Micro-Raman Spectroscopy Investigation of Chlorophyll-doping effects on Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ Thin Film

E K Palupi$^{1*}$, R Umam$^{2}$, BB Andriana$^{2}$, H Sato$^{2}$, B Yuliarto$^{3}$, H Alatas$^{1}$, and Irzaman$^{1}$

$^1$Department of Physics, Faculty of Mathematics and Natural Science, Bogor Agricultural University, Bogor, Indonesia
$^2$School of Science and Technology, Kansei Gakuin University, Sanda, Japan
$^3$Department of Physics Engineering, Faculty of Industrial Engineering, Bandung Institute of Technology, Bandung, Indonesia

*palupi_19@apps.ipb.ac.id

Abstract. This study is to find out how the effect of chlorophyll doping of spinach and papaya leaves on thin film BST that analyzed using micro-Raman Spectroscopy. Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ (Barium Strontium Titanate) doped of chlorophyll of spinach and papaya leaves was grown on a p-type silicon substrate (100). Film growth method uses a chemical solution deposition method with a spin coating technique. This deposition technique is an application of centripetal force so that the solution can be spread evenly on the film. The solution is dripped, three drops of solution three times, where the spin coating reactor’s rotational speed is 8,000 rpm for 30 seconds with a delay between repetitions of 60 seconds. The annealing process is carried out as a high-temperature heating step which aims to restore the physical and crystalline properties of the film which may change during the film growth process. The specified annealing temperature is 850°C with a holding time of 8 hours. The effect of chlorophyll doping was observed by applying variations in chlorophyll concentration of spinach leaves and papaya leaves which were 0%, 2.5%, and 5%.

1. Introduction

Micro-Raman spectroscopy has been employed to study different kinds of materials. Raman scattering spectroscopy has proven to be a powerful technique for studying the matter. In fact, the Raman-effect is able to make solids, liquids, and gases scatter light, and this phenomenon is applied as a technique in various cases ranging from mono-components to multi-components, which in turn can consist of organic and inorganic materials [1].

Raman scattering is a very sensitive technique for investigating the environment of local atoms. The nature of vibration is basically determined by mass, type of bond and symmetry of atoms in units of gas or liquid (molecular), or solid (primitive unit cells) [2]. In this way, the environment of the particular atom has a strong influence on its dynamics; therefore, the emergence of any physical factor affecting short-term orders, such as defects or dirt, has a direct impact on the vibrational properties of atoms. Photon energy from Raman scattering can be changed in two ways, namely energy loss caused by the creation of the phonon (Stokes process) or energy obtained from phonon absorption (anti-Stokes process). In both cases, the energy change from photon scattering is separate and is directly related to the vibrational nature of the specimen. Each peak in the Raman spectrum corresponds to the vibrational...
mode of a particular atom in the sample, and its energy measures the frequency of the corresponding 
normal atomic mode [3].

Growth and application of ferroelectric-based thin films have been carried out. However, there is not 
much use of micro-Raman to investigate thin films. One of the latest in a decade is research conducted 
by S.Y.Wang who used Ce doping on BST films [4].

In recent years, Barium Strontium Titanate (BST) thin films have attracted the attention of 
researchers in various parts of the world. BST thin films are one of the semiconductor materials that are 
widely applied in the production of Dynamic Random Access Memory [5] infrared sensor [6], light 
sensor [5], temperature sensor [7], gas sensor[8] because it has high dielectric and optoelectronic 
properties [9]. Irzaman revealed that the unique advantage possessed by BST is that its ferroelectric 
characteristics can be controlled by adjusting the Barium-Strontium ratio [5]. By studying the optical 
and electrical characteristics from that research, it was felt necessary to study the optical properties of 
BST with a ratio of 0.2: 0.8 taking into account fewer barium availability than strontium. The physical 
properties of BST films are strongly influenced by composition, dopants, deposition conditions, internal 
stresses, and electronic structures. BST is also an insulator at room temperature because of the large 
bond-gap value.BST performance can be improved by doping. Doping is a material that can change 
physical properties, such as electronic structure, core level, and dielectric properties of the film[10].

