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Characterization of Optical and Structural of Lanthanum Doped LiTaO₃ Thin Films

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Undoped, 5%, and 10% lanthanum doped lithium tantalate thin films were annealed at 550°C temperature for 12.5 hours and their properties were characterized. The results showed that the dopant addition affects the crystal formation of LiTaO₃, especially the 10% La₂O₅ dopant, where the lattice of $a = 5.11 \text{ \AA}$, $c = 13.30 \text{ \AA}$, and its crystal was hexagonal. The observed functional groups were O-H, N-H, C = C, Li-O, Ta-O. The higher La₂O₅ dopant concentration leads to the higher absorption of Ta-O and Li-O, the lower the energy gap, the higher the refractive index, and the smaller the particle size of thin films.

Keywords Lithium tantalite; lanthanum dopant; optical properties; structure; thin films

1. Introduction

Development of Lithium Tantalate (LiTaO₃) films can be carried out by using various methods, such as Chemical Solution Deposition (CSD), Metal Organic Chemical Vapor Deposition (MOCVD), rf sputtering, and Pulsed Laser Ablation Deposition (PLAD) [1], and it does not need complicated treatment [1,2]. LiTaO₃ is one of the widely used optoelectric materials to its ferroelectric, piezoelectric, and pyroelectric properties [1,3-8,15-16,]. It is also an attractive materials for integrated-optic applications due to its nonlinear optical properties [9-13], large electrooptic and piezoelectric coefficient and its superior resistance to laser-induced optical damage [16-19,24,35,37,38,44]. In other hand, it is a ferroelectric crystal which undergoes high Curie temperature of 608 °C and it also has high melting temperature at 1650 °C [34].

However, most of the techniques used to make LiTaO₃ are not only expensive but also involve difficult stoichiometric quantification and complex equipment. Sol-gel processing [10], a solution-based method, is interesting due to its ease of production and lower cost, and large area thin film. However, the commonly used alkoxide precursors to produce

LiTaO₃ films by sol-gel method are highly reactive and require careful control of the hydrolysis-condensation reaction [3].

In this research, LiTaO₃ thin films were coated on p-type silicon substrates by using CSD method, followed by spin-coating technique and annealed at the temperature of 550°C then characterized using X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), UV-Vis Wave Analyzer, and Particle Size Analyzer (PSA). This research aims to manufacture the lanthanum doped LiTaO₃ thin films and determine its optical and structural properties.

2. Experimental

The thin films preparation was started by cutting the Si substrate with the size of 8 mm × 8 mm, each as many as 5 pieces. Then, the substrates were cleaned using aqua bidest and dried [35,37,45]. In this case, three LiTaO₃ solutions were prepared using CSD (Chemical Solution Deposition) method. The first solution was prepared by mixing 0.1650 gram of LiCH₃COO and 0.5524 gram of Ta₂O₅ which were soluted inside 2.5 ml of 2-metoxy methanol which called undoped LiTaO₃ solution. The second solution was prepared by mixing 0.1650 gram of LiCH₃COO and 0.5524 gram of Ta₂O₅ which were soluted LiTaO₃ 2.5 ml of 2-metoxy methanol with the addition of 0.0295 gram of La₂O₅ as dopant which called 5% lanthanum doped LiTaO₃ solution. Afterwards, the third solution was prepared by mixing 0.1650 gram of LiCH₃COO and 0.5524 gram of Ta₂O₅ which were soluted inside 2.5 ml of 2-metoxy methanol with the addition of 0.0590 gram of La₂O₅ which called 10% lanthanum doped LiTaO₃ solution.

After the preparation of those three solutions, they were sonificated for 90 minutes using Branson 2510. Afterwards, the solution was dropped towards the substrate's surface on spin coating rotator with speed of 3000 rpm, conducted twice. The remaining solution then dried at 80°C for 24 hours, then characterized using FTIR and PSA. The dropped substrate was then annealed using Furnace with the increasing rate of temperature at 1.7°C/minute, started from room temperature until it reaches 550°C and held constantly for 12.5 hours, and then cooled down into room temperature. The formed thin films were characterized using XRD and Optical Ocean USB 2000.

