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Stoichiometric $LiNb_3O_8$ thin films from microwave annealing

Anil Tumuluri[1], K. C. James Raju[1,2]

[1]*Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad 500046, India*
[2]*School of Physics, University of Hyderabad, Hyderabad 500046, India*

[*]Corresponding author. E-mail: kcjrsp@uohyd.ernet.in

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ABSTRACT

Mono phase $LiNb_3O_8$ (LN), a compound that comes during the processing of $LiNbO_3$ is synthesized as thin films using sol gel process followed by microwave annealing. Initial studies like phase determination, structure and microstructure of this particular compound are done. XRD pattern confirmed LN as monoclinic with no preferred orientation. From Raman spectroscopy, we found that crystallization is not uniform and new peaks are appearing. Untraceable phases have been identified from Raman imaging. The broadening of peak width is increasing with increase in temperature. Low frequency modes are due to the Li deficiency sites occupied by Nb ions and higher frequency peaks are due to oxygen displacement. Non stoichiometric phases can be identified from color contrast in Raman imaging. Microwave annealing is a successful method to obtain $LiNb_3O_8$ thin films. Copyright © 2014 VBRI press.

Keywords: $LiNb_3O_8$; Raman imaging; non stoichiometry.

Anil Tumuluri completed his M.Sc from TJPS college, Acharya Nagarjuna University, Guntur. Currently, he is pursuing his Ph.D from Advanced Centre of Research in High Energy Materials, University of Hyderabad. He is working on Ferroelectric thin films for Optical devices and dielectric materials for resonator applications.

K. C. James Raju is a faculty member at School of Physics, University of Hyderabad, Hyderabad. He obtained his Ph.D degree from IIT, Madras. His major research focuses on design and simulation of microwave devices using novel materials, synthesis and characterization of dielectric, ferroelectric and piezoelectric materials. He has more than 80 research papers in the International peer reviewed journals, 2 books and two patents. His group is involved in developing multifunctional materials for high frequency applications. He is a member of editorial board of Science Publishing Group journal: American Journal of Modern Physics. Recently, he got elected as a Life Member of National Academy of Sciences, India.

Introduction

$LiNbO_3$ with its versatile applications in optical industry is one of the most studied material and used in many devices **[1-4]**. But $LiNb_3O_8$ and Li_3NbO_4 are the uninvited guests that appear during the processing of thin film $LiNbO_3$ limiting its applications further **[5]**. It is well known that non-stoichiometric phases of $LiNbO_3$ ([Li]/[Nb]<1) are still to be explored for applications. One such compound is $LiNb_3O_8$ (LN). Several new niobate solid solutions have been explored as microwave dielectrics for LTCC applications. The microwave dielectric properties of $LiNb_3O_8$–TiO_2 ceramics have been investigated by varying sintering temperatures and the amount of TiO_2 **[6]**. Although $LiNb_3O_8$–TiO_2 is a material of interest which is still to be explored, synthesis of single phase $LiNb_3O_8$ is also a difficult task because of the control of volatilization of Lithium. Since microwave annealing heats materials from inside out (volumetric heating)**[7-9]**, resulting in faster heating over a short period of time, application of this method is expected to influence the Li loss. The effect of microwave annealing of $LiNbO_3$ films on the structure and microstructure has not been previously reported. In the present work, effect of microwave annealing on the $LiNbO_3$ which resulted in non stoichiometric $LiNb_3O_8$ has been presented and compared with the results obtained from conventional annealing. The obtained $LiNb_3O_8$ thin films can be used as miniaturized microwave components for wireless communication purposes **[10]**.

