Crystalline structure and optical properties of thin film LiTaO₃

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Abstract. The coatings of LiTaO₃ material on p-type Si (100) substrates were fabricated by using Chemical Solution Deposition (CSD) technique. In the fabrication process, the spin coater is used to flatten the LiTaO₃ solution on the p-type Si (100) substrates surface, which was set at 4000 rpm for 30 seconds. Furthermore, the coating on those substrates was annealed in the furnace (Nabertherm type B410) for 15 hours at 750°C, 800°C, and 850°C temperature. The study of crystalline structure was obtained through the X-Ray Diffraction (Shimadzu XRD-7000) measuring with the interval of angular diffraction 2θ from 10° to 80° in the increment of 0.02°. Moreover, the study of optical properties was observed using the spectrometer (Ocean Optics USB4000-UV-VIS). Based on the results of the study, obtained a hexagonal angle diffraction peak for the crystal structure, when viewed from the refractive index, the optical properties are sensitive to visible and ultraviolet light. The results of the crystalline structure and optical properties that are sensitive to visible and ultraviolet light can be used to improve the performance of satellite systems in the term of the optical remote sensing.

1. Introduction
Lithium tantalate (LiTaO₃) is one of perovskite ferroelectric optical crystal materials [1-3]. The presence of external field derived from the sunlight spectrum may affect the position of atoms at the center of the perovskite structure, as it happens when overloaded on one side of the crystal (electro-optics) [4-8]. LiTaO₃ is very interesting to study because in practice it can be used as a sensor. However, over the last few years, LiTaO₃ has been studied intensively because it has unique properties [1, 4, 5]. LiTaO₃ is crystalline ferroelectric having an excellent of pyroelectric, ferroelectric, and coefficients that are non-linear optic [3, 9-11]. LiTaO₃ is crystalline ferroelectric which subjected to the process of high Curie temperature by 608°C and it also has a high melting temperature at 1650°C [2, 3, 12-14]. A good LiTaO₃ ferroelectric characteristic is used on electronic devices and optical devices [15, 16].
In order to choose the best intensity and high purity of LiTaO₃, using X-Ray Diffraction (XRD) method is suggested. X-Ray Diffraction methods can explain the lattice parameter, structure type, different atomic, the arrangement of crystals, presence of crystal imperfection, orientation, grain, and grain size. The XRD characterization aims to determine the crystal system [17, 18]. In this study, LiTaO₃ thin films were obtained from mixing lithium acetate and tantalum methoxide were coated on p-type Si (100) substrate using Chemical Solution Deposition (CSD) method, followed by spin-coating technique and annealed using furnace at variety temperature of 750°C, 800°C, and 850°C, then characterized using X-Ray Diffraction (Shimadzu XRD-7000). Spectrometer (Ocean Optics USB4000-UV-VIS) was used to investigate the energy gap and the refractive index of LiTaO₃ thin films [2, 17, 18].

Related to the electromagnetic spectrum and the optical remote sensing on the satellite system, the purpose of this study is to fabricate and investigate the performance of LiTaO₃ thin film which can be applied for: (1) climate and environmental monitoring (oceanography field), which have required sensor with sensitivity in the visible light range; (2) thermal monitoring (volcanology field), which have required sensor with sensitivity in the ultraviolet light range; and (3) weather and climate monitoring (meteorology field), which have required sensor with sensitivity in the ultraviolet-visible light range [19-21].

2. Research method

In the first process, the used substrate, p-type Si (100), was cut to 1 × 1 cm² size using a glass cutter. Furthermore, the substrates were cleaned sequentially for 15 minutes with acetone, methanol, and deionized water in the tub of the ultrasonicator device [22-25]. Then, 0.16496 gram of lithium acetate [Li(CH₃COO), 99.99%] and 0.84030 gram of tantalum methoxide [Ta(OCH₃)₅, 99%] were weighed using Kern analytical scale. The materials were then mixed and dissolved in 2.5 ml of 2-methoxyethanol (CH₃OCH₂CH₂OH), thereafter stirred using Vortex 3000. Next step, the solution mixture was homogenized using the ultrasonicator device for 30 minutes to obtain a homogenous LiTaO₃ solution.