3. Results and Discussion

3.1 XRD Pattern

Figure 1 shows the XRD pattern of LiTaO₃ thin films with p-type Si (100) substrate after annealing at 550°C. The data were obtained with interval of 0.02° in the range of 20°–80° [32,33]. These three patterns show a peak at $2\theta = 70^\circ$ because the used substrate is silicon.

XRD pattern shows that LiTaO₃ thin films have both crystalline and amorphous structures. Undoped LiTaO₃ thin films have mixed structure with lattice parameter of $a = 5.13 \text{ \AA}$ and $c = 13.54 \text{ \AA}$. Meanwhile, for 5% La doped LiTaO₃ thin films, the structure is not significantly different with the undoped. However, it has smaller lattice parameter of $a = 4.92 \text{ \AA}$ and $c = 14.19 \text{ \AA}$. Moreover, for 10% La₂O₅ doped LiTaO₃ thin films, there is a peak (crystalline) of LiTaO₃ with lattice parameter of $a = 5.11 \text{ \AA}$ and $c = 13.30 \text{ \AA}$.

Decreasing in crystal size is also influenced by the radii of its constituent ions. Ionic radii of Li⁺, Ta⁵⁺ and La³⁺ are 0.90 Å, 0.78 Å and 1.172 Å, respectively. It can be seen that the ionic radius of La³⁺ is closer to that of Li⁺ so that La³⁺ can occupy the positions of

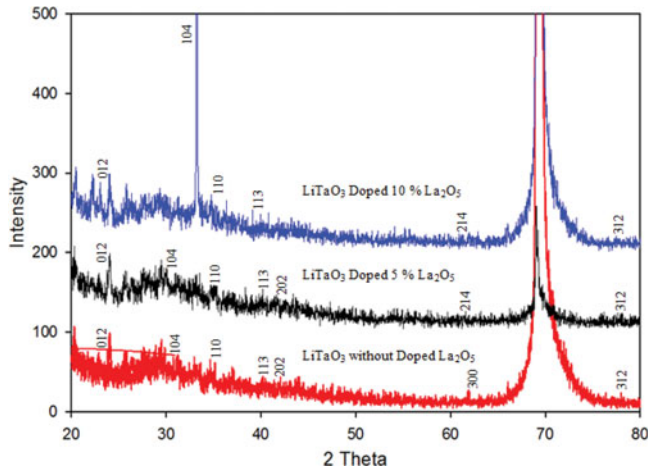


Figure 1. the XRD pattern of LiTaO_3 thin film with p type Si (100) substrate after annealing at 550°C .

Li^+ in the crystal structure. The difference of Ionic radii between dopant and replaced ion affects the formation of spinel phase. This leads to crystal size decreasing which is caused by the existence of dopant cations in the structure of LiTaO_3 .

3.2. FTIR Results

The results show the existence of stretching vibration of OH group, C = C aromatic bonding, Li-O bonding, and Ta-O bonding at wave numbers of $3100\text{--}3900\text{ cm}^{-1}$, $1650\text{--}1450\text{ cm}^{-1}$, $1440\text{--}1420\text{ cm}^{-1}$, and $610\text{--}945\text{ cm}^{-1}$, respectively [29]. According to these results, it is implied that there is a change in absorbance value of LiTaO_3 for

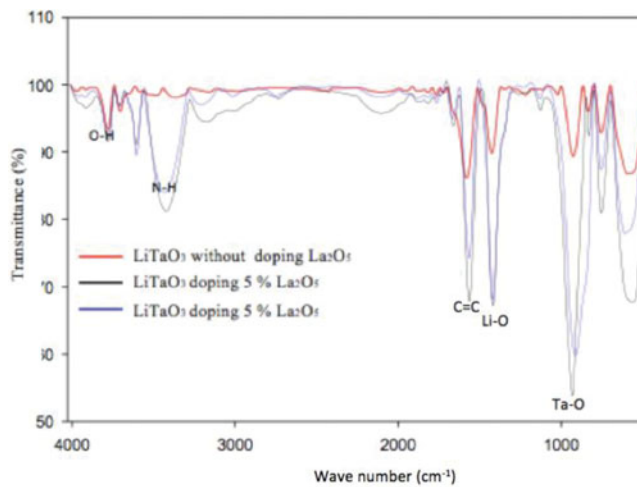


Figure 2. The FTIR spectra of LiTaO_3 thin films.