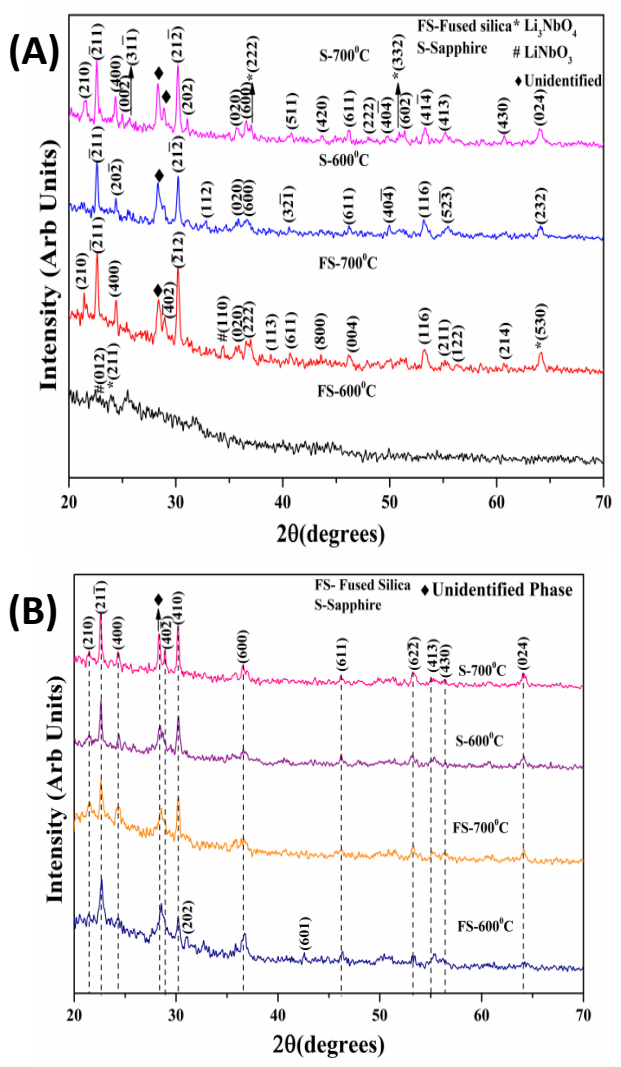

Fig. 1. (A) XRD patterns of conventionally annealed and (B) microwave annealed at different temperatures.

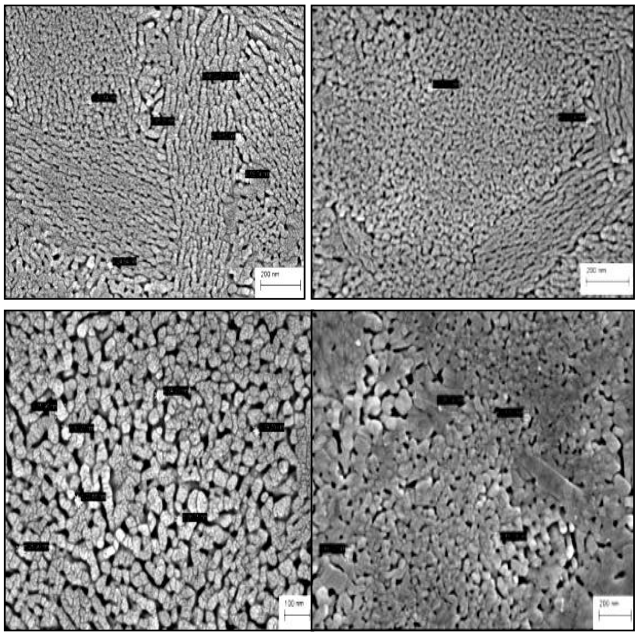

Fig. 2. Microstructure of LN film processed by conventional and microwave annealing.

Experimental

Materials

High Pure $Li(OC_2H_5)$ (1.0M in ethanol) and $Nb(OC_2H_5)$ (99.95%) were procured from Sigma Aldrich. Remaining chemicals (Absolute ethanol, Isopropyl alcohol) were of analytical grade.

Preparation of thin films

The standard route for processing LN films is explained in detail elsewhere **[5]** except that hydrolysis has not been done in the present case. Li (OC_2H_5) and $Nb(OC_2H_5)_5$ in equal molar ratio were dissolved in absolute ethanol and refluxed for 20hr under dry N_2 atmosphere. Substrates were cleaned with Isopropyl alcohol and deionised water and dried. The sol is deposited over fused silica and sapphire substrates using spin coater at 3000rpm for 20sec. After drying, the films were annealed in both conventional and microwave furnaces.

