Methodical engineering of defects in Mn$_x$Zn$_{1-x}$O ($x = 0.03$, and 0.05) nanostructures by electron beam for nonlinear optical applications: A new insight

Albin Antony$^a$, P. Poornesh$^{a,*}$, I.V. Kityk$^b$, K. Ozga$^b$, J. Jedryka$^b$, Reji Philip$^c$, Ganesh Sanjeev$^d$, Vikash Chandra Petwal$^e$, Vijay Pal Verma$^e$, Jishnu Dwivedi$^e$

$^a$ Department of Physics, Manipal Institute of Technology, Manipal Academy of Higher Education, Manipal, Karnataka, 576104, India
$^b$ Institute of Optoelectronics and Measuring Systems, Faculty of Electrical Engineering, Czestochowa University of Technology, Armii Krajowej 17, PL-42-201, Czestochowa, Poland
$^c$ Light and Matter Physics, Raman Research Institute, C. V. Raman Avenue, Sadashivanagar, Bengaluru, 560 080, India
$^d$ Department of Physics, Mangalore University, Mangalore, Karnataka, 574199, India
$^e$ Industrial Accelerator Section, PSIAD, Raja Ramanna Centre for Advanced Technology, Indore, 452012, M.P, India

ABSTRACT

A series of Mn$_x$Zn$_{1-x}$O ($x = 0.03$, 0.05) nanostructures have been grown via the solution based chemical spray pyrolysis technique. Electron beam induced modifications on structural, linear and nonlinear optical and surface morphological properties have been studied and elaborated. GXRD (glancing angle X-ray diffraction) patterns show sharp diffraction peaks matching with the hexagonal wurtzite structure of ZnO thin films. The upsurge in e-beam dosage resulted in the shifting of XRD peaks (101) and (002) towards lower angle side, and increase in FWHM value. Gaussian deconvolution on PL spectra reveals the quenching of defect centers, implying the role of electron beam irradiation regulating luminescence and defect centers in the nanostructures. Irradiation induced spatial confinement and phonon localization effects have been observed in the films via micro Raman studies. The later are evident from spectral peak shifts and broadening. Detailed investigations on the effect of electron beam irradiation on third order nonlinear optical properties under continuous and pulsed mode of laser operation regimes are deliberated. Third order absorptive nonlinearity of the nanostructures evaluated using the open aperture Z-scan technique in both continuous and pulsed laser regimes shows strong nonlinear absorption coefficient $\beta$ of the order $10^{-4}$ cm/W confirming their suitability for passive optical limiting applications under intense radiation environments. Laser induced third harmonic generation (LITHG) experiment results supports the significant variation in nonlinearities upon electron beam irradiation, and the effect can be utilized for frequency conversion mechanisms in high power laser sources and UV light emitters.

1. Introduction

In the past few decades wide band gap semiconductors (WBG) materials have attracted much interest due to its applications in optics and solid state electronics [1–3]. Among the widely investigated WBG semiconductor materials ZnO belonging to II-VI group with energy band gap of 3.36eV has gained a lot of studies due to possible applicability in various fields especially as a perspective material for ultrafast UV light modulators and near-UV emitters [1–6]. The devices based on nonlinear optical effects are at pressing need. The available conventional nonlinear optical materials have reached its technical limit. Furthermore there is a demand for nanostructured nonlinear optical materials which can be easily integrated into nonlinear optical devices [6–11]. It’s important for future optoelectronics and photonics to search and design of new nonlinear optical materials with large nonlinear optical responses [9–10]. These new materials seems to be promising and enable novel devices with high performance and new functionalities like reduced cost of production, easily downscaling to industry standards and enhanced performance etc... Studies related to the nanostructured ZnO thin films [12,13] pointed out that this material exhibits a strong and efficient second and third harmonic generations. But in order to meet the requirements of cutting-edge nonlinear optical devices with reduced cost and better-quality performance, the traditional physical and chemical properties and method of synthesis of ZnO...
nanostructures should be modified.

