Influence of Defects States on the Nonlinear Absorption Mechanism in ZnO and Li doped ZnO Thin films

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***Abstract*: The role of substitution of Li atoms at different ratio (1, 2 at wt%) on the linear and third order nonlinear optical (NLO) properties of ZnO films is revealed in the present work. The interstitial sites in the ZnO crystal structure are occupied by the Li^+ ions with increasing doping ratio. The redshift in energy gap confirms the existence of extended defect levels below the conduction band. The open aperture Z-scan experiment revealed the reverse saturable absorption mechanism in all the films. The values of nonlinear absorption coefficient are decreased with increasing doping ratio which confirms the ground state bleaching due to the enhanced defect states. The Li doped ZnO films possess optical parameters suitable for NLO applications.**

***Keywords: Compressive stress, Redshift, RSA, Nonlinear absorption coefficient, Optoelectronics*.**

I. INTRODUCTION

Semiconducting materials exhibiting nonlinear optical (NLO) properties are very widely studied by many researchers [1].The higher order of nonlinear parameters such as nonlinear absorption coefficient (β), nonlinear susceptibilities and the stability of semiconductors attracted industries and researchers since few decades. ZnO is a group II-VI semiconducting material which exhibits higher order nonlinearity as well as structural stability [2]. Many authors have studied the NLO properties of ZnO employing single beam z-scan technique [3,4]. In general, the open aperture Z-scan experiment is adopted to study the reverse saturable absorption (RSA) mechanism in ZnO. However, there are only few study accounted for the saturable absorption (SA) mechanism due to enhanced defect states [reference]. Thus, the internal electronic structure of the ZnO is vital in order to understand the NLO properties. In the present study, the role of different doping concentration (1 at wt% and 2 at wt%) on the NLO properties of Li doped ZnO (LZO) films are investigated. The effect of doped Li^+ ions on the values of β and $\chi_i^{(3)}$ are explained using XRD, UV-VIS spectroscopy and Z-scan experiments. The present study identifies the possible application of LZO films in optoelectronics.

II. Materials and Methods

The undoped and LZO films were prepared using simple sol-gel spin coating technique. The initial precursor solution consists of a starting material (Zin acetate dehydrate), solvent (2-methoxy ethanol), and stabilizer (MEA). Lithium hydroxide hexahydrate was used as a source for Li dopant. The dopant ratio of Li was 1 at wt% and 2 at wt%. The films were prepared using the procedure followed by Jyothi *et al* [5]. The films were fabricated on amorphous corning glass substrates at 4000 rpm. Each layer was pre annealed at 150˚C for ten minutes followed by a post annealing at 500˚C for one hour. All the films were coated 5 times to achieve uniform thickness in all the films. The prepared films were characterized by X-ray diffraction and UV-Vis spectral technique, and Z-scan measurements.

III. RESULTS AND DISCUSSION

Figure 1 shows the crystallinity and phase formation of ZnO and LZO films with various doping ratio. All the films exhibit the poly crystalline nature. The major preferred orientation in all the films is (002) plane (or c-axis). The intensity of the c-axis is observed to be enhanced as the Li doping ratio is increased which suggest enhancement in film quality upon doping Li into ZnO matrix. However, the orientation of grains along (102) and (110) also been observed at higher doping ratio indicates polycrystalline nature of the film. All the planes identified from the XRD spectra confirm the hexagonal wurtzite structure of the films. No other peaks except peaks related to wurtzite structure in all the films clearly represent the absence of secondary phase formation. However, the diffraction angle related to c-axis has variations compared to the bulk ZnO sample (34.42°). The undoped ZnO film has higher diffraction angle (34.45°) while doping Li, the diffraction angle shift towards lower angles (34.41° and 34.39° in 1%LZO and 2%LZO respectively). This shift towards lower angle compared to bulk material is due to the increased lattice constants in the films. The increased lattice constant is attributed to the interstitial sites occupied by the Li^+ ions in the ZnO matrix. Also, the authors of [6] reported that the increased lattice constant leads to the compressive stress in ZnO films. The values of compressive stress are calculated using the equation,

$$\varepsilon = -233\left(\frac{c - c_0}{c_0}\right) \text{ [Gpa]}$$

Where c is the calculated lattice parameter of the samples, and c_0 is the unstrained lattice parameter of the bulk ZnO. Thus, from the calculated values of the stress, undoped ZnO film shows tensile stress (positive value) where LZO films show compressive stress (negative value). The compressive stress in LZO films leads to the generation of defects.