The substrate was placed on the center of spin coater plate with sellotape to cover 1/3 of the substrate surface [22]. The dripped LiTaO₃ solution on the p-type Si (100) substrate was fixed to the stage of spin coater [11, 22]. LiTaO₃ coating process on the surface of each substrate and rotating process using a spin coater at 4000 rpm speed for 30 seconds were repeated three (3) times (disposition and rotation) with one (1) minutes break in between [1, 6, 22-25]. LiTaO₃ thin film on p-type Si (100) substrate was then annealed using Nabertherm type B410 for 15 hours at 750°C, 800°C, and 850°C temperature. The filming and crystallization of LiTaO₃ thin films were obviously affected by the heat treatment process [18].

After the growth and annealing process was completed, the formed thin films were characterized using X-Ray Diffraction (XRD), measuring it with the interval of angular diffraction 2θ from 10° to 80° in the increment of 0.02° and it was characterized using spectrometer (Ocean Optics USB4000-UV-VIS) to measure the reflectance.

3. Result and discussion

3.1. XRD pattern

X-Ray Diffraction (XRD) was used to observe the crystalline structure of LiTaO₃ thin films crystallized on the surface of the substrate p-type Si (100) with different annealing temperatures (750°C, 800°C, 850°C). In this study, the thin films were characterized using X-Ray Diffractometer (Shimadzu XRD-7000) with Cu Kα radiation whose wavelength (λCu) is 1.54060 Å. The spectrum was recorded at a diffraction angle of 2θ from a range of 10° ≤ θ ≤ 80° with the interval of 0.02°/minute. Measurement results (figure 1) show the peaks diffraction angle with the hexagonal crystal structure,
while the peak diffraction intensity showed the Miller index values. The Miller index is used to
determine the lattice parameters of LiTaO$_3$ thin films with the Cramer and Cohen equations [26-28].

$$
\sum \alpha \sin^2 \theta = C \sum \alpha \gamma + B \sum \alpha \delta
$$

$$
\sum \gamma \sin^2 \theta = C \sum \alpha \gamma + B \sum \gamma \delta
$$

$$
\sum \delta \sin^2 \theta = C \sum \alpha \delta + B \sum \gamma \delta + A \sum \delta^2
$$

(1)

with: $\alpha, \gamma, \delta =$ lattice parameters (Å)

$\theta =$ Bragg angle (degree)

$A, B, C =$ lattice constants

Figure 1. XRD patterns of LiTaO$_3$ thin films with different annealing temperatures.

Table 1 shows the lattice parameter values of LiTaO$_3$ thin films. Based on the table, the lattice
parameter values show some differences from the JCPDS data. Small differences caused by the peaks
diffraction value that appears at the 2θ diffraction angle are not the same as the diffraction angle from
the JCPDS data. The obtained diffraction peaks experience a shift at an angle of 2θ. This diffraction
angle shift was caused by the magnitude of the annealing temperature.

| Lattice parameter  | LiTaO$_3$ annealing at 750°C (Å) | LiTaO$_3$ annealing at 800°C (Å) | LiTaO$_3$ annealing at 850°C (Å) | JCPDS (No. 29-0836) (Å) |
|--------------------|----------------------------------|----------------------------------|----------------------------------|------------------------|
| $c$                | 17.376750                       | 17.453590                       | 21.258570                       | 13.750                 |
| $a$                | 5.699490                        | 5.722771                        | 5.716996                        | 5.153                  |

The crystallite size of LiTaO$_3$ thin films can be calculated based on the FWHM of the diffraction
peaks produced using the Scherrer equation [17]:

$$
D = K \frac{\lambda}{\beta \cos \theta}
$$

(2)

with: $D =$ crystallite size (Å)

$K =$ constant (0.96)

$\lambda =$ wavelength (1.506 Å)

$\beta =$ the graph width of FWHM (radian)

$\theta =$ maximum angle (radian)
Based on the Scherrer equation, the calculation of the crystallite size of LiTaO$_3$ thin films was listing in table 2. The average calculation value of the crystallite size of LiTaO$_3$ thin films on the surface of the substrate p-type Si (100) shows the decrement along with the increment of annealing temperature. It means that the increment of temperature can reduce the crystallite size.