The application of chlorophyll as a thin film dopant material is currently being actively carried out, 
mainly focused on how to improve performance in the ferroelectric aspects of semiconductor materials 
[11]. All of them are from leaf plant extraction, but no one has taken chlorophyll extract from the leaves 
of vegetable plants, while chlorophyll formation is strongly influenced by two important factors, namely 
the sun's light intensity and leaf age. Chlorophyll from the leaves of vegetable plants is interesting to 
study because it has been known that the leaves of vegetable plants have relatively fast leaf life and 
harvesting age, which is around 25-30 days after planting. In this study, an investigation with 
Micro-Raman Spectroscopy on BST thin films was doped with chlorophyll of spinach leaves and papaya 
leaves. BST films that are not doped with chlorophyll are also presented in the same conditions to be 
compared [12].

2. Material and Methods

The spinach and papaya leaves are separated from the leaves and then weighed 500 grams each. 
Furthermore, the leaves are cleaned under running water to remove macro impurities. The leaves that 
have been cleaned are then left to dry and then purified using a blender. Aquades used are 1000 ml. The 
leaf solution is filtered and the filter results are heated with a heating temperature of 60°C until the 
solution is separated into two parts, namely chlorophyll, and water. This lump is filtered and rinsed with 
distilled water. Flushing is done in order to remove the red pigment component in the sample. The next 
process is drying. At this stage, drying is done using a digital oven with a temperature of 50°C for 1 
hour. The dried chlorophyll mixture is smoothed using a mortar, then filtered with a 200 mesh filter to 
obtain better results. Powder mass measurement is done to find out the results of chlorophyll content of 
every 500 grams of fresh leaves. Calculation of chlorophyll levels using the equation [12-13].

\[ C= [(20 \times A_{649})-(6.1 \times A_{665})] \frac{V}{1000 \times w} \]  

With, C is the total chlorophyll content of \( A_{649} \). \( A_{649} \) and \( A_{665} \) are the intensity of absorbance at 
wavelengths 649 and 665 nm.

The main material preparation is carried out according to the plan as in Table 1. The mechanism of 
making a solution includes several steps as follows. First, barium acetate and strontium acetate are 
dissolved with acetic acid. Second, the solution from the first stage results is added titanium 
isopropoxide. The third stage is the addition of ethylene glycol, and the fourth stage is the addition of 
chlorophyll wherein each stage is stirred using a hot plate stirrer for 1 hour [14].

| Table 1 | The mass stoichiometry of strontium titanate barium solution |
| Ingredients         | Mass         | Solvent                  | Percentage of chlorophyll extract          |
|---------------------|--------------|--------------------------|--------------------------------------------|
| Ba(CH$_3$COO)$_2$   | 63,8538 mg   | Acetic acid and ethylene glycol (3:1) | Chlorophyll (0%, 2.5%, and 5%)            |
| Sr(CH$_3$COO)$_2$   | 205,708 mg   |                          |                                            |
| Ti (C$_{12}$H$_{28}$O$_4$) | 0.370093 ml |                          |                                            |

Deposition is carried out using a spin coating reactor. P-type silicon substrate (100) measuring 1cm$^2$ was given three drops of precursor solution on one-third surface, rotated at 8,000 rpm for 30 seconds three times with a 60-second pause between repetitions made three times[15]. Annealing is a heat treatment that aims to get back the physical properties and get back the crystal structure that changes during the film deposition process. This process is carried out using a Vulcan TM-3-130 model furnace[11]. The heating stage starts from room temperature and then is increased to the desired annealing temperature (850°C) with a temperature increase of 1.7°C/ minute. After reaching 850°C, the temperature was kept constant for 8 hours, then lowered again at room temperature[9].

