and filtered using a 200 mesh filter.

2.2. Preparation of substrate

The Silicon substrate (100) was cut with a size of 1 cm² then washed using 150 ml of aquadest.

2.3. Preparation of BST Solution

Samples were weighed in accordance with the results of the calculations for the mole fraction of 0.2 Barium acetate, 0.8 Strontium acetate, and 1 Titanium isopropoxide (Table.1). The mixing of the material using stirring process was done according to the literature [15] and can be seen at Figure 1. The dopant material were mustard greens, spinach, cassava, and papaya chlorophyll each of which was 2.5% from the mass of BST. There are 5 bottles consisting of 5 types of solution; BST solution, BST doped

of mustard greens chlorophyll solution, BST doped of spinach chlorophyll solution, BST doped of cassava chlorophyll solution, and BST doped of papaya chlorophyll solution.

Table 1. Measurement of materials BST

Materials	Measurement	Solvent	Measurement	Dopant chlo.	Measurement
$\text{Ba}_{0.2}(\text{CH}_3\text{COO})_2$	63,8538 mg	Acetic acid	0,9375 ml	0%	0 mg
$\text{Sr}_{0.8}(\text{CH}_3\text{COO})_2$	205,708 mg	Ethylene glycol	0,3125 ml	2.5% Mustard greens	15,6213 mg
$\text{Ti}(\text{C}_{12}\text{H}_{28}\text{O}_4)$	370,093 ml			2.5% Spinach	15,6213 mg
				2.5% Cassava	15,6213 mg
				2.5% Papaya	15,6213 mg



Figure 1. The process of mixing the material using a stirring technique.

2.4. The deposition of $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ film

The deposition of the film is carried out using a spin coating reactor where the substrate is placed on a plate that has been mounted double-tape at the center of the disc. Then 1/3 of the surface of the substrate is covered with masking tape to avoid the entire surface of the substrate covered with a solution of $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$. Then 3 drops of $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ solution dropped on the substrate, then the reactor rotates at a speed of 8000 rpm for 30 seconds. The process of dripping the solution is done 3 times with a difference of 60 seconds between each repetition [16].

2.5. The annealing process

Annealing is a heat treatment that aims to regain physical properties and regain crystalline structures that change during the growth process of the coating. The annealing process was performed on the $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ substrate using a furnace of the Vulcan TM-3-130 model. The heating process is carried out gradually, starting from room temperature then upgraded to desired annealing temperature (850°C), with a temperature rise rate of 1.7°C/ min, after reaching 850°C, the temperature is maintained constant for 8 hours. After that, the temperature is lowered until it reaches room temperature again. The annealing process is shown in Figure 2.

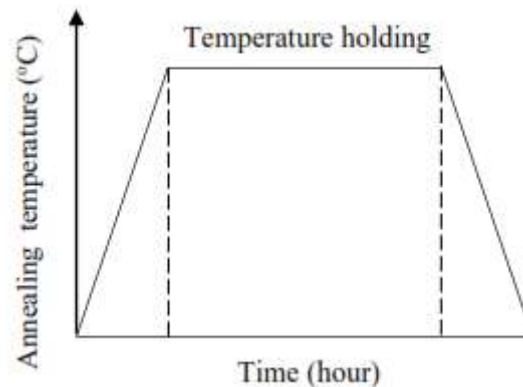


Figure 2. The annealing process.

