Effect of heavy metals (Ni, Cu, Pb) doped ZnO on the nonlinear optical properties

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Abstract

In this paper, the non-linear optical properties of undoped and doped ZnO thin films were investigated. The films were doped with Ni, Pb, and Cu. An increase in the refractive index against wavelength is apparent for all films up to a certain value of wavelength. Z scan technique is used for measuring the nonlinear optical parameters via open and closed aperture configurations. Third order nonlinear susceptibilities ($\chi^{(3)}$) of samples were calculated. The sign of nonlinear refractive index ($\nabla$) of ZnO was changed from positive (self-focus) to negative (de-focus) upon metal doping. Doping ZnO with heavy metals changes the sign of nonlinearity although the nonlinear absorption coefficient ($\beta$) is positive for all samples; the doped materials behave as optical limiters at high intensity. These materials are promising for optoelectronic devices and optical limiting applications.

1. Introduction

There is a growing body of literature that recognizes the importance of nonlinear optical materials; they have numerous applications such as optical limiting, optical switching, and phase conjugation. Nanostructures semi-conductors exhibit optical nonlinearities features which expand their applications in as optical amplifiers, optoelectronic switching, and construction of lasers [1–5]. Recently, there has been renewed interest in zinc oxides for a wide range of technologies, Zinc oxide is a promising semiconducting material used in many branches of construction of lasers [1–5]. It is used wherever a source for UV and blue range, and also used as an optical waveguide [3], solar cells window [4, 5], photo-catalyst [6], piezoelectric transducers [7], varistors [8], transparent conductive films [9], photo electrode [10], and gas sensors [11].

Optical nonlinearity of zinc oxides are studied in different matrices, as Barium-Zinc-Borate glasses with Er doping [12], Er doped Ag-ZnO films [13], polymeric betanin—ZnO matrix [14], Gd-doped in ZnO NCs [15], and tin zinc oxide composite films [16]. Theses matrices exhibit good optical nonlinearity for photonic applications.

Although the nonlinear optical properties of ZnO are in growth using different laser parameters [17–20]; However, the study of ZnO doped with metals using nanosecond laser is still limited. The current work focuses on the study of the non-linear properties of undoped and doped ZnO thin films, with the doping were Ni, Pb, and Cu at a constant level of 3 wt% in the starting solution. Thin films were prepared using a spray pyrolysis technique [10] at constant parameters with different dopants. Phase identification has been confirmed elsewhere [10]. The nonlinear refraction, the nonlinear absorption, and the third order susceptibility were calculated based on Z scan measurements, the nonlinearity sign is changed under doping ZnO with heavy metals. This study offers some important insights for the optical nonlinearity of ZnO.

2. Experimental methods

As mentioned above, films were prepared via a spray pyrolysis technique and characterized in Aboud et al work [10]. The linear refractive index has been determined using the optical data obtained by measuring the transmission spectra of all films using the Prava program [10].
The nonlinear optical studies of the doped and undoped ZnO thin films were analyzed using open and closed aperture configurations of Z-scan technique. The third-order NLO properties of the prepared spray-coated ZnO and ZnO:X (Ni, Pb, Cu) films are calculated based on Z-scan measurements; 532-nm pulsed Nd:YAG laser (Continuum PL 7030) were used with pulse energy 1.3 mJ, 5 ns pulse duration, and repetition rate 10 Hz. energy of pulses was controlled by using density filter (DF) and pulses focused by lens (15 cm focal length). The schematic diagram of the Z-scan experimental setup is shown in figure 1. All films are scanned across the focal region in laser beam propagation direction by using the translation stage (TS) provided by Thorlabs instruments of type APT version 1.0.21. The transmitted beam has been divided into two equal intensity beams using a beam splitter (BS). The axial beam passing through an aperture (1 mm diameter) placed in the far-field was measured by a photo detector (PD1); this line is the closed aperture Z-scan sensitive to the nonlinear refractive index measurement. The vertical beam was focused by the lens into PD2 without prior pinhole; this part is the open aperture Z-scan which sensitive to the nonlinear absorption. PD1 and PD2 were fed into digital power meter (DPM) which connected to the computer (PC) with controlled software PM320E. To study the optical limiting; We measured the transmittance by holding the sample at the focal point as a function of laser energy.

