



# Sol-gel Synthesis of Lithium Niobate Powder and Thin Films Using Lithium 2,4-Pentanedionate as Lithium Source

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**Abstract.** Lithium niobate powder was prepared at 500°C by a sol-gel method using lithium 2,4-pentanedionate as the lithium source. This method offers an advantage over the double alkoxide method as lithium 2,4-pentanedionate is less prone to moisture as compared to lithium ethoxide precursor and also it is easily soluble in 2-methoxyethanol. Microstructural investigation revealed sub-micrometer gel powder heat treated at 600°C. Thin films of lithium niobate with no preferred orientation were obtained at 350°C by spin coating of the above precursor solution onto platinum coated silicon substrates.

**Keywords:** sol-gel synthesis, crystallization, microstructure

## 1. Introduction

Lithium niobate,  $\text{LiNbO}_3$ , exhibits a large non-linear optical coefficient, a large birefringence, a high electro-optic coefficient, a high Curie temperature, good piezoelectric and excellent acousto-optic properties which makes it suitable for many applications such as optical wave guides, optical modulators, optical switches and SAW (surface acoustic wave) devices [1]. Single crystals of  $\text{LiNbO}_3$  are grown by Czochralski method from melts with non-stoichiometric congruent composition of 48.5 mol%  $\text{Li}_2\text{O}$  [2]. Polycrystalline powders are generally prepared via solid-state reaction between lithium carbonate and niobium pentoxide [3] which require high temperatures that might lead to compositional defects due to volatilization of  $\text{Li}_2\text{O}$  [4]. Also since several properties such as refractive index and Curie temperature of  $\text{LiNbO}_3$  are very sensitive to even slight compositional fluctuations [5], low temperature chemical processing with a good control over stoichiometry is highly desirable for reproducible properties. Two such chemical processes have been reported in literature for the synthesis of  $\text{LiNbO}_3$  powders. Lanfredi et al.

[6] described an evaporative method based on thermal decomposition of a precursor salt obtained by coprecipitation, while Hirano and Kato [7], Castings et al. [8] derived  $\text{LiNbO}_3$  from metalorganic precursors. In the recent years, in order to produce integrated electro-optic devices, significant efforts have been focused on the fabrication of  $\text{LiNbO}_3$  thin films using liquid phase epitaxy, chemical vapor deposition, and rf-sputtering and sol-gel methods. Since sol-gel technique offers low processing temperature and precise control over stoichiometry, epitaxial growth of  $\text{LiNbO}_3$  films on sapphire,  $\text{LiNbO}_3$ , MgO doped  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$  substrates in particular have been thoroughly investigated [9–18]. All the above sol-gel based methods made use of lithium alkoxide as lithium source. Besides lithium alkoxide or lithium acetate was also used as lithium source [19]. Since lithium ethoxide is extremely hygroscopic and since lithium acetate has limited solubility in 2-methoxyethanol (solvent used in sol-gel process), use of lithium 2,4-pentanedionate has been explored. This paper describes the use of lithium 2,4-pentanedionate as lithium precursor for the fabrication of  $\text{LiNbO}_3$  powders and thin films.

## 2. Experimental

Figure 1 depicts the synthesis of  $\text{LiNbO}_3$  precursor solution. 0.1 mole Lithium 2,4-pentanedionate (Alfa chemical company, USA) was mixed with 2 moles of 2-methoxyethanol and refluxed at  $125^\circ\text{C}$  in argon for 12 h. Likewise niobium ethoxide (Aldrich chemical company, USA) was mixed with 4 moles of 2-methoxyethanol and refluxed separately at  $125^\circ\text{C}$  in argon for 12 h. The above two solutions were refluxed and cooled to room temperature and again refluxed for 6 h under the same conditions as above. Concentration of the final solution was 0.3 molar. The resultant precursor solution thus obtained was

stable when stored in a closed container and was filtered through a 0.2 mm syringe filter for spin coating onto platinum coated Si (100) substrate using a spin coater (Integrated Technologies P-6000) operated at 4000 rpm for 30 s. Prior to deposition the Pt coated silicon substrates were thoroughly cleaned using a standard semiconductor processing technique. To obtain a thin film of suitable thickness, six coatings were performed on layers previously heat treated at  $350^\circ\text{C}$  for 10 min. Phase identification of the films annealed at different temperatures (using a ramp rate of  $20^\circ\text{C}$ ) was performed by an X-ray diffractometer (Scintag, Model DMC 105) with a Ni filtered  $\text{CuK}\alpha$  radiation. The microstructure and thickness of the