2.6. Characterization process using UV-Vis Spectroscopy

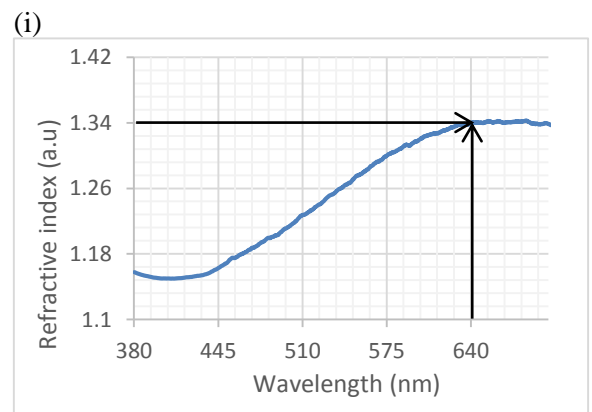
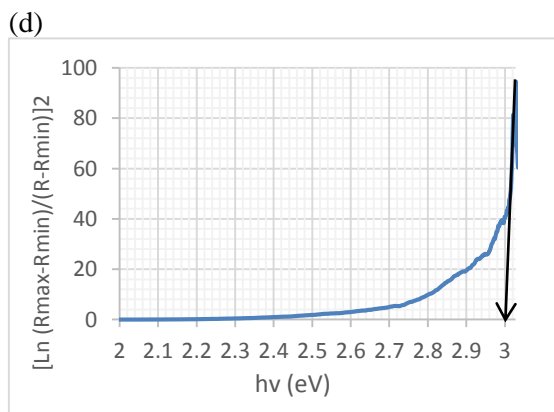
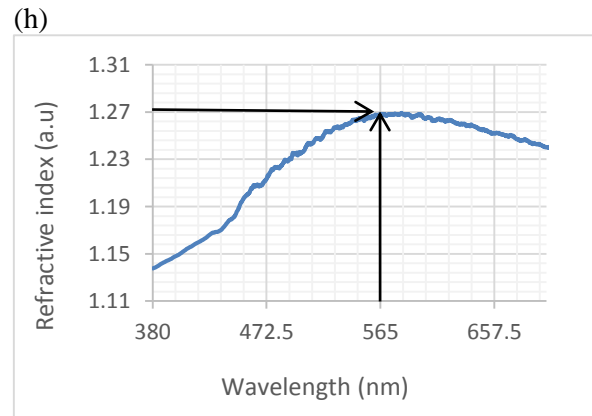
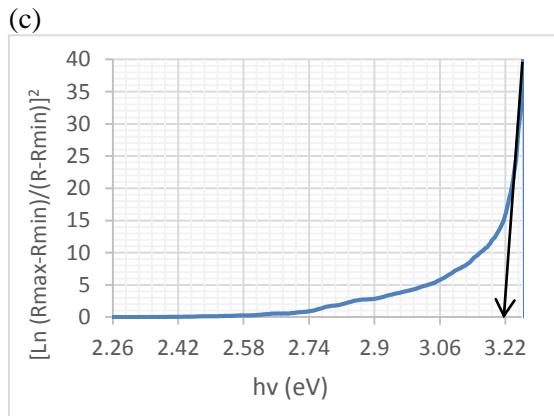
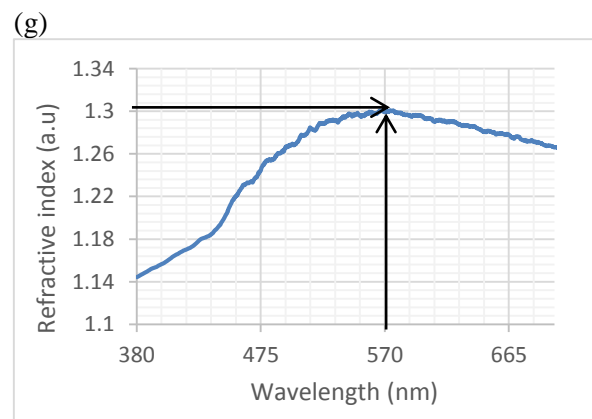
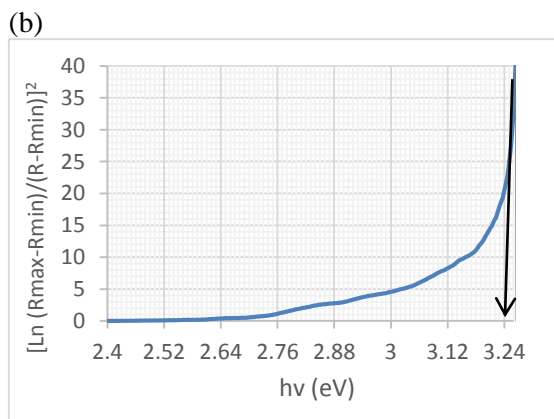
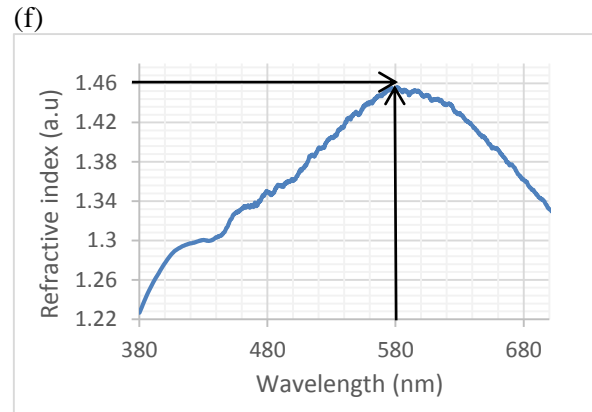
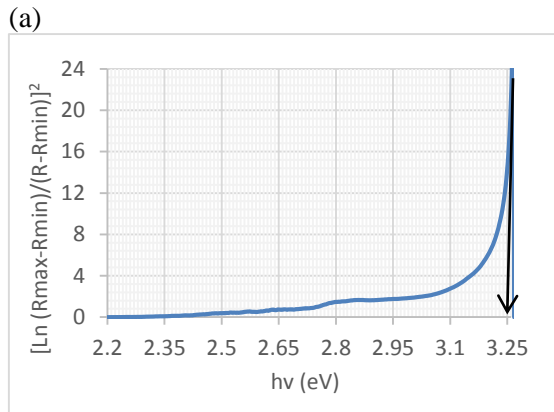
The surface of the silicon substrate that has undergone annealing process is seen to have two distinct parts. 1/3 part is pure silicon as calibration value and 2/3 other part is silicon that has been modified with BST and dopant chlorophyll layer as test value. Both of part were tested by high energy sources using UV-Vis Ocean Optics USB4000 spectrophotometer. The data obtained is reflectance. Analysis of reflectance value is calculation of energy gap value and refractive index.