![Figure 1 Annealing Process](image)

In this analysis, the type of Raman used was Micro Raman Spectroscopy DU420 BROD semicolon indoor technology co. Ltd., Northern Ireland. Samples that have been placed at the point of laser shooting, previously set in advance using the x and y position control devices. Furthermore, because the focus point of sampling is very small, setting the accuracy of using a microscope is very necessary so that the incoming laser can be precisely located in a good area and depth. In this case, the wavelength used is 785nm with a laser power of 50 mW, a working distance of 200-800μm, space resolution of 10μm, slit 100 μm, and exposure time of 3x20 seconds.

When the laser is fired into the sample, the transmitted light will be turned using a convex double lens and passed to the HNF and a small slit or gap as a filter to reduce the reflection effect, then Grating resolution is used as a reflection of light to separate the spectrum of light which then lights with a large wavelength of spectrum certain captured by the detector to be translated in the form of asc data [1]. The results of the Raman analysis are the data of the intensity value of the absorbance of the wavelength. However, this data needs to be processed before being interpreted. The stages in data processing are [1]:

- Interpolation serves as a linking value at a certain wavelength to the surrounding values numerically. Other functions to shorten spaces of a row of values. Because interpolation can determine the value absorbed between 2 measured absorbance values.
- Baseline correction serves to place the spectral value in the correct position because the Raman spectra often shift due to the fluorescence effect.
- Background subtraction serves to reduce noise during measurement. Functions like high-pass and low-pass filters, it's just that this method is more specific to the original data and can reduce or eliminate data noise.
- Normalization serves to smooth the data. So it doesn't experience line shifts on the graph.
The Raman spectrum of the pure Barium Titanate analyzed was showed by previous studies and in Figures 3A and 3B. In large quantities, BST from tetragonal structures can be clearly found, including broad peaks centered on 226 cm\(^{-1}\), weak shoulder tops at 303 cm\(^{-1}\), asymmetric peaks near 515 cm\(^{-1}\), and broad, weak peaks at 730 cm\(^{-1}\), which is very similar to the results reported by a previous study by [3]“barium titanate powders” and by [4]about “Ce-doping effects on Ba\(_{0.5}\)Sr\(_{0.5}\)TiO\(_3\) thin films”.

**Figure 2** Data retrieval process using Micro-Raman Spectroscopy

**Figure 3 A.** Raman spectrum of BaTiO\(_3\) powder [3]; **B.** Raman spectra of (a) ceramic BST-0.3, (b) ceramic BST-0.5, (c) undoped BST film, (d) 1% CeBST film, (e) 5% CeBST film, and MgO substrate [4]

3. Result and Discussion

Based on the literature [16], it is known that the total chlorophyll content of spinach and papaya leaves is 23.0222 mg/g and 29.5975 mg/g, while our chlorophyll has a higher level of calculation as available [17] obtained levels of chlorophyll spinach and papaya are 36.20234 mg/g and 49.35242 mg/g. This maximum result can be affected by the position of the leaves, moisture content, and available light intensity factors.

In this case, the spectrum observed from **Figure 4** consists of 2 peaks at 515-530 cm\(^{-1}\) and 700-730 cm\(^{-1}\), which are the characteristics of the BaTiO\(_3\) tetragonal phase. From the results of the analysis, it
was seen that the 2 peaks experienced a peak shift after adding chlorophyll extract. Based on Figure 4, BST that uses a comparison of Acetic acid and ethylene glycol and added chlorophyll extract experienced a significant peak shift. Chlorophyll extract which has an influence on increasing the absorption of the largest spectrum is spinach. According to the comparison of the percentage of chlorophyll extract, 5% had a greater effect than 2.5%. Thus, it can be expected that the more percentage of chlorophyll extract used, the greater the absorbance value in the use of chlorophyll extract will be greater. The increase in absorbance value has increased, especially in frequency 521 cm$^{-1}$.