In the present study host ZnO lattice was doped by Mn with different concentration. Mn has the advantage because of its half-filled 3d orbitals which aids its incorporation into the ZnO lattice and relatively comparable ionic radii between Zn$^{2+}$ and Mn$^{2+}$ [14]. Another point to be highlighted is the method of thin film deposition and choice of substrate. Different method of thin film synthesis led to different growth behavior, hence different physical properties and thus nonlinear behavior of the samples can also be varied. In the present study we employed solution based air assisted spray pyrolysis technique [15] for the growth of Mn$_{1-x}$Zn$_x$O nanofilms. It is a cost-effective, scalable and well explored method to grow Mn$_{1-x}$Zn$_x$O nanostructures from aqueous salt solutions of Mn and Zn. It allows a large range of diverse geometries by wafering the films growth conditions [16]. Furthermore the chemical and physical properties of the deposited films can be tailored by imposing various external conditions such as substrates, annealing temperature, strain, electric and magnetic field, electron and ion beam irradiations [17,18] etc. Up today there are no reports concerning the influence of energetic electron beam irradiation on nonlinear optical properties of Mn$_{1-x}$Zn$_x$O nanostructures. Therefore, investigating irradiation induced effects and subsequently en-hancing or modulating the physical and chemical properties of Mn$_{1-x}$Zn$_x$O thin film is significant to understand and further modification of the materials for nonlinear optical device applications such as frequency converters, optical limiters, modulators, triggers etc... Herein the effect of 8 MeV electron beam irradiation on third order optical susceptibilities for Mn$_{1-x}$Zn$_x$O nanostructures were studied and elaborated for the first time. The electron beam induced modifications in linear optical, morphological, and structural properties of the films were studied via Glancing angle X-ray diffraction(GXRD), Atomic force microscopy (AFM), Photoluminescence and Raman spectroscopy.

2. Experimental details

2.1. Thin film preparation

To grow Mn$_x$Zn$_{1-x}$O thin nanocrystalline films with Mn concentration(X) of 3% and 5% we implemented a cost effective spray pyrolysis film growth technique [15]. Appropriate proportions of powders of Zinc chloride and Manganese chloride tetra hydrate were dissolved in a 1:3 solution of ethanol and double distilled water. The molar content of the solutions were fixed to be 0.05M. The prepared Mn dopant solution were added to host solution by prefixing the dopant concentration as 3% and 5%. The deposition parameters followed for the growth of Mn$_x$Zn$_{1-x}$O thin films were reported elsewhere [15].

2.2. Characterization

The physical properties such as structural, linear optical and morphological features for deposited films were studied using various characterization tools. The morphological changes in the Mn$_{1-x}$Zn$_x$O (x = 0.03, 0.05) thin nanofilms were studied using Bruker Icon Atomic force microscopy (AFM). The variations of the topological parameters were done using Bruker Nanoscope analysis software. Electron beam simulated with respect to crystallinity, orientation and other structural parameters were analyzed by X-ray diffractometer (GXRD) within a 2θ range of 20$^\circ$-80$^\circ$. Shimadzu 1800 UV-Visible spectrophotometer were applied for linear absorption spectra measurements. The non-radiative and radiative recombination in the grown films were investigated by Raman spectroscopy (Horiba JOBINYVON LabRAM HR) and Photoluminescence spectroscopy (Horiba Fluoromax-4 Spectrofluorometer).

2.3. Open aperture Z-scan technique

Open aperture Z-scan measurement were applied to study the third order nonlinearity of the deposited films [19,20]. The measurements have been executed both in continuous as well as pulsed laser regimes. The excitation source used for the measurement in continuous wave regime was He-Ne laser with a wavelength of 632.8 nm and input power of 20 mW. The pulsed regime measurements were carried out using Continuum Minilite IQ-switched Nd: YAG laser with nanosecond pulses (532 nm, pulse energy 100 μJ, pulse duration 5ns, pulse fre-queency repetition 10Hz).

2.4. Third harmonic generation

An Nd-YAG fundamental laser with 8 ns pulse duration, 1064 nm wavelength and 10 Hz pulse frequency repetition rate were employed as the fundamental beam and the photo induction to the samples were done by modulated cw 532 nm CW laser [21]. The studied samples were put on a rotating table. Levels of obtained fundamental and third harmonic signals were measured using a Tektronix MSO 3054 oscilloscope with sampling of 2.5 GS. The obtained data points were averaged around 400 points throughout the film surfaces.

2.5. Electron beam irradiation

Electron beam line from linear accelerator (LINAC) at RRCAT Indore, India were employed for the electron beam irradiation experiments. The Mn$_{1-x}$Zn$_x$O (X = 0.03, 0.05) thin films were irradiated at predetermined dosages starting from 5 kGy to 20 kGy in steps of 5. The energy of the electron beam line was fixed to 8 MeV. The time of beam exposure to samples were designed based on the dosage to be delivered.