3. Results and discussion

Figure 2 shows the refractive index variation. All films show a general increase in the refractive index against wavelength. Such an increase in the refractive index with increasing wavelength is known as anomalous dispersion. The anomalous behavior of the optical constants in thin films have been recorded by many workers [21–23]. Rao et al [22] recorded the anomalous behavior of ZnO thin films prepared by spray pyrolysis at a certain substrate temperature of 400 °C. The possible causes of the anomalous behavior of the refractive index was listed in the paper of Robers et al [23]:- size effects, anisotropy, film morphology, and surface engineering. In the work of Mahmoud et al [24] anomalous behavior is observed for NiO thin films prepared at low substrate temperature using the spray pyrolysis technique. They account this behavior to several reasons listed as follows

1. Transformation to crystalline phase considering the substrate temperature.
2. Adsorption of water deposited at low temperatures in films during film handling.
3. Formation of a bigger clusters of the films materials which increase the surface roughness.

The nonlinear properties of ZnO thin film were measured using nanosecond laser at operating wavelength 532 nm as mentioned early. The nonlinear absorption is measured via an open aperture z scan where the transmitted light is measured in the far-field after the sample is scanned through a gradient of laser intensities through the focal point. The normalized transmission for the open aperture is given by equation [25, 26].

\[
T_{\text{open}}(Z) = \sum_{m=0}^{\infty} \frac{(-q_0)^m}{(m + 1)^{3/2} \cdot (1 + z^2/z_r^2)^m}
\]

Where \( q_0 = \beta_0 I_{\text{eff}} \) and, \( z_0, I_0, \beta, \text{L}_{\text{eff}} \) being Rayleigh length, peak intensity at the focal plane \((z = 0)\), the nonlinear absorption coefficient, and effective sample thickness respectively.
The nonlinear refraction is determined by the closed aperture (CA), where a pinhole is in the center of the detector in the far-field, as seen in figure 1. The nonlinear refractive index value ($n_2$) was obtained by fitting closed aperture data to equation (2) [27].

$$T = 1 + 2 \frac{\rho x^2 + 2x - 3\rho}{(x^2 + 9)(x^2 + 1)} \Delta \varnothing$$  \hspace{1cm} (2)

Where $x = z/z_0$, and

$$\Delta \varnothing = \frac{2\pi}{\lambda} n_1 I_{off} \rho = \frac{\Delta \psi}{\Delta \varnothing} \text{ and } \Delta \psi = \beta I_{off} / 2$$  \hspace{1cm} (3)

Where $\Delta \psi$ and $\Delta \varnothing$ are the nonlinear phase shifts due to the nonlinear absorption and nonlinear refraction, respectively.

The third-order susceptibility is considered a complex quantity, given by,

$$\chi^{(3)} = \chi_R^{(3)} + i \chi_I^{(3)}$$  \hspace{1cm} (4)

Where $\chi_R^{(3)}$ is the real part and $\chi_I^{(3)}$ is the imaginary part of $\chi^{(3)}$ are given by,

$$\chi_R^{(3)} = \frac{c^4 \varepsilon_0 \varepsilon_a n_2}{\pi}$$  \hspace{1cm} (5)

$$\chi_I^{(3)} = \frac{n_2^2 \varepsilon_0 c^2}{4\pi^2} \chi \beta$$  \hspace{1cm} (6)

It is obvious from equation CC(5) and (6) that $\chi_R^{(3)}$ and $\chi_I^{(3)}$ is related to the nonlinear refractive index $n_2$ and the nonlinear absorption coefficient $\beta$, respectively.

Z-scan measurements are shown in figures 3 and 4. Figure 3 shows open and closed Z-scan of ZnO thin film. Figure 3(a) shows the valley signal around the focal point, the transmitted intensity decreased as the laser intensity reached its maximum value in the focal point. Figure 3(b) for closed aperture Z-scan shows a valley (pre-focal transmittance minimum) followed by peak (post-focal maximum), which is the signature of positive $n_2$, while the peak-valley feature indicates a negative $n_2$. It means that ZnO thin film has positive nonlinear refraction; the beam is collimated and leads to beam narrowing at the aperture (increase in the transmission: self-focusing). The nonlinear parameters $\beta$ and $n_2$ are extracted corresponding to fitting to equations (1) and (2), respectively. Further, no NLO response for the glass substrate alone, consequently the obtained nonlinearity originates from ZnO samples.