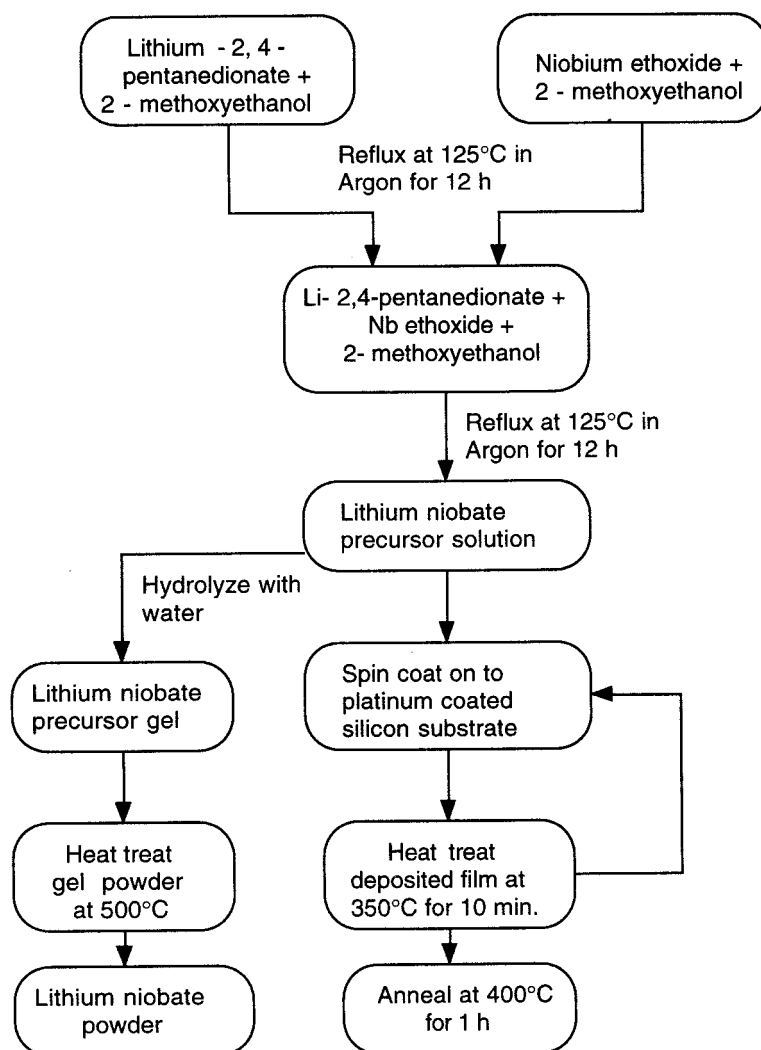


Fig. 1. Flow chart depicting the synthesis procedure for  $\text{LiNbO}_3$  precursor gel powder and thin films.

films were obtained by a scanning electron microscope (Model ISI-DS 130, Akashi Beam Technology Corporation, Japan).

A portion of the precursor solution was gelled separately by hydrolyzing with 8 moles of theoretical amount of water and was dried at 60°C. Thermal behavior of precursor gel powder was studied using a thermogravimetric analyzer (Delta series TGA7, Perkin Elmer) and a differential thermal analyzer (Model DTA1700, Perkin Elmer). Phase identification of gel powders subjected to different heat treatment temperatures was done by an X-Ray Diffractometer. Microstructure of  $\text{LiNbO}_3$  powder was obtained by a Scanning electron microscope.