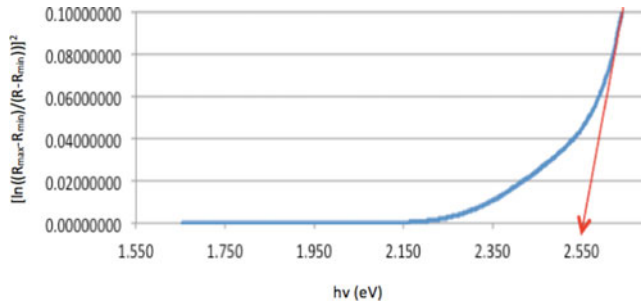


Figure 3. Energy gap of undoped thin films.

each of dopant addition. Thus, the absorption value tends to increase with the increasing in dopant concentration.

3.3. Optical Analysis

3.3.1 Energy Gap. The results show the energy gap of undoped, 5% La doped, and 10% La doped thin films are 2.550 eV, 2.020 eV, and 2.199 eV, respectively (Figs. 3–5). It can be concluded that the higher dopant concentration leads to the lower energy gap, which means the electron will be easier to move from the valence band area into the conduction band.

In this research, the overall values of energy gap of thin films from silicon substrate are in the range of 2.0–3.45 eV for all concentrations. According to other researches, the energy gap of pure silicon is in the range of 1.0–1.3 eV [5–53]. Silicon itself is usually used as semiconductor material and has been applied on many electronic devices for its unique energy gap [56, 57]. In this research, the usage of Si as substrate makes a medium level of energy gap, makes the obtained thin films are capable to be applied in high-voltage electronic components [52].

From the results, it is also found that there is energy gap increasing from 5% to 10% dopant. According to several researches, energy gap can increase after the dopant addition [56–66]. This is the result of Burstein-Moss effect, increasing in band gap value of a thin film-doped semiconductor due to their electrons in the conduction band push the fermi level [67] which lead to the increasing band gap.

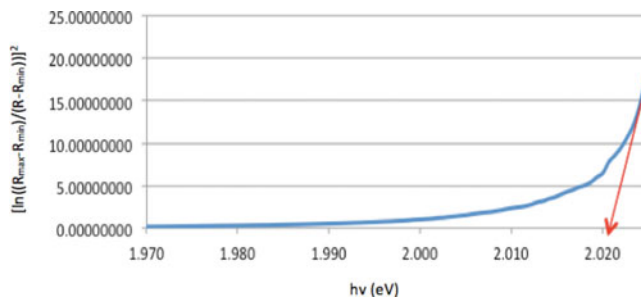


Figure 4. Energy gap of 5% lanthanum doped thin films.

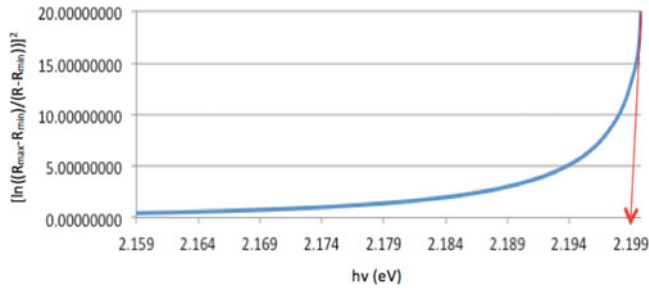


Figure 5. Energy gap of 10% lanthanum doped thin films.

