Crystalline structures properties doped RuO$_2$ (0, 2, 4, 6%) of thin film LiNbO$_3$

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Abstract. Lithium Niobate (LiNbO$_3$) can be applied as a thin film coating because it has superior piezoelectric, optoelectronic, pyroelectric, and photorefractive properties. The growth of LiNbO$_3$ thin film using Chemical Solution Deposition (CSD) method with spin coating technique speed of 8000 rpm for 30 seconds on a p-type silicon substrate (100) with variations in concentration of RuO$_2$ container (0%, 2%, 4%, 6%) and annealing temperature (750 ºC, 800 ºC, 850 ºC). The annealing temperature is kept on hold for 8 hours with an increase of 1.67 ºC/minute. The result of LiNbO$_3$ of the analysis using the Cramer and Cohen method obtained hexagonal crystal structure ($\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$) with a lattice parameter value of 5.3856 Å to 5.6566 Å and c lattice parameter value of 15.4054 Å to 17.8404 Å.

1. Introduction
The development of increasingly rapid science and technology especially in the field of physics can produce functional materials that can be used as electronic devices because they have ferroelectric properties. A ferroelectric material is a material that has electric polarisation due to the presence of an external electric field [1]. Initially, producers have made this ferroelectric material in bulk, but the development of science and technology have made this material in the form of thin films that have a thickness reaching nano. The thin layer is a fragile layer of organic, inorganic, metal and metal-organic mixtures that have the properties of conductors, semiconductors, superconductors and insulators [2].

LiNbO$_3$ is a ferroelectric material that has pyroelectric, piezoelectric, refractive, electro-optical and nonlinear optical properties. LiNbO$_3$ is suitable for application to non-linear optics, integrated optics, acoustic wave devices, and holography optics [3]. In this paper, we have made a thin film of lithium drug (LiNbO$_3$) by adding ruthenium oxide (RuO$_2$) receptacle. The substrate used is p-type silicon material (100), using the CSD method (Chemical Solution Deposition). A CSD method is a method of making thin films by depositing chemical solutions on the substrate, then preparing using spin coating at a certain rotational speed. In this paper, we have done the spin coating with a rotating speed of 8000 rpm. Based on the literature shows that at this speed thin films formed are thinner (in micrometre order) [4]. The CSD method has several advantages, such as stoichiometric control, homogeneity, temperature and relatively low costs [5].
2. Research Objective
This research objective is to determine the effect of variations in the concentration of the RuO$_2$ receptacle and the annealing temperature on the thin films of LiNbO$_3$ on the crystal properties of the film.

3. Methods

3.1. Tools and Materials
The materials used in this study were lithium acetate (Li$_2$C$_2$H$_3$O$_2$) 99.6% powder, niobium oxide (Nb$_2$O$_5$) 99.9%, with ruthenium oxide (RuO$_2$) dopant, methyl ester sulfonic acid (MESA) surfactant, a p-type silicon substrate (100), and double distilled water. While the tools used are an analytic balance, spin coater reactor, Vulcan TM-3000 brand furnace, and UV Opt-Opt Ocean USB Optical Spectroscopy.

3.2. Substrate Preparation
The substrate used is the p-type silicon substrate (100). The substrate was cut to a square size of 1 cm x 1 cm using a diamond eye knife. We have cleaned The substrate by dipping in double distilled water using tweezers for half a minute.

3.3. Making LiNbO$_3$ solution
We have made The LiNbO$_3$ solution was made by mixing lithium acetate (Li$_2$C$_2$H$_3$O$_2$) powder, niobium pentoxide (Nb$_2$O$_5$), and ruthenium oxide (RuO$_2$) into 2.5 ml of acetic acid solvent and MESA surfactant. Then stirred using a magnetic stirrer with a rotating speed of 600 rpm for 30 minutes which solved 2 M. LiNbO$_3$.

3.4. The growth of thin films
The LiNbO$_3$ film was grown on a p-type silicon substrate 1 cm x 1 cm using the chemical solution deposition (CSD) method. We have done the deposition of a film on the substrate by spin coating. We have set the spin coating reactor playback with a rotating speed of 8000 rpm for 30 seconds and a 60-second pause for each drop. The penetration process is done three times to obtain three layers on the substrate. Then the film is annealed using a furnace.