### 3. Results and Discussion

Figure 2(a) depicts the thermogram from 50–850°C of  $\text{LiNbO}_3$  precursor gel powder heat treated at 200°C for 6 h. As it can be seen from this figure, the gel powder showed a continuous loss upto about 460°C with two steep losses between 350–450°C followed by a minor loss upto 600°C. These losses may be attributed to the decomposition of organics and subsequent oxidation of carbon, respectively. Figure 2(b) shows differential thermal analysis (DTA) curve of same gel powder as above. The DTA curve indicates one broad endotherm at 197°C followed by four exothermic peaks of which two peaks at 271 and 443°C are sharp while the other two peaks at 316 and 571°C being broad. As all these peaks lie within the continuous weight loss region (Fig. 2(a)), the crystallization peak, if any, cannot be assigned unambiguously since this will be masked by other peaks due to loss of organics. Hence, the gel powder is subjected to separate heat treatments at 275, 500 and 800°C for 4, 2 and 1 h, respectively. The X-ray diffraction (XRD) pattern of gel powder heat treated at 275°C is characteristic of an amorphous powder. XRD patterns of gel powder heat-treated at 500 and 800°C as shown in Fig. 3 indicate that phase pure  $\text{LiNbO}_3$  was formed at 500°C itself. In this study, gel powders were heat treated only in air in contrast to the simultaneous use of water vapor and flowing oxygen gas used in some studies reported in literature. According to Puyoo-Castings et al. [4], crystallization of  $\text{LiNbO}_3$  from ethanolic solutions of Li and Nb alkoxides began at 400°C and increased upto 600°C. Eichorst et al. [6] formed a mixed metal alkoxide

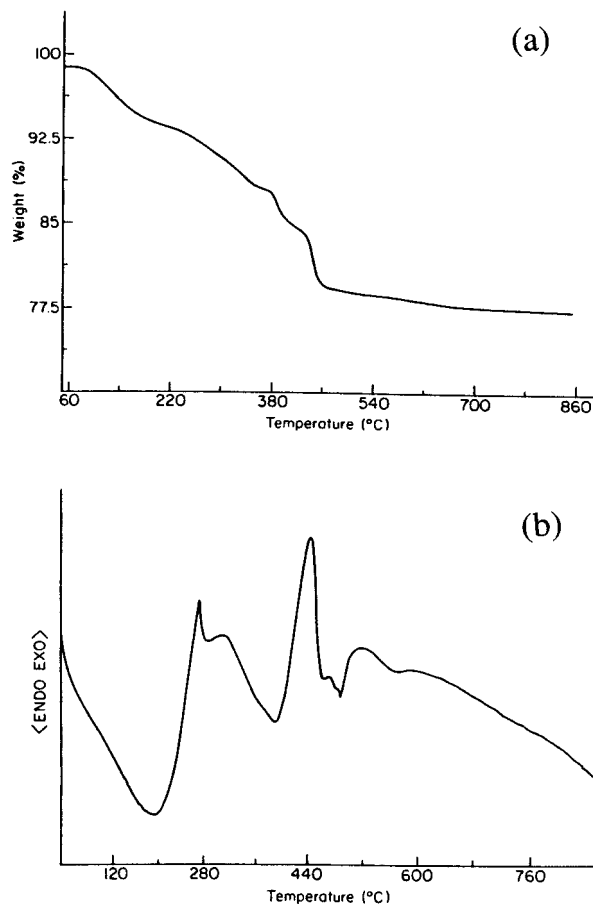


Fig. 2. (a) Thermogram and (b) DTA curve of  $\text{LiNbO}_3$  gel powder heat treated at 200°C for 6 h.