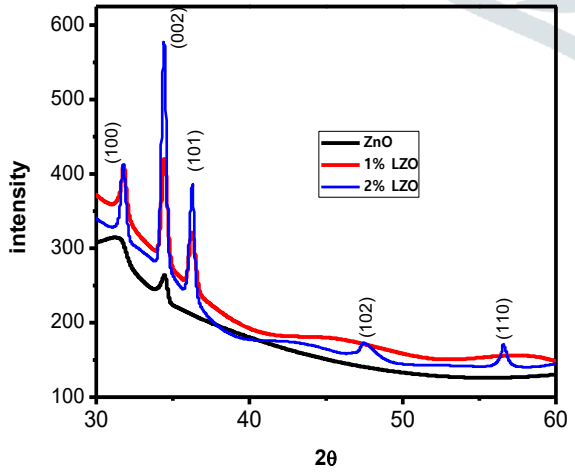


FIG 1. XRD spectrum of the films

The authors of [7] have observed the similar mechanism in Mn doped ZnO nanorods and they attributed this to the enhanced defects in the nanostructures. The enhanced

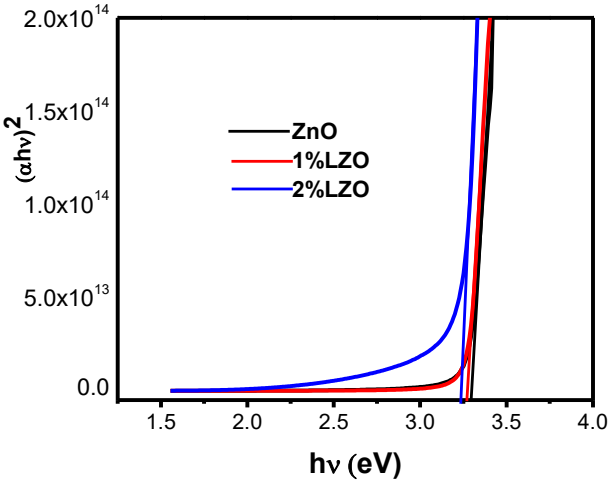


FIG 1. Energy gap determination of the prepared films.

The energy gap of the films is calculated using Tauc plot. The energy gap values are redshift as the doping ratio is increased. The decreased band gap in the films is due to the formation of extended states below the conduction band. The extended states below the conduction band act as defect states. This leads to the shrinkage of band gap. To understand the role of defect states in the LZO films Urbach energy is calculated. The increased Urbach energy with increasing Li doping ratio clearly suggest the enhanced defect states in the LZO films.

Single beam Z-scan technique (open aperture) [2] is performed in order to extract β and $\chi_i^{(3)}$ values. The source used was Nd:YAG laser with pulse width 7ns and wavelength 532 nm. From the fig. 3a, b and c it is observed that all the films show RSA mechanism. RSA is the representation of positive two photon absorption coefficient (β). A theoretical fit to the open aperture curve is performed using the equation

$$T(Z) = 1 - \frac{\beta I_0 L_{eff}}{2^{2/3}(1 + x^2)} \qquad 1$$

Where I_0 represents the on-axis irradiance at focus and L_{eff} is effective length of the sample given by,

$$L_{eff} = \frac{(1 - e^{-\alpha L})}{\alpha},$$

Where α and L represent absorption coefficient and thickness of the samples respectively.

From Table 1, the values of β showed inverse trend with Li doping ratio in LZO film. This shows that the doping of Li affects the RSA process. This is the result of enhanced defects in the LZO films.

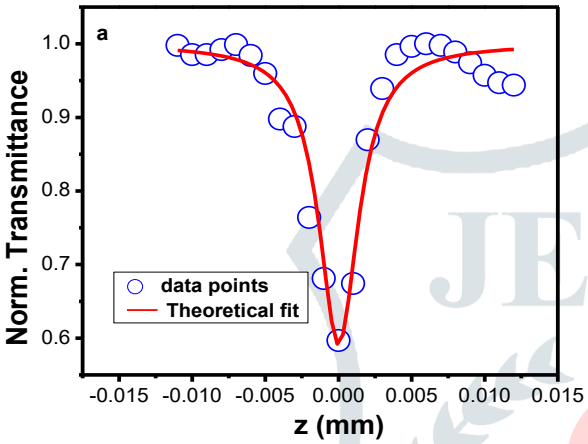
defect levels in LZO films have longer lifetime and these defect levels trap the carriers. This, in turn, results in the depletion of carriers in the ground states and increases the number of carriers in the higher states and thus the RSA