3. Results and discussion

3.1. Influence of electron beam treatment on linear optical properties

Linear absorption spectra of Mn$_x$Zn$_{1-x}$O (X = 0.03, 0.05) thin films were noted within the wavelength range varying within 350 nm-1000 nm and are depicted in Fig. 1 for different irradiation dosage. The increase in the optical scattering loss of light from the grain boundaries favours an enhancement of the absorption as evident from figure. The aggregation of the grains in the irradiated films will effect in the formation of large grain boundaries enhancing the optical scattering effects [22]. The red spectral shift observed in the absorption edge of the films results in the shrinkage of band gap. The band gap of the irradiated films were found out by implementation of Tauc plot method [23] and is shown in Fig. 2. The obtained band gap energy values are depicted in Table 1. The formation of localized defect states upon electron beam irradiation results in the decrease of the band gap energy values. The more discussion on the formation of localized defect states were done in Sec 3.3.

3.2. Electron beam irradiation effects on structural and surface morphological properties

GXRD pattern are obtained using Cu Ka radiation source with λ = 1.54A$^0$ and shown in Fig. 3. The results are used to study the effect of irradiation on crystallographic structure, nanocrystalline size, lattice strain and bond length. GXRD pattern showing sharp diffraction peaks and they are matched with hexagonal wurtzite structure of ZnO thin films (JCPDS-036-1451). The observed XRD diffraction peaks in the films are indexed to (002), (101), (102), (110), (103), (112), and (201) with preferred growth orientation along (002) C-axis direction. The angle shift of the diffraction peak position observed with irradiation dosages are attributed to elongation of lattice parameters which results in compressive strain in the nanostructures [17,18]. The absence of Mn related peaks in the GXRD pattern may indicate incorporation of Mn into ZnO lattice due to substitution of Zn atoms position or in other way the impurity content of Mn in the films are lower than the detection limit of GXRD used. The changes noticed in the lattice parameters are
also an indication of expansion of crystal lattice. Enhancement in the intensity of diffraction peak corresponds to the influence of irradiated electron beam on the scattering factors of Mn$_x$Zn$_{1-x}$O unit cell [17]. The discrepancies observed in the intensity of diffraction peaks fall out the variations in the crystalline origin of the films on irradiation.

The electron beam induced variations on structural parameters were found out and depicted in Table 2. The peak at 2θ ~34.6$^\circ$ is observed to be strongest for all films except pristine Mn$_{0.03}$Zn$_{0.97}$O which shows at 2θ ~36.6$^\circ$. Crystallite size, D of the films were evaluated using Debye Scherer formula reported elsewhere [22]. The irradiation effects results in the decrease in the crystallite size as observed from Table 2. The decrement of crystallite size owes to the decrease in the grain size or deterioration of crystallinity. The decrement in the crystallinity or increase in the FWHM can be attributed to the incorporation of lattice defects in the nanostructure by e-beam ir-radiation [17,24]. The broadening of the x-ray diffraction peak which results in the decrease in the crystallite size further associated with the formation of localized strain in the lattice. These arised strains in the films are due to the creation of extended defects or point defects which in turn results in the systematic modifications of atoms positions from their original position [24]. Close inspection of Fig. 3 indicates a shift in the diffraction angle upon irradiation. The prominent diffraction along (101) and (002) plane exhibits a lower angle shift on higher dosages as evident from Fig. 4. Irradiation induced elongation in the lattice parameters which results in the elongation of bond length can be attributed to the observed shift in the diffraction peak towards lower 2θ. Electron beam induced irregularity in the crystal structure or the amount of defects induced in the lattice can be explained by finding out the dislocation density of the nanostructure. Dislocation density represents the magnitude of defects in the samples which can be find out using equation (1) and depicted in Table 2.

\[
\delta = \frac{1}{D^2} \tag{1}
\]

Table 1: Variation in energy band gap at different irradiation dosage.

| Dosage (kGy) | Mn$_{0.03}$ Zn$_{0.97}$ O (eV) | Mn$_{0.05}$ Zn$_{0.95}$ O (eV) |
|--------------|-------------------------------|-------------------------------|
| 0            | 3.26                          | 3.25                          |
| 5            | 3.17                          | 3.25                          |
| 10           | 3.14                          | 3.24                          |
| 15           | 3.11                          | 3.22                          |
| 20           | 3.15                          | 3.19                          |

The peak at 2θ ~34.6$^\circ$ is observed to be strongest for all films except pristine Mn$_{0.03}$Zn$_{0.97}$O which shows at 2θ ~36.6$^\circ$. Crystallite size, D of the films were evaluated using Debye Scherer formula reported elsewhere [22].
Table 2
Variation in structural parameters upon electron beam irradiation.