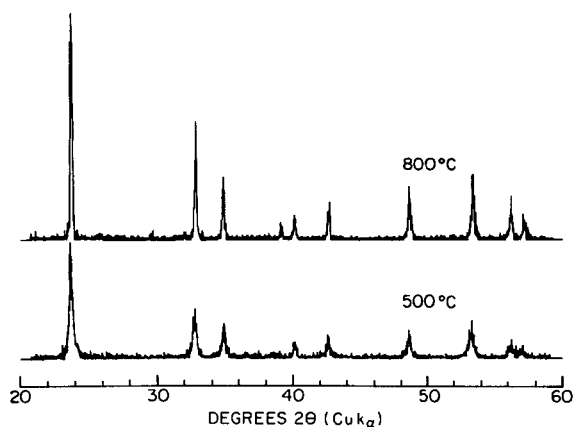


Fig. 3. XRD patterns of  $\text{LiNbO}_3$  gel powder separately heat treated in air at 500°C for 2 h and 800°C for 1 h.

$\text{LiNb}(\text{OR})_6$  where  $\text{R} = \text{CH}_3\text{OCH}_2\text{CH}_2$ , the hydrolysis of which yielded  $\text{LiNbO}_3$  after heat treatment at 490 and 510°C for basic and neutral gels respectively. In all of the studies so far, only lithium ethoxide was used as lithium precursor while the present study shows lithium 2,4-pentanedionate which is less prone to degradation by moisture can be used as an alternative lithium source. Also the refluxion time after mixing the individual precursors in the present study is not critical as was the case for double alkoxide precursor formation. Figure 4 shows the microstructure of gel powder heat treated at 600°C for 1 h. Very fine grains of submicrometer size are evident from the above figure. Figure 5 shows the XRD patterns of thin films obtained by spin coating of non-hydrolyzed precursor solution onto platinum coated silicon substrates and heat treated at 350, 400, 500 and 750°C. From these XRD patterns it can be clearly seen that no preferred orientation is observable. According to the study of Eichorst, Payne and Wragg [12]  $\text{LiNbO}_3$  films on Si(111) crystallized in air at 650°C and exhibited well developed microstructure at 800°C. Hirano and Kato's study of  $\text{LiNbO}_3$  films made by dip coating onto Si(100) substrates indicated that crystallization occurred at 400°C for first two dippings while subsequent dippings showed  $\text{LiNbO}_3$  film formation at as low as 250°C. In these studies Hirano and Kato used a mixture of water vapor and oxygen gas followed by further 0.5 h drying in oxygen gas for heat treatment. No preferred orientation of

$\text{LiNbO}_3$  films on Si(100) was reported. In the present study,  $\text{LiNbO}_3$  films with no preferred orientation are formed at 350°C under an ordinary air atmosphere. Microstructure of these films is shown in Fig. 6 which indicates an average grain size less than 0.1  $\mu\text{m}$  for the film annealed at 750°C while no characteristic morphology is noticeable for heat treatment at 400°C.

#### 4. Conclusion

From the above studies it may be concluded that  $\text{LiNbO}_3$  powders and films can be easily formed by using lithium 2,4-pentanedionate as lithium source in place of lithium ethoxide which is extremely moisture sensitive. Heat treatment of gel powder yielded polycrystalline powder at 500°C while spin coated thin films with no preferred orientation on platinum coated Si(100) substrate were obtained at a temperature as low as 350°C for heat treatment in an ordinary atmosphere.

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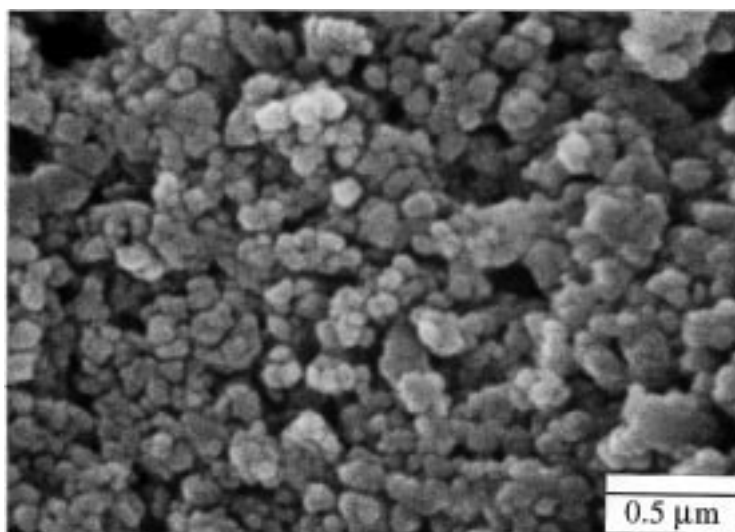


Fig. 4. SEM micrograph of  $\text{LiNbO}_3$  gel powder heat-treated at 600°C for 1 h.