Characterization

The phase analysis is carried out by GI-XRD (Bruker D8 Discover with Cu Kα=1.5405A^o source). The microstructure is observed using FESEM (Carl Zeiss, Ultra 55). Raman scattering experiments were recorded using Nd:YAG 532nm wavelength in the back scattering geometry in a CRM spectrometer equipped with a confocal microscope and 100x objective(1μm diameter focal spot size) with a CCD detector (model alpha 300 of WiTec, Germany).

Results and discussion

Phase confirmation

Fig. 1(A) and **(B)** shows the XRD patterns of LN films. The planes were indexed based on PDF#75-2154, 88-0289 and 75-0907. This confirmed the single phase formation of $LiNb_3O_8$ in case of **Fig. 1(B)**. Sample annealed at 600^{0}C on fused silica is almost amorphous with two distinct phases. (012) peak that corresponds to $LiNbO_3$ has been observed whereby it disappeared with further increase in temperature. The sample annealed at 700^{0}C on fused silica is highly crystalline in nature and almost all the peaks were corresponding to $LiNb_3O_8$ except two. Films annealed at 600^{0}C and 700^{0}C on sapphire are also crystalline with mixed phases of Li_3NbO_4, $LiNb_3O_8$ and untraceable phases. Not only this, it can be observed that the intensity of some peaks is completely suppressed and some new peaks were emerged and there is not particular pattern in the arousal of peaks with increase in temperatures over different substrates. Therefore, from **Fig. 1(A)**, we can confirm that films annealed conventionally have miscellaneous phases of $LiNbO_3$, Li_3NbO_4, $LiNb_3O_8$ and untraceable phases. The reason behind this may be due to the evaporation of Li content and the heating programs. **Fig. 1(B)** is the XRD patterns of the microwave annealed samples. It has been observed that there are no mixed phases and as temperature is increasing the intensity of the peak also got increased irrespective of the substrate. It can also be inferred that the nature of substrate has no influence on the crystallinity of the film. All peaks are exactly matching with Monoclinic

$LiNb_3O_8$. There is no observable changes occurred with the increase in temperature. In conclusion, Films did not show any preferred orientation. Non stoichiometry by way of Li loss is observed in the films with increase in temperature which leads to the formation of $LiNb_3O_8$.

Microstructure

Microstructure of the films annealed with conventional (**Fig. 2**) and microwave revealed nano grains with highly porous inter and intra granular structures. Microwave annealed films have grain size ranging from 20-80nm. From microstructure, it can be confirmed that the grains are oriented in different directions. This random orientation is observed only in the case of films deposited on fused silica which is amorphous. Films annealed on sapphire also have intra granular porosity but the grains are not randomly oriented as in the case of fused silica. This confirmed that the films are highly oriented in the case of single crystal substrate. The grain orientation is highly dependent on the nature of the substrate. But, the grain structure and size of the films does not change with the nature of the substrate i.e., either amorphous or crystalline.