Table 2. The crystallite size of LiTaO$_3$ thin films.

| Annealing temperature (°C) | Diffraction angle $2\theta$ (degree) | FWHM | Crystallite size (Å) |
|---------------------------|----------------------------------|------|----------------------|
| 750                       | 23.5198                          | 0.11 | 770.8524654          |
|                           | 32.6350                          | 0.09 | 961.0708700          |
|                           | 34.5885                          | 0.09 | 966.0269819          |
|                           | 44.4985                          | 0.15 | 597.9111105          |
|                           | 64.8000                          | 0.09 | 1092.264842          |
|                           | 77.9800                          | 0.09 | 1186.404787          |
| Average Crystallite Size (ACS) |                                   |      | 929.0885095          |
| 800                       | 23.5480                          | 0.14 | 605.7008116          |
|                           | 32.6900                          | 0.14 | 617.9180784          |
|                           | 34.5800                          | 0.12 | 724.5035234          |
|                           | 44.4795                          | 0.19 | 472.0031116          |
|                           | 64.8166                          | 0.13 | 756.2528047          |
|                           | 77.8850                          | 0.15 | 711.3662991          |
| Average Crystallite Size (ACS) |                                   |      | 647.9574381          |
| 850                       | 23.4316                          | 0.16 | 529.8764096          |
|                           | 34.5000                          | 0.12 | 724.3464565          |
|                           | 44.4700                          | 0.18 | 498.2086376          |
|                           | 64.8500                          | 0.18 | 546.2835689          |
|                           | 77.8650                          | 0.19 | 561.5258775          |
| Average Crystallite Size (ACS) |                                   |      | 572.0481900          |

3.2. Energy gap and refractive index

The energy gap of LiTaO$_3$ thin films was presented in figure 2, which determined through extrapolation by withdrawing straight line on the coordinate axis using the following equation [30]:

\[
\begin{align*}
y-axis: \quad 2 \alpha d &= \ln \left( \frac{R_{\text{max}} - R_{\text{min}}}{R - R_{\text{min}}} \right)^2 \\
x-axis: \quad E_g &= \frac{h c}{1.602 \times 10^{-19} J(\lambda)}
\end{align*}
\]

with: $\alpha$ = absorbance coefficient
$d$ = film thickness (μm)
$R$ = reflectance values (from measurement using an Ocean Optics USB4000-UV-VIS)
$R_{\text{max}}$ = maximum reflectance value
$R_{\text{min}}$ = minimum reflectance value
$E_g$ = energy gap (eV)
$h$ = Planck’s constant ($6.626 \times 10^{-34}$ J·s)
$c$ = speed of light ($2.998 \times 10^8$ m·s$^{-1}$)
$\lambda$ = wavelength (m)
In this study, the refractive index values of LiTaO$_3$ thin films were pointed out in figure 3 and listed in table 3. In figure 3, the coordinate axes were plotted to form the curve of the energy gap with the refractive index through the temperature dependent dispersion relation by using the Sellmeier equation [31, 32]:

$$n_e^2(\lambda, T) = A + \frac{B + b(T)}{\lambda^2 - [C + c(T)]^2} + \frac{E}{\lambda^2 - F^2} + \frac{G}{\lambda^2 - H^2} + D \lambda^2$$

(5)

with:
- $n_e =$ refractive index
- $A, B, C, D, E, F, G, H =$ constants (Sellmeier coefficients)
- $b(T), c(T) =$ temperature dependent
- $\lambda =$ wavelength ($\mu$m)

![Figure 2](image2.png)

(a) 
(b) 
(c)

**Figure 2.** Energy gap of LiTaO$_3$ thin films: (a) 750°C (b) 800°C (c) 850°C.

![Figure 3](image3.png)

**Figure 3.** Refractive index of LiTaO$_3$ thin films with annealing treatment at 750°C, 800°C, and 850°C.
Table 3. The energy gap and the refractive index of LiTaO$_3$ thin films.

| Annealing temperature ($^\circ$C) | Energy gap (eV) | Refractive index |
|----------------------------------|----------------|-----------------|
| 750                              | 3.10           | 2.24            |
| 800                              | 4.80           | 2.68            |
| 850                              | 5.50           | 3.32            |

4. Conclusion
The thin layer from LiTaO$_3$ solution was deposited on p-type Si (100) substrates using Chemical Solution Deposition (CSD) technique and it was flattened at 4000 rpm for 30 seconds using spin coater device. Then, crystallization of LiTaO$_3$ thin layer was formed because of annealing temperature treatment. Further, the crystalline structure was characterized by X-Ray Diffraction (XRD) and the optical properties were identified based on measurement using spectrometer (Ocean Optics USB4000-UV-VIS). The study of crystalline structure exhibits that thin films were polycrystalline with the direction of orientation along (104) and (110). Moreover, optical properties indicated the sensitiveness to the visible and ultraviolet light. For its application as the visible and ultraviolet light sensor, these thin films can improve the performance of satellite systems that contribute to the optical remote sensing.