**Figure 4** Analysis of BST with the addition of chlorophyll extract of spinach leaves and chlorophyll extract of papaya leaves.

The reflectance measurement of BST thin film aims to observe the maximum reflection and wide of reflection spectra of thin films of BST. BST thin films with 5% doping of papaya chlorophyll have the highest reflectance value than the others. **Figure 5 (a)** shows the difference of dopant percentage on BST thin film VS reflectance intensity. The greater dopant percentage, the greater reflectance intensity value of the thin film. Some condition on the relation between reflectance intensity VS energy (**Figure 5b**). Generally, the reflectance peaks for all types of films have the same curve shape and there is no shifting.

From the curve in **Figure 6**, can be seen that there is a shift of optical 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 materials, whether is a conductor, an insulator, or a semiconductor. In a conductor material, no gap between the band. This will allow the electrons to move freely from the conduction band to the valence band. A semiconductor material has a little gap and wide gap on the insulator materials. So, a smaller energy gap, the material is increased to the semiconductor or conductor character. The use of dopant material can reduce the refractive index of the film. The wavelength of reflectance, band gap values, and the refractive index was determined and listed in Table 2.

![Figure 6](image1.png) The energy gap of undoped BST film, doped with chlorophyll of papaya and spinach.

![Figure 7](image2.png) Refractive index of undoped BST film, doped with chlorophyll of papaya and spinach.

**Table 2** Relationship of dopant chlorophyll variation, wavelength, energy gap, and the refractive index of BST thin films

| Sample                                      | Wavelength (nm) | Energy Gap (eV) | Refractive Index |
|---------------------------------------------|-----------------|-----------------|------------------|
| Undoped BST                                 | 405             | 3.07            | 2.283026287      |
| 2.5% Chlorophyll of papaya leaves doped BST | 417             | 2.98            | 2.283026274      |
| 5% Chlorophyll of papaya leaves doped BST   | 373             | 3.33            | 2.283026327      |
| 2.5% Chlorophyll of spinach leaves doped BST| 372             | 3.34            | 2.283026328      |
| 5% Chlorophyll of spinach leaves doped BST  | 368             | 3.37            | 2.283026334      |

In this study, it can be seen that the addition of chlorophyll affects the energy gap of BST films. The energy gap BST without doping is 3.07 and the energy gap is getting bigger with the addition of doping chlorophyll spinach 2.5%, 5% spinach, and 5% papaya. The only one that can reduce energy gap is doping 2.5% papaya chlorophyll. The factor that is thought to be influential here is the condition of the chlorophyll solution formed which is very concentrated so that it forms coagulation and this becomes not the same as 2.5% papaya chlorophyll. The factors in stirring have been explained by previous studies [15,19]. Energy gap doping BST 2.5% papaya chlorophyll can reduce energy gap up to 2.98 eV accompanied by increasing sensitivity to a wavelength from 405 to 417, where the wavelength is a visible light spectrum with violet color.

The decrease in value also occurs in the refractive index (Figure 7) of the film wherein the undoped BST film is 2.283026287 and decreases to 2.283026274 in the 2.5% Chlorophyll of papaya leaves doped BST.

**4. Conclusion**

Based on the results of the analysis obtained, it can be concluded that BST which has been added to the chlorophyll extract experienced an increasingly significant amount, respectively. This increase in reflectance intensity is linear to the addition of the percentage value of chlorophyll extract. Meanwhile, according to the comparison of chlorophyll extract of spinach leaves and papaya leaves, it can be seen that spinach leaves have a better chlorophyll extract to increase the absorbance value of BST which has
been added by chlorophyll extract. On the other hand, although the percentage of chlorophyll extract used is the same, but based on the comparison band gap value, the 2.5% chlorophyll doped of BST has a lower value than another sample.

Acknowledgments

We gratefully acknowledge the funding from USAID through the SHERA Centre for Development of Sustainable Region (CDSR) program. We also gratefully acknowledge the funding from Penelitian Dasar Unggul Perguruan Tinggi (PDUPT) program with grant number 129/SP2H/PTNBH/DRPM/2018.