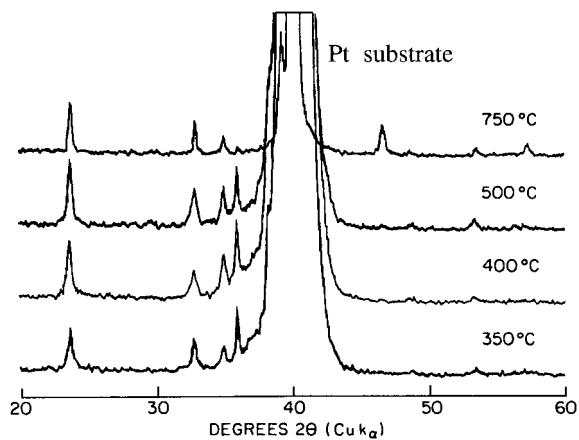


Fig. 5. XRD patterns of thin films heat-treated at 350, 400, 500 and 750 °C for 1 h.

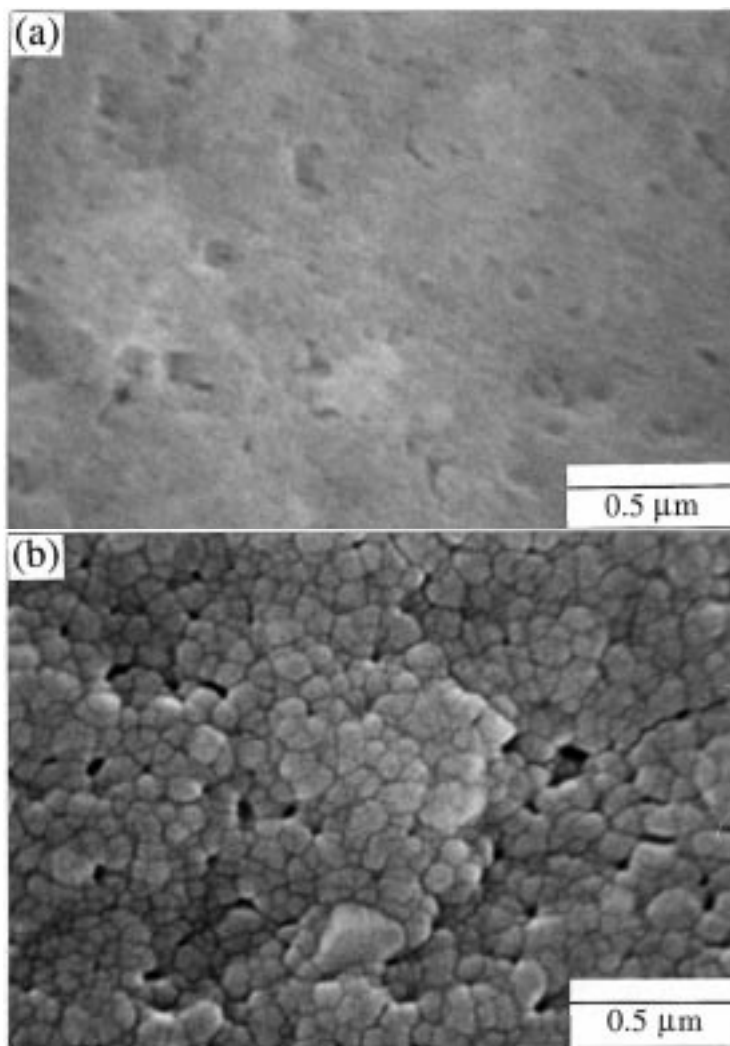


Fig. 6. SEM micrographs of  $\text{LiNbO}_3$  thin film annealed at (a) 400 and (b) 750 °C for 1 h.

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