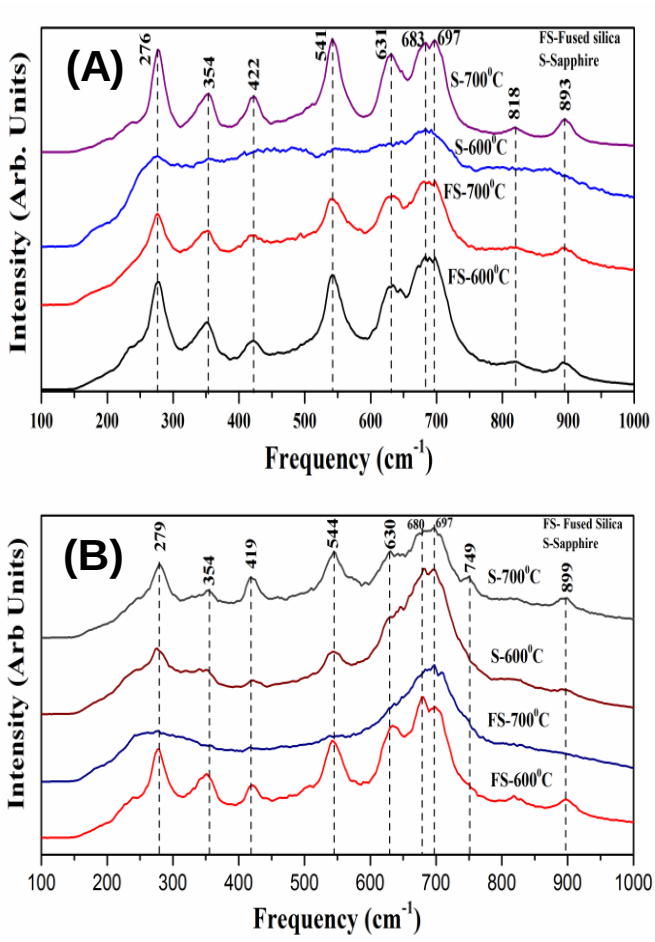

Fig. 3. (A) Raman Spectra of conventionally annealed and (B) Microwave annealed at different temperatures.

Raman spectroscopy

Raman spectroscopy is sensitive to the deformation of the lattice and to the presence of defects in crystal. Several studies reported the stoichiometry variation from half widths of Raman modes **[9]**. We have obtained the Raman spectra of samples in order to study the changes in the peak widths and shifts induced by the lack of stoichiometry. Raman Spectra for all the films annealed conventionally and microwave have given in **Fig. 3**. Films annealed using fused silica substrates are well crystallized and there in no observable peak shift with increase in temperature. But, in case of sapphire the crystallization in not uniform at 600^{0}C and intensity of the peaks were not good when compared with film annealed at 700^{0}C. Microwave annealed films are well crystalline and there is no observable peak shift or broadening with change in substrate or temperature. In order to study in more detail, Raman spectra have been taken at different spots in a single film. Interestingly, the color contrast in the image has been observed indicating the non uniform crystallization. The detailed analysis of the Raman modes taken at different spots is discussed further.

