Nonlinear spectra of ZnO: reverse saturable, two- and three-photon absorption
Nonlinear spectra of ZnO: reverse saturable, two- and three-photon absorption

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Abstract: We present a broadband (460 - 980 nm) analysis of the nonlinear absorption processes in bulk ZnO, a large-bandgap material with potential blue-to-UV photonic device applications. Using an optical parametric amplifier we generated tunable 1-kHz repetition rate laser pulses and employed the Z-scan technique to investigate the nonlinear absorption spectrum of ZnO. For excitation wavelengths below 500 nm, we observed reverse saturable absorption due to one-photon excitation of the sample, agreeing with rate-equation modeling. Two- and three-photon absorption were observed from 540 to 980 nm. We also determined the spectral regions exhibiting mixture of nonlinear absorption mechanisms, which were confirmed by photoluminescence measurements.

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1. Introduction

Zinc oxide (ZnO) is a wide-bandgap semiconductor that is being extensively investigated for the development of optoelectronic devices operating in the blue-to-near-UV spectral region [1,2]. In addition to its large bandgap energy (~3.3 eV), ZnO possesses a large exciton binding energy (~60 meV) [2,3] and can easily be handled to yield uniform and high-quality ZnO nanostructures without the use of highly toxic precursors [4–6]. In order to better understand ZnO’s optical processes under femtosecond laser excitation, it is necessary to characterize its nonlinear absorption behavior. Some studies have been conducted on the nonlinear properties of ZnO in a narrow wavelength range or using MHz repetition-rate laser [7–11].

In this paper we perform systematic energy-resolved Z-scan studies at a 1kHz repetition rate that yield the nonlinear absorption coefficient of ZnO as a function of excitation energy [12]. By tuning an opticalparametric amplifier across a large spectral range (460 nm to 980 nm) we fully characterize the various regimes of nonlinear absorption. The low repetition rate used decouples excitation effects from the thermal contribution to the measured nonlinear absorption processes. The data suggest that there are excitation wavelength regimes under which the absorption process is a result of one-photon absorption (1PA), two-photon absorption (2PA) and three-photon absorption (3PA) or a mixture of these processes. Using modeling as well as photoluminescence measurements, we have confirmed the presence of such spectral regions of mixed multiphoton absorption mechanisms.

2. Experimental

The Z-scan experiment uses laser pulses from an optical parametric amplifier pumped by 150 fs pulses at 775 nm from a Ti:sapphire chirped pulse amplified system, operating at 1-kHz repetition rate [12]. For the Z-scan measurements the beam waist size employed ranges from 14 to 22 µm. The same laser system was used to excite, at normal incidence, the ZnO photoluminescence, which was collected perpendicularly to excitation through a photomultiplier attached to a spectrometer. The intensity of fluorescence as a function of the pump irradiance, for several wavelengths, was measured at 550 nm (close to the green fluorescence peak). The linear absorption was determined using a Cary 17 UV-Vis-NIR spectrophotometer. The c-plane ZnO single-crystal sample (thickness of 0.6 mm) was purchased from Crystec GmbH (Berlin, Germany).

3. Results

Prior to conducting nonlinear spectroscopy experiments, we measured the linear absorption spectrum of ZnO. The sample presents a bandgap of 3.3 eV, in agreement with other studies carried out at room temperature [13].

We determined the nonlinear absorption spectrum of ZnO by performing Z-scan measurements [14]. The Z-scan measurements were carried out with intensities ranging from 10 to 160 GW/cm², depending on the order of the multi-photon absorption processes. Figure 1 shows the open-aperture Z-scan curves for excitation wavelengths at 500 nm (2.48
eV), 730 nm (1.70 eV) and 820 nm (1.51 eV). At 500 nm, the decrease observed in the Z-scan curve corresponds to a reverse saturable absorption due to linear absorption involving deep levels of ZnO that will be discussed in detail in the next section. For 730 nm and 820 nm, below the bandgap of ZnO, the decrease in normalized transmittance at the focal point ($z = 0$) indicates two- and three-photon absorption processes, respectively. By fitting the Z-scan curves we determine the absorption coefficients for two-photons and three-photons.

