# Third order nonlinearity in pulsed laser deposited LiNbO3 thin films

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Citation: AIP Conference Proceedings **1728**, 020365 (2016); doi: 10.1063/1.4946416
View online: http://dx.doi.org/10.1063/1.4946416
View Table of Contents: http://scitation.aip.org/content/aip/proceeding/aipcp/1728?ver=pdfcov
Published by the AIP Publishing

# Third order nonlinearity in pulsed laser deposited $LiNbO_3$ thin films

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**Abstract.** Lithium niobate ($LiNbO_3$) thin films were prepared using pulsed laser deposition technique. Structural properties of the same were examined from XRD and optical band gap of the thin films were measured from transmittance spectra recorded using UV-Visible spectrophotometer. Nonlinear optical properties of the thin films were recorded using Z-Scan technique. The films were exhibiting third order nonlinearity and their corresponding two photon absorption, nonlinear refractive index, real and imaginary part of nonlinear susceptibility were calculated from open aperture and closed aperture transmission curves. From these studies, it suggests that these films have potential applications in nonlinear optical devices.

## INTRODUCTION

Lithium niobate ($LiNbO_3$) with its distinct features possess unique combination of versatile properties like non-linear optical, piezoelectric, ferroelectric, electro-optical, pyroelectric by making this material suitable for wide range of applications like non-linear optical devices, transducers, electro optic modulators and pyroelectric sensors [1]. The phenomenal growth of $LiNbO_3$ crystal for versatile applications encouraged for further studies till date. Research on single crystal X-cut, Y-cut and Z-cut $LiNbO_3$ are highly in demand to meet the device structures and the performance can be enhanced with oriented single crystal of $LiNbO_3$ [1].

Reports on deposition of $LiNbO_3$ thin films using different techniques like sol-gel, RF magnetron sputtering, pulsed laser deposition is widely available [2]. Most of the literature explains the optimization of conditions for the successful deposition of stoichiometric $LiNbO_3$ thin films. Epitaxial growth of $LiNbO_3$ thin films with ZnO as buffer layer is meagre. $LiNbO_3$ is well known for its second order nonlinearity and several groups reported the enhancement of nonlinearity using different techniques [3]. But, third order nonlinear optical properties of $LiNbO_3$ thin films have not been explored much [3].

In the present paper, deposition of $LiNbO_3$ thins films and their third order nonlinear optical properties measured from femtosecond Z scan technique was explained in detail.

## EXPERIMENTAL

The $LiNbO_3$ target of one inch diameter was prepared from commercially available $LiNbO_3$ powder (Alfa aesar, 99.99% purity) with 5wt% of $Li_2CO_3$ (Sigma Aldrich, 99.99% purity) addition for Li loss compensation. The $LiNbO_3$+$Li_2CO_3$ mixture is pressed using Poly Vinyl Alcohol (PVA) as binder followed by sintering at 1100 $^oC$ for 2h. Al:ZnO (Al:0.5 wt%) target of 1 inch diameter was prepared by ball milling $Al_2O_3$ (Alfa aesar, 99.9% purity) and ZnO (Sigma Aldrich, purity) and pressing with PVA as binder followed by sintering at 900 $^oC$ for 2 h. These densified targets were mounted on to a rotating target holder that can accommodate maximum of 6 targets by maintaining the target to substrate distance fixed to be 5 cm. The fused silica and quartz ($SiO_2$) substrates were

*International Conference on Condensed Matter and Applied Physics (ICC 2015)*
AIP Conf. Proc. 1728, 020365-1–020365-5; doi: 10.1063/1.4946416
Published by AIP Publishing. 978-0-7354-1375-7/$30.00

cleaned by ultrasonication in acetone and then dried to get impurity free substrate wafers. These substrates were mounted on to substrate holder facing target with an angle of $180^{o}$ to get maximum plume condensed on to the wafer. The chamber (Excel instruments, India) is initially evacuated to a base pressure of ~ $4\times10^{-6}$ mbar. Initially ZnO target is ablated with fused silica and Z-cut $SiO_2$ substrates followed by $LiNbO_3$ deposition. In the present case, KrF excimer laser (λ=) was used.

The structural studies of deposited thin films were confirmed from GI-XRD (BRUKER). The optical transmission spectra of all the films were recorded using UV-Vis-NIR spectrophotometer. Nonlinear optical properties of all the thin films were measured using Z-Scan with femtosecond laser pulses.