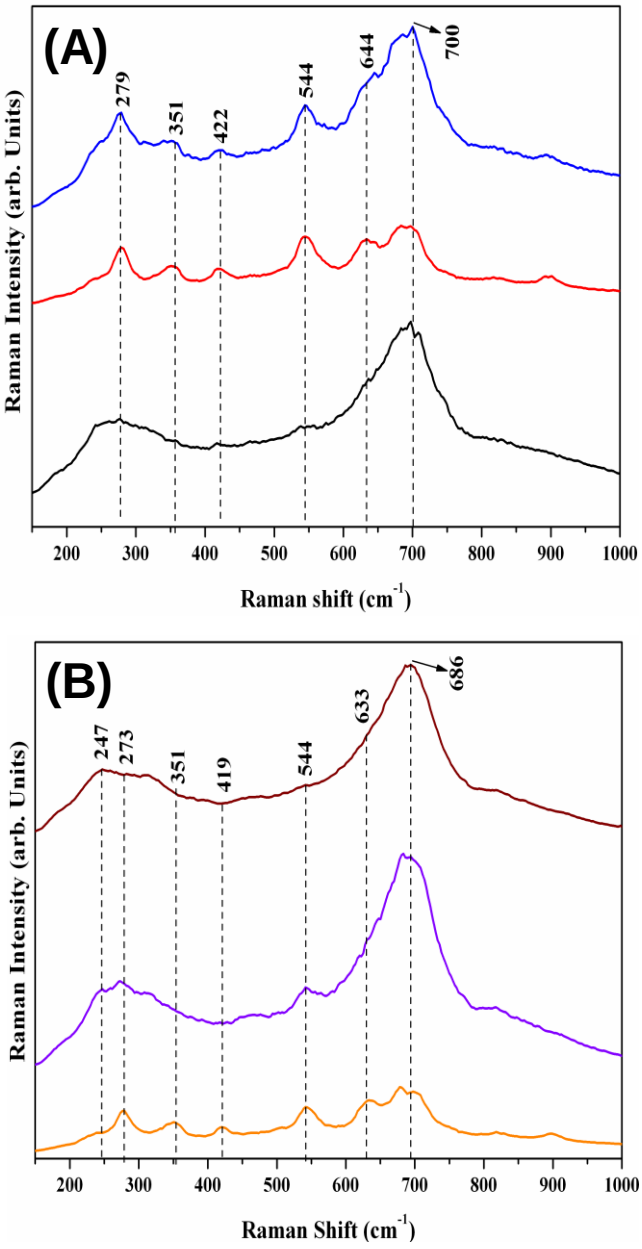

Fig. 4. (A) Conventional annealed at 600^{0}C and (B) Microwave annealed at 600^{0}C.

The examination of **Fig. 4(A)** reveals that the films annealed at 600^0C is not uniformly crystallized. As the [Li]/[Nb] ratio in the crystal increases, the widths of the phonons decrease and new peaks appear at one or both sides of the previous phonon peak. This confirms the presence of $LiNb_3O_8$, as [Li]/[Nb] ratio increases from $LiNbO_3$ to $LiNb_3O_8$. In **Fig. 4(B)**, the width of the phonons increases where only two broad peaks at 247 and 686cm^{-1} has been observed.

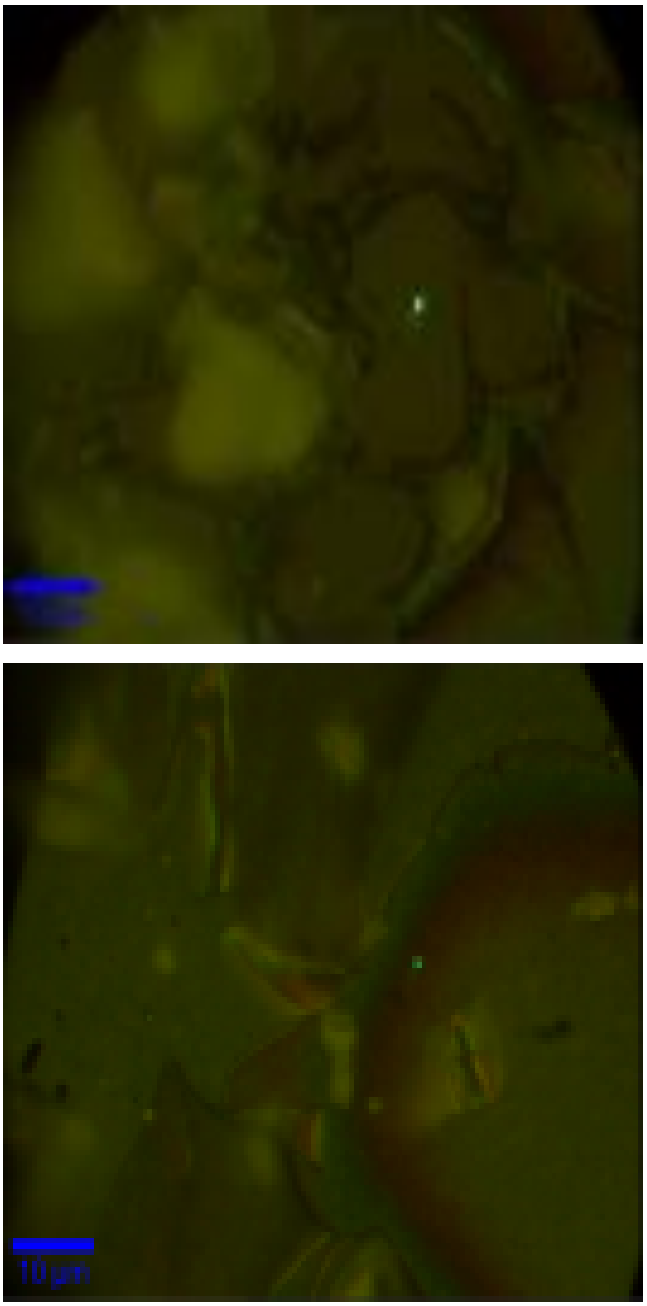

Fig. 5. Color contrast observed in Raman imaging.