3.3.2 Refractive Index. The addition of 5% La dopant significantly increases the refractive index from the undoped thin films. However, 10% La dopant decreases the refractive index (Figure 6). Previous researches [68, 69] showed that the refractive index tends to increase with the increasing in dopant concentration, which is caused by the occurrence of disorder in structure, changes in stoichiometry, and internal strain caused by polarizability. Consequently, if containing dopant materials have high polarizability, the refractive index will thus increase [70]. In addition, the phenomenon in dopant increasing decreases the refractive index may be caused by the thinning of the material or the widening of energy gap [71, 72]. From the previously observed energy gaps, it can be seen that there was indeed an increase of energy gap from thin film with 5% dopant to 10% dopant, so that it is likely the cause of decreasing in refractive index.

3.4. PSA

To determine the particle size of LiTaO_3 thin films, particle size analyzer (PSA) device with scale of $0.6\text{nm} - 7\mu\text{m}$ was used. Figure 7 shows that the LiTaO_3 thin films have different

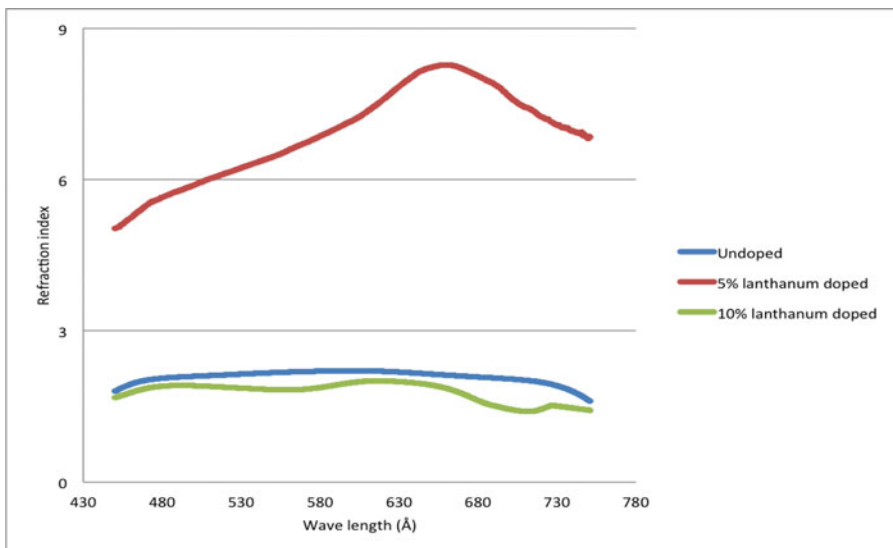


Figure 6. Refractive index of undoped, 5% La doped, and 10% La doped LiTO_3 thin films.

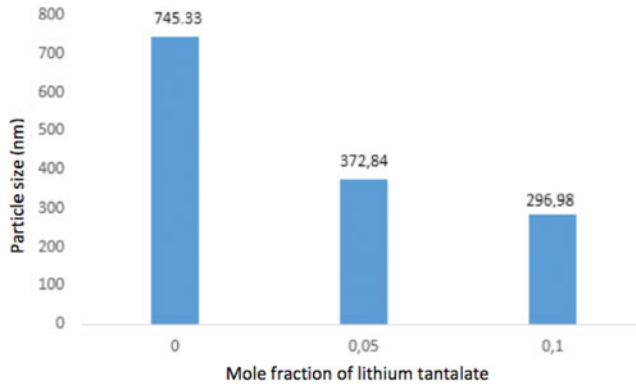


Figure 7. The particle size of LiTaO₃ thin films at various mole fractions.

particle sizes. Undoped LiTaO₃ thin films have the largest particle size range, which is 745.33 nm. Meanwhile, the particle size of 5% and 10% La doped LiTaO₃ thin films were 372.84 nm and 296.98 nm, respectively. These results indicate that the higher dopant concentration, the smaller the particle size.

4. Conclusion

The addition of lanthanum dopant ignites the formation of LiTaO₅ crystal, especially in the addition of 10% lanthanum dopant with the hexagonal-shaped crystals. From FTIR, the higher the dopant concentration given, the larger the absorption of Ta-O and Li-O. Moreover, from PSA, it is found that the dopant addition leads to smaller particle size. The optical measurements show that the higher the dopant concentration leads to the lower the energy gap and the higher the refractive index of thin films.

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