3.5. Annealing process
The annealing process on the substrate starts from the room temperature which we have raised to the desired annealing temperature with an adjusted heating temperature increase of 1.67 °C / minute. After reaching the annealing temperature then the heating temperature is held constant for 8 hours. Then the cooling furnace is carried out until we have recovered the room temperature. Annealing is carried out with three temperature variations namely 750 °C, 800 °C, and 850 °C with the same holding time of 8 hours.

3.6. Determine the value of the LiNbO$_3$ film lattice parameter
To determine the hexagonal crystal lattice parameters used Equations known as the Cramer and Cohan equations (1) [6,7].

\[
\begin{align*}
\Sigma \alpha \sin^2 \theta &= C\Sigma \alpha^2 + B\Sigma \alpha \gamma + A\Sigma \alpha \delta, \\
\Sigma \gamma \sin^2 \theta &= C\Sigma \gamma \alpha + B\Sigma \gamma \gamma^2 + A\Sigma \gamma \delta, \\
\Sigma \delta \sin^2 \theta &= C\Sigma \alpha \delta + B\Sigma \gamma \delta + A\Sigma \delta^2 
\end{align*}
\]

(1)

Film crystallite size can be calculated using FWHM with the Rietveld method using the equation (2) [8].
\[ L = K \frac{\lambda}{(\beta \cos \theta)} \]  

(2)

$L$: grain size (m)  
$K$: constant (0.96)  
$\beta$: wide graph (rad)  
$\Theta$: maximum angle (rad)  
$\lambda$: wavelength (1.506 Å)

4. Results and Discussions

Characterisation using XRD aims to determine the crystal structure, lattice parameters, and the size of the crystalline lithium drug formed. This characterisation uses Shimadzu XRD-7000 with $\lambda$ of 0.1506 Å and diffraction angle 2$\Theta$ from 10° to 80° with step 0.02°. If an examiner has subjected an ingredient to X-rays, the intensity of the X-rays transmitted is smaller than the intensity of the incoming beam. The difference in intensity is due to the absorption by materials and also scattering by atomic atoms in the material. Some of the scattered rays are mutually eliminating because the phases are different and some are mutually reinforcing because the phases are the same. We have referred amplifying X-ray files as diffraction files. The diffraction peaks formed indicate film particles have a crystal orientation distribution. The diffraction peaks can be used to determine the Miller index (hkl). The Miller index obtained is used to determine the lattice parameter.

![X-ray diffraction pattern](image)

**Figure 1.** The X-ray diffraction pattern of the LiNbO$_3$ film which we have annealed at 750 °C to the diffraction angle.
Figure 2. The X-ray diffraction pattern of the LiNbO$_3$ film which we have annealed at 800 °C to the diffraction angle.

Figure 3. The X-ray diffraction pattern of the LiNbO$_3$ film which we have annealed at 850 °C to the diffraction angle.
The difference from the 12 films lies in the level of diffraction intensity produced. The highest intensity is possessed by a LiNb$_{0.94}$Ru$_{0.06}$O$_3$ film which we have annealed at a temperature of 800 °C. The LiNb$_{0.94}$Ru$_{0.06}$O$_3$ film which we have annealed at 800 °C also had lattice parameter values that approached the literature compared to other films, namely a at 0.5336 Å and c at 15.9804 Å. Therefore, a LiNb$_{0.94}$Ru$_{0.06}$O$_3$ film which we have annealed at 800 °C has the best crystal structure compared to other films, because the higher the diffraction intensity obtained shows, the more the number of uniform crystal fields from the same field orientation. Along with the addition of the amount of concentration of the receptacle, the intensity of the peaks that appear decreases and there is a shift in the angle of action caused by Ru$^{4+}$ atoms that enter between the crystal cracks of LiNbO$_3$ replacing Nb$^{5+}$ at the time we have annealed the film. However, the film annealed at 750 °C experienced an increase in the intensity of diffraction peaks along with the increase in the number of Ru containers (Table 1).