- $\left[\ln \left(\frac{R_{max} - R_{min}}{R - R_{min}} \right) \right]^2$ to $h\nu$ is the plot of energy gap and its value is equal to the $h\nu$ axis intersection at the highest gradient of the curve.
- $n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}}$ is the equation to obtain the refractive index.

3. Result and Discussion

The optical properties of BST were obtained from the characterization of UV-Vis spectroscopy. Because of the samples in this study were colored solutions, instruments were used with spectral range of 380 nm to 700 nm (visible spectrum). The data obtained is reflectance. The reflectance is the ability of a material to reflect light. Reflectance characterization can be used to know the percentage of reflectance based on wavelength, refractive index, and energy gap.

From the result of research, wavelength value informs the color spectrum. The value of refractive index informs the comparison between the speeds of light in a vacuum with the fast ripple of light in the medium. While the energy gap informs the minimum energy required by electrons to move from the valence band to the conduction band. Between the valence band and the conduction band, there is a gap, where the electrons will jump from one band to the other. This gap will show the properties of solids, whether the solid is a conductor, an insulator, or a semiconductor. In a solid conductor, the electrons in the valence band are empty compared to the fully charged electron conduction band, and the distance between the valence band and the conduction band is very close. This will allow the electrons to move freely from the conduction band to the valence band. So, the smaller of energy gap material, it means that the material is increasingly directed to the semiconductor or conductor character. The use of dopant material can reduce the refractive index of the film [19-20].



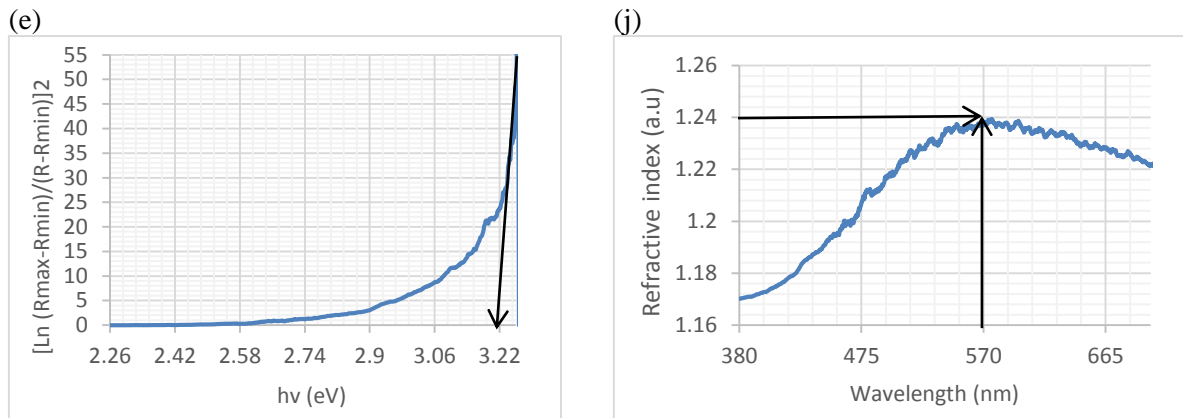


Figure 3. Energy gap of chlorophyll doped $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ film; (a) 0% chlorophyll (b) 2.5% cassava chlorophyll (c) 2.5% mustard greens chlorophyll (d) 2.5% papaya chlorophyll (e) 2.5% spinach chlorophyll. Graphics which on the right side is refractive index of chlorophyll doped $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ film; (f) 0% chlorophyll (g) 2.5% cassava chlorophyll (h) 2.5% mustard greens chlorophyll (i) 2.5% papaya chlorophyll (j) 2.5% spinach chlorophyll.