Figure 1. Open aperture Z-scan curves at 500 nm (● - 15 GW/cm²), 730 nm (■ - 40 GW/cm²), and 820 nm (▲ -120 GW/cm²) with the respective 1PA, 2PA, 3PA and theoretical fitting (solid line).

Figure 2(a) and 2(b), respectively, show the two-photon ($\beta$) and three-photon ($\gamma$) absorption coefficients of ZnO as a function of the ratio between the excitation photon energy and the bandgap energy of ZnO at room temperature. The excitation wavelength range plotted across both graphs is from 550 nm to 980 nm.

Fig. 2. Two-photon (a) and three-photon (b) absorption coefficient vs. $E_{\text{photon}} / E_{\text{gap}}$. The solid lines are fittings using the theoretical calculation of the nonlinear optical absorption coefficient as described by Brandi and Araujo [15].

Each value for the multi-photon absorption coefficient in Fig. 2 is obtained from the fit of the Z-scan measurements performed at particular excitation wavelengths (Fig. 1). The solid lines in Fig. 2(a) and Fig. 2(b) are theoretical fits determined from modelling the nonlinear optical absorption coefficient as described by Brandi and Araujo [15]. For these fittings we used the characteristic parameters (effective mass of the conduction band, reduced effective mass, refractive index and band-gap energy) of ZnO, obtained from the literature [10]. The theory slightly deviates from the measured two- and three-photon absorption coefficients when the $E_{\text{photon}} / E_{\text{gap}}$ ratio increases above the value of 0.71 eV and 0.46 eV, respectively. Such deviation is due to the mixture of nonlinear processes in these regions, which is not predicted by the theoretical model.
Figure 3 shows a log-log graph of the photoluminescence intensity of ZnO (green photoluminescence from the deep levels) as a function of the excitation intensity for various excitation wavelengths, namely 500 nm, 530 nm, 730 nm, 800 nm, and 820 nm. It is well known that the slope derived from a linear fit of the photoluminescence intensity as a function of excitation intensity is indicative of the mechanism of absorption in the material [16]. We find that in ZnO, for an excitation wavelength of 500 nm, the slope is 1.0, signifying single-photon absorption mechanisms. Similarly, we obtain a slope of 2.0 for 730-nm excitation, indicating two-photon absorption at that excitation wavelength, and a slope of 3.0 for excitation with 820 nm light, signifying a three-photon absorption mechanism. The photoluminescence slopes at 530 nm and 800 nm are, respectively, 1.5 and 2.8, indicating a mixture of one- and two-, and two- and three-photon absorption mechanisms. The inset in Fig. 3 shows the broad band photoluminescence spectra of ZnO for three distinct excitation wavelengths. We did not observe any change in the photoluminescence peak position for the range of excitation intensities employed, considering our experimental error.

![Figure 3](image1.png)

Fig. 3. Photoluminescence measurements (log-log scale) that shows the slope at five different excitation wavelengths: 500, 530, 720, 800 and 820 nm, with slopes of 1.0, 1.5, 2, 2.8 and 3, respectively.

![Figure 4](image2.png)

Fig. 4. Excited state relaxation times as function of the excitation wavelength. The inset show the three-level energy diagram used to model the reverse saturable absorption effects.

4. Discussion

The linear absorption spectrum of ZnO reveals high absorption in the short wavelength range (less than 400 nm), as the photon energy is greater than the bandgap. Residual linear absorption is observed from 400 nm until approximately 520 nm due to deep levels attributed to oxygen vacancy [17,18].

When we consider what happens to single-photon absorption in ZnO at higher excitation intensities, we find that near 460 nm (near $E_{\text{photon}}/E_{\text{gap}} = 0.83$), the observed single-photon absorption is intensity dependent as we vary the excitation fluence from 0.8 mJ/cm$^2$ to 2.1 mJ/cm$^2$. Such nonlinear absorption is related to the carrier population in the conduction band [19]. In order to better understand the observed intensity dependence of the measured $Z$-scan at 460 nm, we model ZnO with a three-level energy diagram shown in the inset of Fig. 4, representing the valence band (VB), $|0\rangle$, localized deep level (DL) $|1\rangle$, and the conduction band (CB) $|2\rangle$.