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References
[1] Djohan N, Estrada R, Sari D, Dahrl M, Kurniawan A, Iskandar J, Hardhienata H and Irzaman 2017 The effect of annealing temperature variation on the optical properties test of LiTaO$_3$ thin films based on Tauc Plot method for satellite technology IOP Conf. Ser.: Earth Environ. Sci. 54 012093
[2] Irzaman, Pebriyanto Y, Apipah E R, Noor I, and Alkadri A 2015 Characterization of Optical and Structural of Lanthanum Doped LiTaO$_3$ Thin Films Integrated Ferroelectrics 167 137
[3] Ismagil A, Jenie R P, Irmansyah, Irzaman 2015 Development of lithium tantalite (LiTaO$_3$) for automatic switch on LAPAN-IPB Satellite infra-red sensor Procedia Environ. Sci. 24 329
[4] Ismagil A, Irmansyah, Irzaman 2016 The diffusion coefficient of lithium tantalite (LiTaO$_3$) with temperature variations on LAPAN-IPB satellite infra-red sensor Procedia Environ. Sci. 33 368
[5] Irzaman, Maddu A, Syafutra H, dan Ismagil A 2010 Uji Konduktivitas Listrik dan Dielektrik Film Tipis Lithium Tantalate (LiTaO$_3$) yang Dididah Niobium Pentaoksida (Nb$_2$O$_5$) Menggunakan Metode Chemical Solution Deposition Prosiding Seminar Nasional Fisika 175
[6] Estrada R, Djohan N, Pasole D, Dahrl M, Kurniawan A, Iskandar J, Hardhienata H and Irzaman 2017 The optical band gap of LiTaO$_3$ and Nb$_2$O$_5$-doped LiTaO$_3$ thin films based on Tauc Plot method to be applied on satellite IOP Conf. Ser.: Earth Environ. Sci. 54 012092
[7] Inaguma Y, Matsui Y, Shan Y -J, Itoh M, Nakamura T 1995 Lithium ion conductivity in the perovskite-type LiTaO$_3$–SrTiO$_3$ solid solution Solid State Ionics 79 91
[8] Su Y, Lang J, Du C and Wang X 2016 Perovskite Materials - Synthesis, Characterisation, Properties, and Applications ed L Pan and G Zhu (Rijeka: InTech) Chapter 16 489
[9] Tarafder A, Annapurna K, Chaliha R S, Tiwari V S, Gupta P K, Karmakar B 2010 Structure, dielectric and optical properties of Nd$^{3+}$-doped LiTaO$_3$ transparent ferroelectric glass–ceramic nanocomposites J. Alloy. Compd. 489 281
[10] Aoyagi S, Osawa H, Sugimoto K, Iwata M, Takeda S, Moriyoshi C, and Kuroiwa Y 2015 Crystal structure analysis of LiTaO$_3$ under electric field Jpn. J. Appl. Phys. 54 10NB03
[11] Sari F I W, Djohan N, Kurniawan A, Rohaeti E, Irzaman 2015 Analisis Energy Gap dan Indeks Bias LiTaO$_3$ Didadah Ga$_2$O$_3$ Berdasarkan Metode Reflektansi Prosiding Seminar Nasional Fisika dan Aplikasinya (Jatinangor) I FM-12
[12] Irzaman, Irmansyah, Syafutra H, Arif A, Alatas H, Astuti Y, Nurullaeli, Siskandar R, Aminullah, Sumiarna G P A, Jamal Z A Z 2014 Effect of annealing times for LiTaSiO$_5$ thin films on structure, nano scale grain size and band gap Am. J. Mater. Res. 1 7
[13] Fang S, Wang B, Zhang T, Ling F, Wang R 2006 Growth and photorefractive properties of Zn, Fe double-doped LiTaO$_3$ crystal Opt. Mater. 28 207
[14] Irzaman, Darvina Y, Fuad A, Arifin P, Budiman M, and Barmawi M 2003 Physical and pyroelectric properties of tantalum-oxide-doped lead zirconium titanate [Pb$_{0.9950}$(Zr$_{0.525}$Ti$_{0.465}$Ta$_{0.010}$)O$_3$] thin films and their application for IR sensors Phys. Stat. Sol. (A) 199 416