| Dosages (kGy) | c’(002) Å   | a’(101) Å   | Bond Length(L) Å   | Crystalline size(D) nm | Strain (10⁻³) | Dislocation density (10¹⁵) |
|--------------|-------------|-------------|--------------------|------------------------|---------------|---------------------------|
| 0            | 5.169       | 3.232       | 1.966              | 18.83                  | 1.83          | 2.81                      |
| 5            | 5.197       | 3.250       | 1.976              | 16.02                  | 2.16          | 3.90                      |
| 10           | 5.199       | 3.227       | 1.967              | 16.62                  | 2.08          | 3.61                      |
| 15           | 5.206       | 3.240       | 1.973              | 16.24                  | 2.13          | 3.79                      |
| 20           | 5.190       | 3.231       | 1.968              | 16.60                  | 2.09          | 3.60                      |

| Dosages (kGy) | c’(002) Å   | a’(101) Å   | Bond Length(L) Å   | Crystalline size(D) nm | Strain (10⁻³) | Dislocation density (10¹⁵) |
|--------------|-------------|-------------|--------------------|------------------------|---------------|---------------------------|
| 0            | 5.188       | 3.238       | 1.970              | 18.00                  | 1.92          | 3.07                      |
| 5            | 5.195       | 3.230       | 1.968              | 17.00                  | 2.03          | 3.45                      |
| 10           | 5.188       | 3.238       | 1.970              | 17.10                  | 2.02          | 3.41                      |
| 15           | 5.199       | 3.247       | 1.975              | 16.74                  | 2.07          | 3.60                      |
| 20           | 5.197       | 3.239       | 1.972              | 17.42                  | 1.99          | 3.30                      |

Influence of e-beam irradiation atomic force microscopy (AFM) technique was employed. The films were scanned in tapping mode configuration at a scan area of 5μm×5 μm. The 3D AFM images were recorded and analyzed by the aid of Nanoscope analysis software. The changes observed in the average surface roughness of the films were obtained and tabulated in Table 3. In comparison to non-irradiated MnₓZn₁₋ₓO the e-beam irradiated films demonstrate a variation in surface morphology clearly observed in Fig. 5(a–c). The Root mean square roughness (RMS) value shows an enhancement upon irradiation due to the formation of defects in the sample. It is worthy to be emphasized that e-beam irradiation stimulated large reduction of agglomeration sites which further leads to fragmentation of larger grains into smaller ones with more ordered and shaped grain structures [25]. The changes in shape and size of the grains at higher electron beam dosages are due to the high density of radiative and non-radiative defects induced by the irradiation. There is no any substantial changes observed in the topo-graphical features especially in the average surface roughness and apart from that higher damage threshold shown by the films leads to the credibility of investigated material in nonlinear device application.

3.3. Electron beam induced effects investigated at ambient temperature. Photoluminescence (PL) spectroscopy

Apart from the optical properties PL studies will give an information about structural defects such as Zinc and oxygen interstitials, oxygen vacancy, Zinc vacancy and other surface properties The PL spectra of non-radiated and e-beam irradiated MnₓZn₁₋ₓO (x = 0.01,0.03,0.05) nano-structures were recorded at an excitation wavelength of 325 nm and are shown in Fig. 6(a–c). Gaussian deconvolution fitting is performed for obtained PL spectra of the nanostructures in order to identify the radiative transitions in the films reflecting different native defect centers. The fitting parameters used to perform the deconvolution was kept uniform for all the specimens. Fig. 6 a shows the PL spectra of pristine MnₓZn₁₋ₓO (0.03, 0.05) films. The Gaussian fitting shows existence of luminescent centers which can be attributed to various
defect centers presented in the films. A strong and narrow peaks observed at 3.11 eV, 3.15 eV, 3.12 eV in the UV region can be endorsed to near band edge emission (NBE) possibly raised as a result of exciton recombination effects [26–27]. It is observed from the PL spectra that all the three investigated films exhibit strong visible light emission with different centers which can be recognized to manifestation of various structural defects. Violet emission observed around 2.96 eV, 2.85 eV, 2.94 eV were due to Zinc interstitial (Zni) defect center which traps the electrons while the de-exciting from conduction band to valence band [26–30]. A prominent and strong blue I and blue II emissions demonstrated by all the films is due to the presence of oxygen anti-site defect center (Ozn) in the films [27]. The peaks observed at 2.32 eV, 2.38 eV, 2.37 eV were attributed to green luminescence emission from the nanostructures. Green emission is assigned to oxygen vacancy defects of the titled the films which give rise to the recombination of photo generated holes and electrons. The same observation has been reported in different references [26–30]. The yellow emission peaks observed at 2.19 eV and 2.18 eV in the investigated films are assigned to the presence of absorbed hydroxyl group (OH) and interstitial oxygen (Oi) [27].