## RESULTS AND DISCUSSION

### XRD

The XRD patterns recorded for the films were given in fig. 1. The film deposited on fused silica is found to be polycrystalline in nature (JCPDS diffraction file # 880289). Similarly, the film deposited on $SiO_2$ substrate with Al:ZnO as buffer layer is found to be (300) oriented and is highly crystalline. Al:ZnO acts as a nucleating center for the growth of $LiNbO_3$ in (300) orientation [4]. Al:ZnO is found to be (002) oriented and deposition of $LiNbO_3$ thin film is deposited under minimal stress. Growth of $LiNbO_3$ depends up on various factors such as laser fluence, substrate temperature and partial pressure. The optimized parameters were given in table 1.

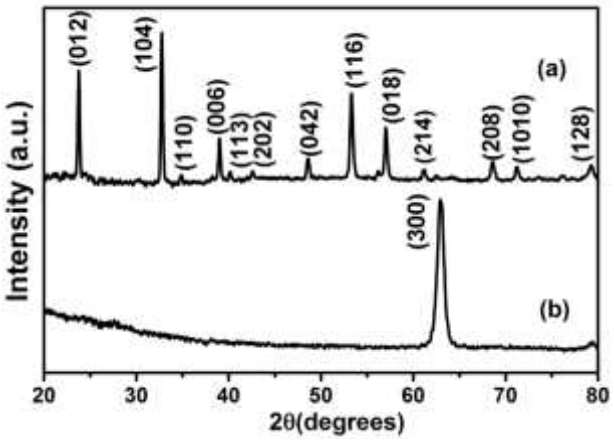


**FIGURE 1.** XRD patterns of (a) LN deposited on fused silica and (b) LN deposited on $SO_2$ with ZnO as buffer layer.

### Linear and nonlinear optical properties

The linear optical properties of $LiNbO_3$ thin films were analyzed from optical transmission spectra. As shown in fig. 2, the film is highly transparent with transmittance around 80% in visible region. The oscillations in the spectra confirm that the films are smooth and possess uniform thickness. The thickness of the films was given in table 1.The optical band gap ($E_g$) of the films was determined from Tauc's plot.

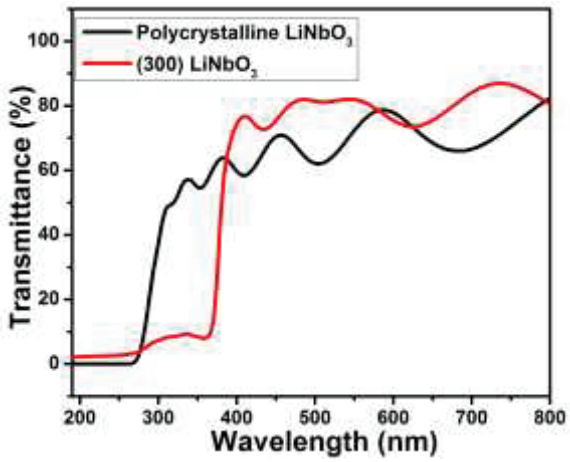


**FIGURE 2.** Transmission spectra of LN thin films

Although literature on band gap of $LiNbO_3$ is plenty, reports on direct and indirect band gap is to be explored more. Anil et.al, deposited $LiNbO_3$ thin films using RF magnetron sputtering and found that band gap varying with change in grain size [5]. Reports on variation in band gap of $LiNbO_3$ were proposed by several authors both theoretically and experimentally [6]. The determination of optical band gap is obtained by Tauc's equation [5]. From fig. 2, it can be inferred that the band gap of LN thin film in case of polycrystalline is around 4.3 eV and red shifted in case of (300) LN which is observed to be 3.9 eV. The decrease in band gap is due to the change in orientation of the film from polycrystalline to (300).

$$\alpha h\nu = A(h\nu - E_g) \tag{1}$$

Where A is a constant
hν is photon energy
$E_g$ is the allowed energy gap
n=1/2 for allowed direct transitions
n=2 for allowed indirect transitions

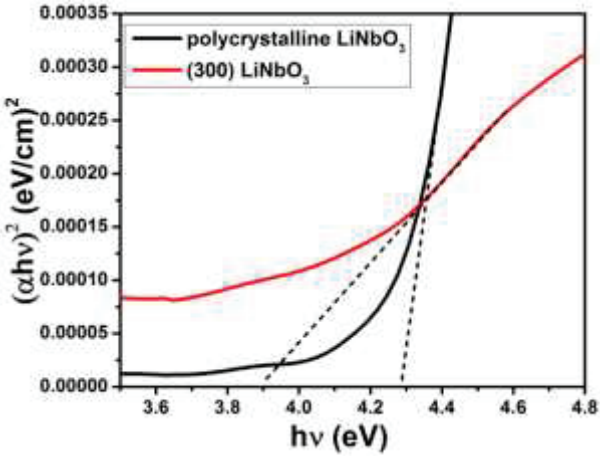


**FIGURE 3.** Tauc's plot for LN thin films

To measure the optical nonlinearities of $LiNbO_3$ thin films, a standard Z-scan technique was employed. For these studies, a tunable Ti:Sapphire femtosecond laser (Chameleon, Coherent) with 150fs,80MHz and 800nm wavelength was used. The experimental details have been reported previously [7]. Fig. 4 displays the OA and CA Z-scan curves of $LiNbO_3$ films deposited on fused silica and quartz. The substrate nonlinearity is subtracted for both the films. The OA Z-scan curve is fitted to the two photon absorption given by the following equation using sheik bahae model [7]