[15] Misbachhussudur M, Ismangil A, Aminullah, Irmansyah, Irzaman 2016 Phasor diagrams of thin film of LiTaO$_3$ as applied infrared sensors on satellite of LAPAN-IPB Procedia Environ. Sci. 33 615
[16] Wendong Z, Qiulin T, Jun L, Chenyang X, Jijun X, Xiujian C 2010 Two-channel IR gas sensor with two detectors based on LiTaO$_3$ single-crystal wafer Opt. Laser Technol. 42 1223
[17] Fakhr M A, Al-Douri Y, Hashim U, Salim E T 2016 XRD Analysis and Morphological Studies of Spin Coated LiNbO$_3$ Nano Photonic Crystal Prepared for Optical Waveguide Application Adv. Mater. Res. 1133 457
[18] Gou J, Wang J, Huang Z H and Jiang Y D 2013 Preparation of LiTaO$_3$ Nano-Crystalline Films by Sol-Gel Process Key Eng. Mater. 531-532 446
[19] McClain C R, Meister G, Monosmith B 2014 Satellite Ocean Color Sensor Design Concepts and Performance Requirements Exp. Methods Phys. Sci. 47 73
[20] Watson I M, Prakash A 2015 Monitoring Volcanoes in the North Pacific: Observations from Space ed K G Dean and J Dehn (Berlin: Springer-Verlag Berlin Heidelberg) Chapter 2 27
[21] Thies B and Bendix J 2011 Satellite based remote sensing of weather and climate: Recent achievements and future perspectives Meteorol. Appl. 18 262
[22] Irzaman, Siskandar R, Nabilah N, Aminullah, Yuliarto B, Hamam K A, and Alatas H 2018 Application of lithium tantalate (LiTaO$_3$) films as light sensor to monitor the light status in the Arduino Uno based energy-saving automatic light prototype and passive infrared sensor Ferroelectrics 524 44
[23] Irzaman, Sitompul H, Masitoh, Misbachhussudur M, and Mursyidah 2016 Optical and structural properties of lanthanum doped lithium niobate thin films Ferroelectrics 502 9
[24] Irzaman, Siskandar R, Aminullah, Irmansyah, and Alatas H 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 Integr. Ferroelectr. 168 130
[25] Irzaman, Putra I R, Aminullah, Syafutra H, Alatas H 2016 Development of ferroelectric solar cells of barium strontium titanate (Ba$_x$Sr$_{1-x}$TiO$_3$) for substituting conventional battery in LAPAN-IPB Satellite (LISAT) Procedia Environ. Sci. 33 607
[26] Cullity B D, Stock S R 2014 Elements of X-Ray Diffraction (Harlow: Pearson Education Ltd)
[27] Suryanarayana C and Norton M G 1998 X-Ray Diffraction: A Practical Approach (New York: Springer Science+Business Media)
[28] Spinolo G and Maglia F 1999 Cohen’s method revisited Powder Diffr. 14 208
[29] Korotcov A, Chen R -S, Hsu H -P, Huang Y -S, Tsai D -S, and Tiong K -K 2007 Well-Aligned IrO$_2$ Nanocrystals J. Nanomater. 2007 84845
[30] Mulyadi, Rika W, Sulidah, Irzaman, Hardhienata H 2017 Barium Strontium Titanate Thin Film Growth with rotational speed variation as a satellite temperature sensor prototype IOP Conf. Ser.: Earth Environ. Sci. 54 012094
[31] Bruner A, Eger D, Oron M B, Blau P, Katz M, Ruschin S 2003 Temperature-dependent Sellmeier equation for the refractive index of stoichiometric lithium tantalate *Opt. Lett.* **28** 194

[32] Weng W -L, Liu Y -W, Zhang X -Q 2008 Temperature-Dependent Sellmeier Equation for 1.0 mol% Mg-Doped Stoichiometric Lithium Tantalate *Chin. Lett.* **25** 4303