The PL spectra of electron beam irradiated Mn0.97Zn0.03O (x = 0.03, 0.05) films have been mainly dominated by four luminescent spectral peaks situated around 2.49 eV, 2.63 eV, 2.77 eV and 2.91 eV which can be formed by four color centers such as blue-green, blue, violet-IV and violet, respectively. Fig. 6(b) and c shows the deconvoluted PL spectra of irradiated nanostructures. The four visible emission centers corresponds to defect center transition and inter-band carrier transitions. The electron transition probabilities between Zni site and valence band are enhanced due to the observed violet emission around 2.91 eV. A prominent Violet II peak emission observed at 2.77 eV and 2.78 eV were consigned to the transfer of electron between the Zni + center and valence band [27,29]. Blue emission peak observed in the films were attributed to presence of oxygen anti-site defect centers for the nanostuctures [27]. The non-equilibrium condition like high energy irra-diation with ions or electron is the required environment for the O2n defect sites to induce in the materials which are likely present in the current investigation. Blue-green emission peak observed in the nanostructures can be attributed to the presence of intrinsic oxygen vacancy defect sites. Moreover, it is observed a substantial decrease in the PL emission intensity upon e-beam incorporation. This behavior can be due to the formation of localized surface states below the conduction band. As a result of these surface states, non-radiative transition of the carriers is enhanced occurring from the conduction band to the surface states below the conduction band. The saturation of PL emission centres observed in irradiated PL spectra can be probably due to the re-combination of Zn and V2+ defect sites. As a consequence a spatial separation between these defects sites will reduce on irradiation which aids to recombination mechanism. This also indicates the saturation of defect concentration in the films upon electron beam irradiation [31].

3.4. Electron beam induced effects investigated by Raman spectroscopy

The non-radiative transitions and structural disorder in Mn0.97Zn0.03O (x = 0.03, 0.05) thin films were investigated by Raman spectroscopy in

| Dosage (kGy) | Surface Roughness (nm) |
|-------------|------------------------|
|             | Mn0.03Zn0.97 O          | Mn0.05Zn0.95 O          |
| 0           | 13.2                   | 19.5                    |
| 5           | 14.6                   | 28.6                    |
| 10          | 11.8                   | 20                      |
| 15          | 10.4                   | 19.4                    |
| 20          | 16.9                   | 22                      |

Table 3

Variation in average surface roughness upon electron beam irradiation.

Fig. 5. 3D AFM image of (a) unirradiated Mn0.03Zn0.97 O (x = 0.03, 0.05) (b) Mn0.03Zn0.97 O (c) Mn0.05Zn0.95 O at different irradiation dosage.
Fig. 6. Deconvoluted PL spectra of (a) pristine Mn$_x$Zn$_{1-x}$O ($x = 0.03, 0.05$) (b) Mn$_{0.03}$Zn$_{0.97}$O (c) Mn$_{0.05}$Zn$_{0.95}$O at different irradiation dosage.

The Raman modes assigned to Mn$_x$Zn$_{1-x}$O ($x = 0.03, 0.05$) were tabulated in Table 4. The presence of narrow peak at 439 cm$^{-1}$ with E2H characteristic phonon modes were dominant in all deposited films is a signature peak of wurtzite ZnO. The variations in the intensity and peak shifting of this modes corresponds to the disordering degree in the films. The line shape of E2H mode at 439 cm$^{-1}$ depends on composition of Mn in the material system. The presence of an intense broad band around 560 cm$^{-1}$ with A1 (LO) vibration modes were observed in all doped films. The incorporation of Mn has increased the intensity of A1 (LO) mode which attributes to the presence of Mn in the films. It's an indication that Mn substitutes Zn in the lattice and 560 cm$^{-1}$ modes related to the local vibrations involving the Mn atom. The presence of 333 cm$^{-1}$ peak in all corresponds to the quality of the deposited samples [32–35].