Table 2. Relationship of dopant chlorophyll variation, energy gap, refractive index, wavelength, and spectrum

$\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ film variation	Energy gap (eV)	Refractive index	Wavelength (nm)	Spectrum
$\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3 + 0\%$	3.25	1.46	580	orange
$\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3 + 2.5\%$ cassava	3.24	1.30	570	green
$\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3 + 2.5\%$ mustard greens	3.22	1.27	565	green
$\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3 + 2.5\%$ papaya	3.00	1.34	640	red
$\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3 + 2.5\%$ spinach	3.22	1.24	570	green

4. Conclusion

Based on experiments conducted to obtain refractive index value and energy gap from BST film using reflectance method, it can be concluded that $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ (without and with dopant chlorophyll) produces sensitivity to the visible light spectrum (orange, green, and red). Overall, a film that has been successfully created on the silicon (100) substrate by chemical solution deposition method with spin coating technique has the potential to be applied as a light sensor.

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6. References

- [1] Dewi Suriyani Che Halin and Ayu Wazira Azhari 2016 *Material Science Forum* **857** 142-145
- [2] SS Kumar, P Manoj, P Giridhar 2015 *J Food Sci Technol* **52** 8131-8139
- [3] T C. Vogelmann and J. R. Evans 2002 *Plant, Cell, and Environment* **25** 1313-1323
- [4] Z Ge, X. Zhou, S. Kellomäki, K. Wang, and H. Peltola 2011 *Photosynthetica* **49** 172-184
- [5] I Terashima, T. Fujita, T. Inoue, W. S. Chow, and R. Oguchi 2018 *Plant Cell Physiol* **50** 684-697
- [6] N R Baker, B Genty, and Jean Marie B 1989 *Biochimica et Biophysica Acta* **990** 87-92

- [7] Irzaman, Darmasetiawan H, Hardhienata H, Erviansyah R, Huriawati F, Akhiruddin MH, Arifin 2011 *J. At. Indonesia* **37** 133–138
- [8] W M Khairul, M F Yusof, R Rahmatullah, A I Daud, S M Jasman, M F A Hasan, H Salleh, H K Adli, and M G Tay 2013 *Int. J. Electrochem. Sci* **8** 8175-8190
- [9] H K Adli, W M Khairul, and H Salleh 2011 *International Journal of Advanced Chemical Technology* **1** 1–5[10]
- [10] B B Panda, P K Mahapatra, and M K Ghosh 2018 *Journal of Electronic Materials* doi: 10.1007/s11664-018-6215-8
- [11] A R Frias, E Pecoararo, S F H Correia, L M G Minas, A R Bastos, S Garcia, S J L Ribeiro, P S Andre, L D Carlos, and R A S Ferreira 2018 *Journal of Material Chemistry A* **8**
- [12] Jun-gu Kang, Joon-Shik Park, and Hoo-Jeong Lee 2017 *Sensors & Actuators: B. Chemical* doi:10.1016/j.snb.2017.03.010
- [13] Irzaman, R Siskandar, Aminullah, Irmansyah, and H Alatas 2016 *Integreted Ferroelectric* **168** 130-150
- [14] Irzaman, R Siskandar, N Nabilah, B Yulianto, K A Hamam, and H Alatas 2018 *Ferroelectrics* **524** 44-55
- [15] M. Dahrul and H. Alatas 2016 *Preparation and optical properties study of CuO thin film as applied solar cell on LAPAN-IPB Satellite* **33** 661–667
- [16] Irzaman, Y Darvina, A Fuad, P Arifin, M Budiman, and M Barmawi 2003 *Physica status solidi* **424** 416–424
- [17] T J Bruno and P D N Svoronos 2006 *CRC Handbook of Fundamental CRC Handbook of Fundamental Spectroscopic Correlation Charts*
- [18] E Karaca, Durmaz B, H Aktuq, Yildiz T, Guducu C, Irqi M, Koksai MG, Ozkinay F, Gunduz C, and Coqulu O 2012 *J Neurooncol* **106** 53-38
- [19] Irzaman, Henni Sitompul, Masitoh, M Misbakhussudur, and Mursyidah 2016 *Ferroelectrics* **502** 9-18
- [20] Irzaman, Y Pebriyanto, E R Apipah, Iman Noor, and A Alkadri 2015 *Integrated Ferroelectrics* **167** 137-145