The width of all modes is decreasing with increase in temperature. This confirms the stoichiometric deviation of [Li]/[Nb] from 1. This may be either due to the concentration of defects or occupancy of Nb at Li sites. It is well known that the Nb-O bond is stronger than Li-O bond. In the non stoichiometric samples, due to the Li evaporation, Nb^{5+} will occupy Li^+ sites and a corresponding number of Li^+ and Nb^{5+} vacancies will be created in order to attain stability.

Fig. 6 shows the Lorentz fit for Raman modes. The peaks were clearly fitted well except a noticeable shift at 424cm^{-1}. A slight shift is observed for 424cm^{-1}, while the frequencies of the other peaks remain unchanged. Observable color contrast in **Fig. 5** (green, light green and brown) supports the presence of inhomogeneous phases apart from $LiNb_3O_8$ that cannot be traced out from XRD.

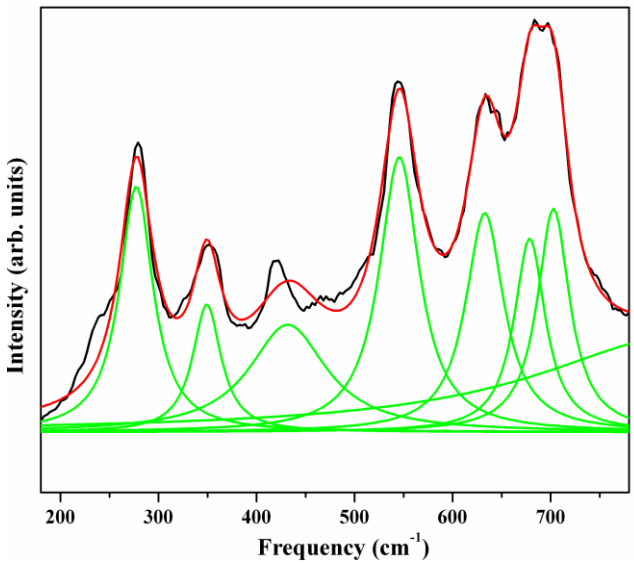

Fig. 6. Lorentzian fit for Raman peaks.

The low frequency modes are associated with Nb ion movements where a Li ion is replaced by an Nb ion. Then its neighboring oxygen ions increase their bonding force with Nb because of the stronger electrostatic interaction between Nb and oxygen. The changes with the higher frequency modes at 633cm^{-1} could be the result of this changed local lattice for some of the oxygen ions with the replacement of Li with Nb **[10]**. The oxygen ion movement not only perturbs the Li-O bond but also Nb-O bonds. Since Nb-O bond is stronger than Li-O bond, the higher frequency phonon modes are highly sensitive to the extra Nb ions located at Li sites. A peak at higher frequency (670-700cm^{-1}) is appearing in each spectra with increasing intensities (**Fig. 4 (A)** and **(B)**) indicating the deviation from stoichiometric composition. It is brought out by a Lorentzian fit of the Raman peaks. This may be due to the oxygen displacement that leads to Nb-O bond stretching **[10]**. When an Nb ion sits at a Li site, its nearest oxygen ions increase their bonding forces because of the strong electrostatic interaction.

Conclusion

LN films have been annealed using both conventional as well as microwave. Microwave annealing aided in rapid thermal treatment. Also, microwave annealing is one of the methods to employ for acquiring single phase $LiNb_3O_8$ thin films for LTCC applications. Microstructure of the film annealed on fused silica gave random grain orientation whereas the film annealed on sapphire has avoided the

random orientation. Thus, the nature of substrate affects the grain growth. But, no effect of substrate has been observed on structure that can be confirmed using XRD. Undetectable minor phases can be traced out using both Raman spectra and imaging. Raman spectra revealed the film has both stoichiometric and Li-deficient as well as Li_2O, NbO_6 octahedra phases where it is not possible to detect with XRD.

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