Raman spectra was obtained for irradiated samples in order to study the formation of defect centers in the samples. The reports of various groups [36–39] predicts that there is a spectral shift in the Raman peaks and also distortions are observed when the samples are undergone ir-radiation treatment. For Mn$_x$Zn$_{1-x}$O ($x = 0.03, 0.05$) films considerable changes are observed upon irradiation. As evident from Fig. 7 the dominant peaks present in the films were assigned to E2H, E2H-E2L and A1 (LO) modes. It is noteworthy that upon e-beam exposure the ob-served Raman peaks underwent a shift in the spectral position with broadened peaks as compared pristine. Table 4 shows the peak posi-tions and corresponding phonon modes assigned. From Fig. 7(a) Raman spectra of Mn$_{0.03}$Zn$_{0.97}$O thin films the E2H mode was observed at 439 cm$^{-1}$ for non-radiated samples and they were blue shifted and A1(LO) mode at 557 cm$^{-1}$ were spectrally red shifted upon electron beam irradiation. The shifting of A1 (LO) phonons also corresponds to the slight variations in the preferred C axis growth orientation upon electron beam irradiation. A1 (LO) phonon can appear only when the c axis of wurtzite ZnO is parallel to the sample surface. The absence and reappearance of E2H-E2L mode at around 330 cm$^{-1}$ attributes to the changes in the samples crystallinity, crystalline size and strain occurred on electron beam treatment. The Raman spectra analysis of Mn$_{0.05}$ Zn$_{0.95}$O thin films also demonstrate identical behavior.

The asymmetric broadening and shifting of spectral peaks to lower and higher frequency sides observed in electron beam irradiated spectra can be likely due to three possible mechanisms arisen in the films [36–41]. The presence of defect centers such as oxygen and Zinc va-cancy, zinc excess, anti-site oxygen and other surface impurities give rise to phonon localization effects. Furthermore spatial confinement effects induced in the samples can also be a possible explanation me-chanism. Electron beam induced heating in nanostructure and induction of tensile strain in sample can also led to peak shifting process.

3.5. Electron beam irradiation effects on nonlinear optical properties

Electron beam induced modifications on third order nonlinear optical properties of Mn$_x$Zn$_{1-x}$O ($x = 0.03, 0.05$) nanostructures were studied using single beam Z-scan technique (both continuous and pulsed regime) and Third harmonic generation technique (THG).
Fig. 7. Raman spectra of (a) $\text{Mn}_{0.03}\text{Zn}_{0.97}\text{O}$ (b) $\text{Mn}_{0.05}\text{Zn}_{0.95}\text{O}$ at different irradiation dosage.
3.5.1. Z-scan technique

The Single beam open aperture Z-scan technique was employed to study the third order absorptive nonlinearity of the films [19, 20]. The measurements have been done in both continuous and pulsed laser regimes. In both cases the nonlinearity arises essentially from the absorption of the excited states [21].

Fig. 8 (a) and 8(b) show open aperture Z-scan trace of Mn$_{1-x}$Zn$_x$O (x = 0.03, 0.05) nanostructures under cw laser excitation. The sig-nature trace obtained from the measurement can be attributed pre-vailing to two different phenomena. The trace which unveils a valley at the focus corresponds to reverse saturable absorption mechanism (RSA) which results from the laser irradiation which further enhances electron excitation and relaxation process. The electrons in defect level can be further excited to the conduction band state which results in the process known as excited state absorption (ESA) which in turn results in RSA mechanism ob-served in the investigated films [46].

From the Z-scan data obtained, the nonlinear absorption coefficient values $\beta_{eff}$ for both continuous and pulsed excitation regimes have been determined using the nonlinear transmission equations given by Sheik Bahae et al. [19, 20], and the resulting data are shown in Table 5. Significant variations were observed in the nonlinear absorption coefficients for both continuous and pulsed laser regime upon electron beam irradiation. The enhancement observed in $\beta_{eff}$ on higher irra-diation dosages confirms the suitability of the investigated materials for optical limiting applications. The creation of intermediate states upon irradiation which further enhances electron excitation and relaxation processes in the materials could be the possible reason behind the ob-served variation in the magnitude of $\beta_{eff}$.