$$T(z) = 1 - \frac{\beta I_o L_{eff}}{2\sqrt{2}(1 + Z^2 / Z_o^{\,2})} \tag{2}$$

β- third order nonlinear absorption coefficient
$L_{eff} - [1\text{-}\exp(-\alpha_o L)]/\ \alpha_o$ is the effective length.
Z is the position of sample
$Z_o$ is the Rayleigh range.

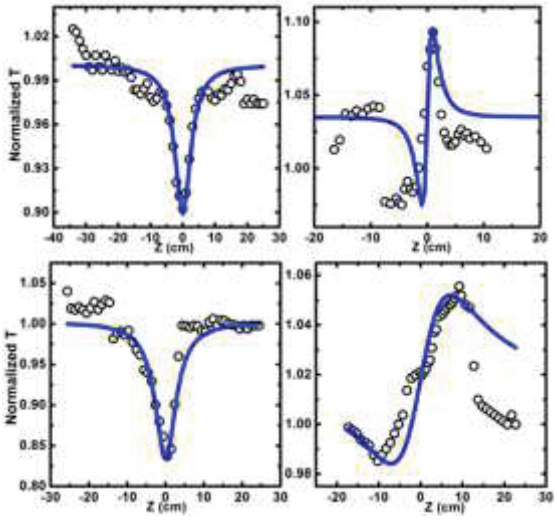


**FIGURE 4.** OA and CA curves for LN thin films

Reverse saturable absorption (RSA) is observed in both films. The optical band gap of both the films were 4.3 and 3.9 eV which satisfies $2h\nu<E_g<3h\nu$ ($h\nu$=1.55 eV is the energy corresponding to laser wavelength of 800 nm), suggesting an indirect two photon absorption via intermediate defect states [8]. In $LiNbO_3$, the defect states are mainly attributed to the antisite defects like Nb replacement in Li site and oxygen vacancies [8]. The CA Z-scan curve is fitted using the following equation for positive nonlinearity.

$$T(z) = 1 + \frac{4x\Delta\Phi_0}{(x^2 + 9)(x^2 + 1)} \tag{3}$$

Where $x=z/z_0$,
Z is the position of the sample
$Z_0$ is the Rayleigh range
$\Delta\Phi_0=2\pi n_2 I_0 L_{eff}/\lambda$ is the phase modulation
$n_2$ is third order nonlinear refractive index

The nonlinear refractive index was estimated from closed aperture Z-scan. Nonlinear optical coefficients like real and imaginary parts of susceptibility, nonlinear refractive index were tabulated in table 1. The nonlinear refractive index of the films is due to third order polarization ($P^{(3)}$) in $LiNbO_3$ [8].

**TABLE 1.** Deposition conditions and nonlinear optical parameters calculated from OA and CA curves of LN thin films

| Sample/ Thickness (nm) | $T_s$(°C) | Femtosecond laser power (mW) | β (cm/W) $\times 10^{-8}$ | $n_2$ ($m^2$/W) | Re$\lvert\chi^{(3)}\rvert$ (esu) | Im$\lvert\chi^{(3)}\rvert$ (esu) | $\lvert\chi^{(3)}\rvert$ (esu) |
|---|---|---|---|---|---|---|---|
| Poly LN/613 | 600 | 3 | 125 | $1.7\times10^{-13}$ | $2.2\times10^{-15}$ | $1.2\times10^{-9}$ | $1.0\times10^{-9}$ |
| (300) LN/963 | 500 | 3 | 165 | $1.1\times10^{-16}$ | $1.4\times10^{-10}$ | $1.3\times10^{-9}$ | $1.3\times10^{-9}$ |

In conclusion, $LiNbO_3$ thin films were deposited using pulsed laser deposition. Third order nonlinear susceptibility of the films was investigated from Z-scan technique at a wavelength of 800 nm. Positive nonlinearity is observed for polycrystalline $LiNbO_3$ and (100) $LiNbO_3$. The two photon absorption is observed with indirect transitions via intermediate defect states. The high optical transparency and third order optical nonlinearity show that $LiNbO_3$ thin films are promising candidate for nonlinear photonic devices.

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