Figure 4 shows the doping effect on Z-scan transmission. ZnO thin films demonstrate minima at the focal point in open aperture Z-scan transmissions. These behaviors are signs of reverse saturation absorption (RSA) performance. The presence of normalized valley in each undoped and doped ZnO film verifies the RSA conduct of the samples underneath the pulsed laser mode. 2PA is a prevailing mechanism in semiconductors although...
RSA can occur from different processes, as two or three-photon absorption (2PA-3PA), and nonlinear scattering, excited-state absorption, and loose carrier absorption.

Nonlinear absorption processes are depending on pulse durations [18]. For semiconductors; only the instantaneous nonlinearities such as ground state two- and three-photon absorption (2PA and 3PA respectively) are accountable for the nonlinear absorption for laser energies (hν) with femtosecond pulse durations (fs) where \( E_g/2 < h\nu < E_g \) where \( E_g \) is the band-gap [18]. On the other hand, for longer pulse durations, excited state nonlinearities such as 2PA triggered excited state absorption (ESA) can also occur [19].

Shortell et al. [28] observed large nonlinear absorption is due to ESA, not pure two-photon absorption in ZnO Nano-cones under 532 nm of nanosecond pulse duration. Zhang et al. mentioned that RSA is caused by high excited states absorption [17] for fs laser pulses in contrary to it occurs from low excited states absorption or deep levels for ns and ps pulses. In our case using nanosecond laser pulses and \( h\nu = 2.33 \) eV which is less than the

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**Figure 3.** Normalized (a) open and (b) closed-aperture Z-scan transmittance curves of ZnO thin film measured at 532 nm laser pulse.

**Figure 4.** Normalized open- (a), (c), (e) and closed- (b), (d), (f) aperture Z-scan transmittance curves of ZnO thin film doped with (Cu, Ni, Pb) measured at 532 nm laser pulse.
calculated energy gap as seen in table 1; a defect-assisted band–band excitation process is responsible for 2PA occurence and the nonlinearity origin of is from the sub-band states shaped by zinc vacancy as explained by Kavitha et al [29].

Figures 4(b), (d), (f); the peak valley shape of closed aperture configuration is an indication of negative optical nonlinear refraction in the films. The beam is broadened at the aperture hence the transmission is decreased (self-defocusing), the doped samples exhibit negative nonlinear refractive index. This indicates the dopant reverses the nonlinearity of ZnO. In the present case, sample thickness (L). The nonlinear absorption coefficient (β), the nonlinear refractive index (n2), nonlinear susceptibilities (χ(3)) based calculations are listed in table 1. The sign of the real part of third order susceptibility is changed under ZnO doping, furthermore the imaginary part was observed to be positive for doped and undoped ZnO. To conclude; doping ZnO with heavy metals changes the sign of nonlinearity although the nonlinear absorption coefficient (β) is positive for all samples, this is promising to use the material in optoelectronic devices and optical limiting applications.

Studies of nonlinear optical properties of ZnO thin film matrices have been recorded by many workers using different laser pulses [18–20, 29]; for examples, many authors investigated the nonlinear properties using a continuous laser such as Al-doped ZnO and irradiated by electron beam [20], Co-ZnO nanoparticles prepared by co-precipitation [31], Ni0.05 Zn0.95 O thin film prepared by pulsed laser deposition [18], Mg-ZnO thin film [19]. continuous lasers have thermo-optic effects, which always hinder the NLO properties exhibited by optical materials [32–34]. Others characterize the nonlinear properties ZnO via pulsed lasers as indicated in table 2.

In table 2, we summarized the nonlinear properties of ZnO prepared with different methods using similar excitation conditions, hence in comparison with our data in table 1; we obtained adequate nonlinear optical parameters for ZnO films prepared via cost effective and simple technique.

Besides the power-dependent measurement of open aperture z scan is indicated in figure 5, where the sample is placed the focal point and the transmittance is measured at different laser intensities using neutral density filters, figure 5 shows the optical limiting for Cu/ZnO is more enhanced than undoped ZnO.