3.5.2. Photo induced third harmonic generation

Photo induced third harmonic generation (THG) measurement technique, may be considered as one of the most instructive technique for the precise assessment of third order nonlinearity raised in the materials due to electronic contribution. Generally the nonlinearity due to thermal, orientational, mechanical effects etc. can be neglected by implementing this technique [49]. The fundamental excitation beam used for the measurement possessed pulse duration was equal to 8 ns. (Nd: YAG pulsed laser with a wavelength of 1064 nm and frequency repetition rate of 10 Hz). The films were photo treated with a CW green laser light of wavelength 532 nm. Fig. 10(a) and (b) shows the photo induced THG signals of electron beam irradiated Mn$_{1-x}$Zn$_x$O (x = 0.03, 0.05) nanostructures. The value of the energy power for fundamental source beam have been varied from 140 J/m$^2$ to 200 J/m$^2$ by Glan polarizer and it was recorded by germanium photodetector supplied with defocused lens. THG signal observed in the films were detected by Hamamatsu photomultiplier by the aid of a filter of 355 nm. From the THG signal intensity vs laser power density graph shown in Fig. 10 it is observed a linear increase in the THG signal intensity on higher laser power density. To eliminate the parasitic background additional filters at 346 nm ad 460 nm have been used. The THG signal was at least on order higher with respect to the fluorescence parasitic scattering background. The measurements were performed after 0.1 s illumination by cw laser to avoid overheating in the 30 different points of the samples to achieve the necessary statistics. For Mn$_{0.03}$Zn$_{0.97}$O and Mn$_{0.05}$Zn$_{0.95}$O the films irradiated with 10 kGy e-beam dosage shows the highest intensity signal compared to other dosages. The substantial increment observed in the THG signal intensity indicates the credibility of electron beam irradiation in tailoring the THG signal intensity which can be used for the fabrication of frequency tripplers in high power laser sources. The observed increase in efficiency of photo induced THG in Mn$_{1-x}$Zn$_x$O (x = 0.03, 0.05) nanostructures can be possibly due to electron beam induced relaxation and photoexcitation process arisen [50].

4. Conclusions

In summary, a series of Mn$_{1-x}$Zn$_x$O (x = 0.03, 0.05) nanostructures have been grown via the solution based chemical spray pyrolysis technique. Electron beam induced modifications on structural, optical and surface morphological properties have been studied and elaborated. Detailed investigations on the effect of electron beam irradiation on third order nonlinear optical properties are being reported for the first time. GXRD pattern shows sharp diffraction peaks matching with the hexagonal wurtzite structure of ZnO thin films. Gaussian decon-volution on PL spectra reveals the quenching of defect centers, implying the role of electron beam irradiation in regulating luminescence and

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**Table 4**

Spectral peak position and Phonon mode assignment on Mn$_{1-x}$Zn$_x$O.

| Concentration | Phonon modes | Electron beam dosage (kGy) |
|---------------|--------------|----------------------------|
| 0             | E$_{2High}$ | 439 440 445 439 444      |
| 5             | A$_{1LO}$   | 557 554 551 560 539      |
| 10            | E$_{2High}$ | - - 322 336 327          |
| 15            | A$_{1}(TO)$ | - - - - - -              |
| 20            | E$_{2High}$ | 439 441 444 448 441      |
|               | A$_{1LO}$   | 565 531 553 540 540      |
|               | E$_{2High}$ | - - 350 322 322 330      |
|               | A$_{1}(TO)$ | - - 391 380 384          |

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**Table 5**

Concentration | Electron beam dosage (kGy) | Electron beam dosage (kGy) |
|---------------|---------------------------|---------------------------|
| 0             | E$_{2High}$ | 439 440 445 439 444      |
| 5             | A$_{1LO}$   | 557 554 551 560 539      |
| 10            | E$_{2High}$ | - - 322 336 327          |
| 15            | A$_{1}(TO)$ | - - - - - -              |
| 20            | E$_{2High}$ | 439 441 444 448 441      |
|               | A$_{1LO}$   | 565 531 553 540 540      |
|               | E$_{2High}$ | - - 350 322 322 330      |
|               | A$_{1}(TO)$ | - - 391 380 384          |
Fig. 8. Open aperture Z-scan traces measured for (a) Mn$_{0.03}$Zn$_{0.97}$O (b) Mn$_{0.05}$Zn$_{0.95}$O under continuous laser excitation.
Fig. 9. Open aperture Z-scan curves measured of (a) $\text{Mn}_{0.03}\text{Zn}_{0.97}\text{O}$ (b) $\text{Mn}_{0.02}\text{Zn}_{0.98}\text{O}$ under pulsed laser excitation.
defect centers in the sample. Non-radiative transitions and structural disorder in MnZn$_{1-x}$O ($x = 0.03, 0.05$) thin films have been investigated by Raman spectroscopy in the back scattering geometry. Irradiation induced spatial confinement and phonon localization effects have been observed in the sample, which are evident from spectral peak shifts and broadening. Third order absorptive nonlinearity of the samples has been studied using the open aperture Z-scan technique. The measurements have been carried out in both continuous and pulsed laser excitation regimes. The strong RSA behavior shown by the samples indicates their suitability for passive optical limiting applications.