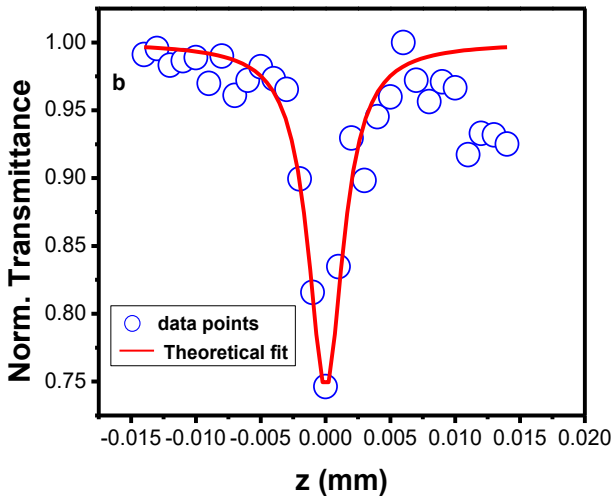
behavior decreases in the doped LZO films. Thus, the decrease in the value of valley in the LZO films is attributed to the dominant bleaching of ground state carriers due to the carrier trapping at the defect states present in the band structure.

The imaginary components of the nonlinear susceptibility are calculated using the expression

$$\psi_i^3(esu) = \frac{(\varepsilon_0 c^2 n_0^2 \lambda)}{4\pi^2} \beta(m/W),$$

The calculated values showed the linear dependence of imaginary components of nonlinear susceptibilities with two photon absorption coefficient.





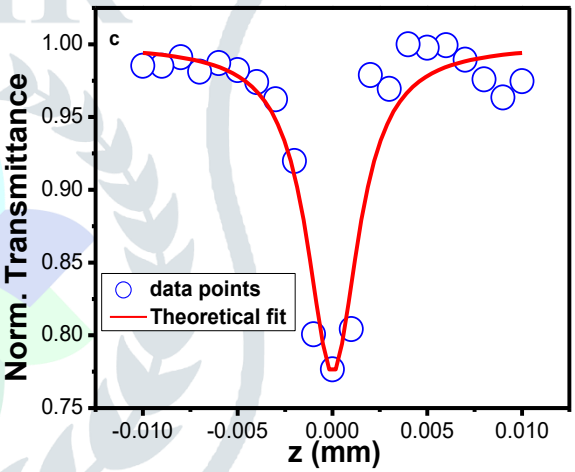


FIG 3. Z-scan open aperture curves of (a) ZnO (b) 1% LZO and (c) 2%LZO films.

TABLE 1. The structural and optical parameters of prepared films

Sample	ε (GPa)	E_g (eV)	E_U (meV)	β (m/W)	$\chi_i^{(3)}$ (esu)
ZnO	0.245	3.30	74.18	5.80×10^{-7}	2.49×10^{-8}
1%LZO	-0.0166	3.27	85.64	3.63×10^{-7}	1.56×10^{-8}
2%LZO	-0.1480	3.23	98.17	1.42×10^{-7}	0.61×10^{-8}

IV. CONCLUSIONS

An effective sol-gel spin coating fabrication techniquw was employed to prepare undoped and Li doped ZnO thin films at optimal conditions. The XRD analysis showed the compressive stress in LZO films. The increased Li doping ratio resulted in enhanced defect levels in the band structure. The presence of extended states below the conduction band edge resulted in the redshifting of band gap in LZO film. The open aperture Z- scan measurements showed RSA mechanism in all the films. The enhanced defect levels in the Li doped ZnO films results in saturation of linear absorption. The nonlinear absorption

coefficient is decreased with increased Li concentration. Thus, the prepared films are the potential candidates for NLO devices.

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REFERENCES

1. Wang Z L, J. Phys. Condens. Matter, 2004, **16**, R82.
2. Brown M P and Austin K, *Appl. Phys. Letters, 2004* **85**, 2503–2504.
3. Nagaraja K K, Pramodini S, Santhosh Kumar A, Nagaraja H S, Poornesh P, and Kekuda D, *Opt. Mater*. **35**, 431 (2013).
4. Zhang X, Fang H, Tang S, and Ji W, *Appl. Phys. B Lasers Opt*.,1997 **65**, 549.
5. Irimpan L, Deepthy A, Krishnan B, Kukreja L M, Nampoori V P N, and Radhakrishnan P, *Opt. Commun*., 2008 **281**, 2938.
6. Serrao F J, Sandeep K M, and Dharmaprakash S, *J. Sol-Gel Sci. Technol*. (2016). doi:10.1007/s10971-016-3958-7.
7. S. Saha and V. Gupta, *J. Appl. Phys*. **110**, (2011).
8. Singh A, Kumar S, Das R, Sahoo P K, *Rsc adv*. **5**, 88767 (2016).