![Figure 5. Energy dependence of Transmission at the focal point for ZnO and ZnO: Cu.](image)

**Table 1.** NLO coefficients β, n2, and χ(3) of undoped ZnO and doped films in the ns regime.

| sample   | L (nm) | E<sub>g</sub> (eV) [10] | β (cm G<sup>-1</sup> W<sup>-1</sup>) | n<sub>2</sub> (cm<sup>2</sup>/GW) | Im χ<sup>(3)</sup> (e.s.u) | Re χ<sup>(3)</sup> (e.s.u) | χ<sup>(3)</sup> (e.s.u) |
|----------|-------|-----------------------|---------------------------------|-------------------------------|--------------------------|--------------------------|------------------------|
| ZnO      | 753   | 3.2                   | 0.45                            | 8.07*10<sup>-6</sup>          | 1.35*10<sup>-11</sup>    | 5.088*10<sup>-13</sup>  | 1.35*10<sup>-11</sup>  |
| Cu 3 wt% | 535   | 3.2                   | 0.17                            | -4.1*10<sup>-6</sup>          | 4.16*10<sup>-12</sup>    | -2.45*10<sup>-13</sup>  | 4.17*10<sup>-12</sup>  |
| Ni 3 wt% | 482   | 3.2                   | 0.27                            | -5.5*10<sup>-6</sup>          | 7.18*10<sup>-12</sup>    | -3.58*10<sup>-13</sup>  | 7.19*10<sup>-12</sup>  |
| Pb 3 wt% | 600   | 3.3                   | 0.19                            | -3.9*10<sup>-6</sup>          | 5.12*10<sup>-12</sup>    | -3.1*10<sup>-13</sup>   | 5.13*10<sup>-12</sup>  |
| Sample                  | Parameter                          | Pulse duration | Pulse Energy | Preparation method               | $\beta$ (cm GW$^{-1}$) | $n_2$ (cm$^2$/GW) | References |
|------------------------|------------------------------------|----------------|--------------|----------------------------------|------------------------|-------------------|------------|
| ZnO                    | Pulsed NG: YAG 532                 | 10 ns          | 100 $\mu$J  | Co-precipitation method           | 3.1                    |                   | [17]       |
| ZnO: Co5%              |                                    |                |              |                                  |                        |                   |            |
| In–ZnO nanorods        | Nd:YAG lasers, $\lambda = 532$ nm | $\tau = 4$ ns  | 80 $\mu$J   | Chemical vapor deposition         | 5.7                    |                   | [35]       |
|                        |                                    | $\tau = 15$ ps | 500 nJ      |                                  | 0.4                    |                   |            |
|                        |                                    | $\tau = 100$ fs| 100 nJ      |                                  | 4.4 $\times$ 10$^{-2}$|                   |            |
| ZnO                    | Nd:YAG 532 nm                      | 25 ps          |              |                                  | 4.2                    | $-0.9 \times 10^{-5}$| [36]       |
| Gd20%+ZnO             | 400 nm                             | 30 fs          | 0.3 $\mu$J  |                                  | 2.4 $\times$ 10$^{-2}$| 0.59 $\times$ 10$^{-6}$| [15]       |
| Er$^{3+}(x=2)$-BaO-ZnO-B$_2$O$_3$ | 532 nm                          | 5 ns           |              | melt quench technique            | 0.797                  | 1.431 $\times$ 10$^{-7}$| [12]       |
| Betanin/ZnO           | 532 nm                             | 7 ns           |              |                                  |                        |                   | [14]       |
| s-ZnO nanocones       | Nd:YAG 532 nm                      | 5 ns           |              | Solution precipitation            | 0.8                    |                   | [29]       |
| h-ZnO nancones        |                                    |                |              | Hydrothermal method              | 2.5                    |                   |            |
Our results are comparable to the previously reported [29] prepared by precipitation. We can summarize, ZnO, prepared by the simple, cheap method as spray pyrolysis, are good candidates for optoelectronics applications and optical limiting.

4. Conclusions

Nonlinear optical properties were measured using the Z-scan technique for doped and undoped ZnO thin films. The dopants were Ni, Pb and Cu. A positive sign of nonlinear refractive index in undoped ZnO film reveals the occurrence of self-focusing effect, whereas self-defocusing effect with negative refraction in doped ZnO films. In addition to, the nonlinear absorption coefficient (β) is positive for doped and undoped films. The third order susceptibilities were calculated based on nonlinear absorption coefficient and nonlinear refraction values. The prepared materials behave as optical limiter at high intensity. ZnO films may have prospective applications in optoelectronic, photonic and optical limiting devices.

5. Disclosures

'The authors declare no conflicts of interest.'

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