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References

[1] H. Shen, M. Wrabaek, J. Pamulapati, S. Liang, C. Gorla, Y. Lu, Properties of epitaxial ZnO thin films for GaN and related application, MRS Internet J. Nitride Semicond. Res. 4S1 (1999) G3.60.

[2] M.J. Fejer, Nonlinear-optical frequency-conversion, Phys. Today 47 (1994) 25.

[3] A. Andrews, A. Schepartz, J. Sweedler, P. Weiss, Chemistry and the BRAIN initiative, J. Am. Chem. Soc. 136 (1) (2014) 1–2.

[4] P. Weiss, Where are the products of nanotechnology? ACS Nano 9 (2015) 3397.

[5] B. Pelaz, S. Jaber, D. de Aberasturi, V. Wulf, T. Aida, J. de la Fuente, J. Feldmann, H. Gaub, L. Josephson, C. Kagan, N. Kotov, L. Liz-Marzán, H. Mattoussi, P. Muharrey, C. Murray, A. Rogach, P. Weiss, I. Willner, W. Park, The state of nanoparticle-based nanoscience and biotechnology: progress, promises, and challenges, ACS Nano 6 (2012) 8468.

[6] Anton Autere, Henri Justsal, Yunyun Dai, Yadong Wang, Harri Lipsanen, Zhipeng Sun, Nonlinear optics with 2D layered materials, Adv. Mater. (2018) 1705963.

[7] Y.R. Shen, The Principles of Nonlinear Optics, Wiley Press, NewYork, 1984.

[8] E. Garmire, Nonlinear optics in daily life, Optic Express 21 (25) (2013) 30532–30544.

[9] G.P. Agrawal, Applications of Nonlinear Fiber Optics, Academic Press, London, UK, 2001.

[10] B.E.A. Saleh, M.C. Teich, Fundamentals of Photonics, Wiley, Hoboken, NJ, USA, 2007.

[11] R.W. Boyd, Nonlinear Optics, Academic Press, New York, 2007.

[12] G.I. Petrov, V. Shcheslavskiy, V.V. Yakovlev, I. Ozerov, E. Chelnokov, W. Marine, Efficient third-harmonic generation in a thin nanocrystalline film of ZnO, Appl. Phys. Lett. 83 (2003) 3893.

[13] Albin Antony, P. Poornesh, K. Ozga, J. Jedryka, P. Rakus, I.V. Kityk, Enhancement of the efficiency of the third harmonic generation process in ZnO:F thin films probed by photoluminescence and Raman spectroscopy, Mater. Sci. Semicond. Process. 87 (2018) 100–109.

[14] Paiton Montraphong, Supree Prinssontorn, Prasit Thongbai, Mn-doped ZnO nano-particles: preparation, characterization, and calculation of electronic and magnetic properties, Microelectron. Eng. 108 (2013) 158–162.

[15] A.H. Reshak, K. Nouneh, I.V. Kityk, J. Bila, S. Auluck, H. Kamarudin, Z. Sekkat, Structural, electronic and optical properties in earth abundant photovoltaic absorber of Cu2ZnSnS4 and Cu2ZnSnSe4 from DFT calculations, Int. J. Electrochem. Sci. 9 (2014) 955.

[16] I.V. Kityk, J. Ebothe, AelHichou, M. Addou, A. Bougrine, B. Sahraoui, “Linear electro-optics effect in ZnO:F film-glass interface”, Phys. Status Solidi 234B (2002) 553.

[17] H.A. Khawal, B.N. Dole, “A study of the 160 MeV Ni7+ swift heavy ion irradiation effect of defect creation and shifting of the phonon modes on MnZn$_{1-x}$O thin films”, RSC Adv. 7 (2017) 34736.

[18] S.K. Neogi, S. Chattopadhyay, A. Sarkar, Ravi Kumar, Effect of 50 MeV Li3+ irradiation on structural and electrical properties of Mn-doped ZnO, J. Phys. Condens. Matter 23 (20) (2011) S801.

[19] M. Sheik-Bahae, A.A. Said, E.W. Van Stryland, High-sensitivity, single-beam n2 measurements, Opt. Lett. 14 (1989) 955.

[20] M. Sheik-Bahae, A.A. Said, T.H. Wei, D.J. Hagan, E.W. Van Stryland, Sensitive