| Temperature | Lithium Niobate Film | Experimental Result (Å) | JCPDS(Å) [5] |
|-------------|----------------------|-------------------------|--------------|
| 750 °C      | LiNb$_{1.00}$Ru$_{0.00}$O$_3$ | 5.6566 | 16.7106 | 5.149 | 13.86 |
|             | LiNb$_{0.98}$Ru$_{0.02}$O$_3$ | 5.6123 | 16.6404 |
|             | Li$_{0.96}$Ru$_{0.04}$NbO$_3$ | 5.5925 | 16.3872 |
|             | Li$_{0.94}$Ru$_{0.06}$NbO$_3$ | 5.6070 | 17.4038 |
| 800 °C      | LiNb$_{1.00}$Ru$_{0.00}$O$_3$ | 5.3856 | 15.4054 |
|             | LiNb$_{0.98}$Ru$_{0.02}$O$_3$ | 5.5917 | 16.6518 |
|             | Li$_{0.96}$Ru$_{0.04}$NbO$_3$ | 5.5999 | 16.5828 |
|             | Li$_{0.94}$Ru$_{0.06}$NbO$_3$ | 5.5336 | 15.9804 |
| 850 °C      | LiNb$_{1.00}$Ru$_{0.00}$O$_3$ | 5.6278 | 16.7086 |
|             | LiNb$_{0.98}$Ru$_{0.02}$O$_3$ | 5.6053 | 16.6961 |
|             | Li$_{0.96}$Ru$_{0.04}$NbO$_3$ | 5.6207 | 16.9115 |
|             | Li$_{0.94}$Ru$_{0.06}$NbO$_3$ | 5.6486 | 17.8404 |

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Table 2. Crystalite Particle Size of LiNbO$_3$ films

| No | LiNb$_1$Ru$_0$O$_3$ | LiNb$_{0.98}$Ru$_{0.02}$O$_3$ | LiNb$_{0.96}$Ru$_{0.04}$O$_3$ | LiNb$_{0.94}$Ru$_{0.06}$O$_3$ |
|----|-------------------|------------------------------|------------------------------|------------------------------|
| 1  | 339.7             | 338.5                        | 353.7                        | 424.3                        |
| 2  | 430.0             | 358.1                        | 537.1                        |                              |
| 3  | 380.0             | 527.6                        | 640.6                        |                              |
| 4  | 619.2             | 427.5                        | 614.5                        |                              |
| 5  | 409.7             | 464.0                        | 464.0                        | 444.7                        |
| 6  | 485.0             |                              |                              |                              |
| ACS| 443.9             | 423.1                        | 522.2                        | 481.7                        |

The crystallite size can be calculated based on FWHM from the diffraction peaks produced by the Rietveld method. Table 2 shows that the size of film crystallite at annealing 850 °C ranges from 338.5 Å to 640.6 Å with an average crystallite size of 443.9 Å for LiNb$_1$Ru$_0$O$_3$, 423.1 Å for LiNb$_{0.98}$Ru$_{0.02}$O$_3$ films, 522.2 Å for LiNb$_{0.96}$Ru$_{0.04}$O$_3$ films and 481.7 Å for LiNb$_{0.94}$Ru$_{0.06}$O$_3$ films.

5. Conclusions

LiNbO$_3$ thin films were grown on a p-type silicon substrate using the CSD method using 0%, 2%, 4%, 6% pendants and annealing with temperatures of 750 °C, 800 °C, and 850 °C successfully made. The results of the analysis using the Cramer and Cohen method obtained hexagonal crystal structure ($\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$) with a lattice parameter value of $5.3856 \, \text{Å}$ to $5.6566 \, \text{Å}$ and c lattice parameter value of $15.4054 \, \text{Å}$ to $17.8404 \, \text{Å}$.

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References

[1] Irzaman, PEBRIYANTO Y, APIPAH E R, NOOR I and ALKADRI A 2015 *Integr. Ferroelectr.* **167** 137–145
[2] Irzaman, Maddu A and Syafutra A 2010 Uji konduktivitas listrik dan dielektrik film tipis lithium tantalate (LiTaO$_3$) yang didahad niobium pentaoksida (Nb$_2$O$_5$) menggunakan metode chemical solution deposition *Pros. Semin. Nas. Fis.* **175–83**
[3] Sistesya D and Sutanto H 2013 *Youngster Phys. J.* **2** 71–80
[4] Abrahams S, Reddy J M and Bernstein J 1966 *J. Phys. Chem. Solids* **27** 997–1012
[5] Irzaman, Sitompul H, Masitoh, Misbakhussudur M and Mursyidah 2016 *Ferroelectrics* **502** 9–18.
[6] Umiati N A K, Irzaman I, Budiman M and Barmawi M 2001 *Indones. J. Phys.* **12** 94-98
[7] Liu M and Xue D 2007 *J. Alloys Compd.* **427** 256–259
[8] Bharath S, Pimputkar K, Pronschinske A and Pearl T 2008 *Appl. Surf. Sci.* **254** 2048-2053