References

[1] H. Sato, B. B. Andriana, H. Shinzawa & Y. Matsuura 2014 An optical biopsy system with miniaturized Raman and spectral imaging probes; in vivo animal and ex vivo clinical application studies
[2] A. Mahardika, A. B. Susanto, R. Prameshi, H. Matsuyoshi & B. B. Andriana 2018 Application of imaging Raman spectroscopy to study the distribution of Kappa carrageenan in the seaweed Kappaphycus alvarezii
[3] M. Boulos et al 2017 Elaboration and characterization of barium titanate powders obtained by the mechanical activation of barium nitrate and titanate oxide and electrical properties of the ceramics sintered by SPS To cite this version
[4] S. Y. Wang et al 2006 Raman spectroscopy studies of Ce-doping effects on Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ thin films
[5] Irzaman et al 2018 Application of lithium tantalate (LiTaO$_3$) films as a light sensor to monitor the light status in the Arduino Uno based energy-saving automatic light prototype and passive infrared sensor
[6] F. Niklaus & C. Vieider 2008 MEMS-Based Uncooled Infrared Bolometer Arrays – A Review
[7] Irzaman, R. Siskandar, Aminullah, Irmansyah & H. Alatas 2016 Characterization of Ba$_{0.55}$Sr$_{0.45}$TiO$_3$ films as light and temperature sensors and its implementation on automatic drying system model
[8] J. Kang, J. Park & H. Lee 2017 Pt-doped SnO$_2$ thin film based micro gas sensors with high selectivity to toluene and HCHO Sensors & Actuators: B. Chemical
[9] H. Hardienata, Irzaman, H. Alatas & Akhiruddin Maddu 2017 The Effects of Lanthanum Dopant on the Structural and Optical Properties of Ferroelectric Thin Films 6 140
[10] F. L. Traversa, F. Bonani, Y. V Pershin & M. Di Ventra 2014 Dynamic Computing Random Access Memory
[11] S. Garc 2018 Sustainable luminescent solar concentrators based on organic-inorganic hybrids Modified with chlorophyll
[12] T. C. Vogelmann & J. R. Evans 2002 Profiles of light absorption and chlorophyll within spinach 1313–1323
[13] W. M. Khairul, M. F. Yusof, R. Rahamathullah & A. I. Daud 2013 Single Molecule Thin Film Featuring Disubstituted Thiourea (TU) Doped with Chlorophyll as Potential Active Layer in Photovoltaic Cell 8 8175–8190
[14] A. Kurniawan, D. Yosman, A. Arif, and J. Juansah 2015 Temperature sensor for satellite technology,” Procedia Environmental Sciences. 24 335–339
[15] I. N. & A. Irzaman, Yunus Pebriyanto, Epa Rosidah Apipah, and Alkadri 2016 Characterization of Optical and Structural of Lanthanum Doped LiTaO$_3$ Thin Films Characterization of Optical and Structural of Lanthanum Doped LiTaO$_3$ Thin Films 4587
[16] N. Setiari 2009 Eksplorasi Kandungan Klorofil pada beberapa Sayuran Hijau sebagai Alternatif Bahan Dasar Food Supplement Abstrak 11 1.
[17] M. F. Pompelli, S. C. Franca, R. C. Tiri, M. T. De Oliveira, M. Sacilot & E. C. Pereira 2013 Spectrophotometric determinations of chloroplastidic pigments in acetone, ethanol, and
dimethylsulphoxide 52–58.

[18] H. Syafutra & S. Pramudito 2017 Uji Konduktivitas Termal pada Daun Bayam 13–18.
[19] S. Ebraheem & A. El-saied 2013 Band Gap Determination from Diffuse Reflectance Measurements of Irradiated Lead Borate Glass System Doped with TiO 2 by Using Diffuse Reflectance Technique 324–329.