At room temperature a certain fraction of the electrons in the DL will be thermally activated into the conduction band. Therefore, some DL are empty and electrons from the valence can be excited to the DL. Then, electron from the DL can be re-excited to conduction band by stepwise two-photon absorption, as the pulse duration is much shorter than the...
lifetime of the donor level. To describe the fraction of electrons in each state, we used the rate equation model, given by:

\[ \frac{dn_0}{dt} = -w_{01}n_0 + w_{em}n_1 + \frac{n_1}{\tau_{10}}, \]  

(1)

\[ \frac{dn_1}{dt} = +w_{01}n_0 - w_{em}n_1 - w_{12}n_1 - \frac{n_1}{\tau_{10}} + \frac{n_2}{\tau_{21}}, \]  

(2)

\[ \frac{dn_2}{dt} = +w_{12}n_1 - \frac{n_2}{\tau_{21}}, \]  

(3)

where \( n_i \) are the population fractions of the states \( i \) with \( n_0 + n_1 + n_2 = 1 \). The \( w_{01} = \sigma_{01}I(t)/\nu \) and \( w_{12} = \sigma_{12}I(t)/\nu \) are the one-photon transition rates, with \( \sigma_{01} \) and \( \sigma_{12} \) being the ground and excited state absorption cross-sections, respectively. The \( w_{em} = \sigma_{em}I(t)/\nu \) is the stimulated emission rate with \( \sigma_{em} \) being the stimulated emission cross-section that has the same order of magnitude of the ground state one \( (\sigma_{em} \approx \sigma_{01}) \). The set of differential equations are numerically solved using a Gaussian temporal profile for the laser pulse. The time dependence of absorption coefficient during the excitation is given by:

\[ \alpha(t) = N\left\{n_0(t)\sigma_{01} + n_1(t)\sigma_{12}\right\}^{1/2}, \]  

(4)

where \( N \) is the concentration of empty donor states in ZnO (estimated as \( \approx 1 \times 10^{17} \) cm\(^{-3} \)). The transmittance can be calculated by integrating Beer’s law, \( dI/dz = -\alpha(t)I(t) \), over the sample thickness and the full pulse width (over \( t \) from \( -\infty \) to \( +\infty \)). The absorption coefficient, \( \alpha(t) \), is obtained from the linear absorption spectrum and is directly related to the ground state absorption cross-section by \( \sigma_{01} = \alpha(t)/N \).

By fitting the Z-scan data in the one-photon absorption regime (460–500 nm) with the rate-equation model, we obtained \( \sigma_{12} = (14 \pm 2) \times 10^{-16} \) cm\(^2 \). Such value is higher than the ground state absorption cross-section in the same region \( (\sigma_{01} = 9.5 \times 10^{-18} \) cm\(^2 \) at 500 nm and \( \sigma_{01} = 22.5 \times 10^{-18} \) cm\(^2 \) at 460 nm), giving rise to reverse saturated absorption. This result indicates ZnO as a promising candidate for optical limiting applications at ultraviolet and blue wavelength region [20].

The excited state dynamics within the conduction band have a time constant on the order of tens of femtoseconds, and are shown as a function of excitation wavelength in Fig. 4. The results suggest that the relaxation time to DLs increase when the energy differences between the excited impurity states and the edge conduction band decrease.

This energy difference is associated with the distribution of electronic states density between the conduction band minimum and the DL state below the conduction band [21]. The value obtained for the ground state relaxation time \( (\tau_{10}) \) is 2.8 ns, consistent with previously published results [11].

In order to investigate the multiphoton absorption mechanisms, we obtain Z-scan measurements using longer excitation wavelengths (460 nm to 980 nm). At excitation wavelengths ranging from 540 nm to 760 nm \( (E_{\text{photon}}/E_{\text{gap}} \text{ from } 0.5 \text{ to } 0.71) \), we see in Fig. 2(a) that the two-photon absorption theoretical model fits our data well. Near the value of \( E_{\text{photon}}/E_{\text{gap}} \) = 0.70, however, the theory for two-photon absorption deviates from the data. That is due to the onset of a mixture of absorption mechanisms; both single-photon absorption and two-photon absorption are present in the material because of the close proximity of the excitation wavelength to the absorption tail of ZnO. We see that \( E_{\text{photon}}/E_{\text{gap}} \) = 0.71 is a turning point that demarks the boundary at which absorption in ZnO is based on single-photon absorption versus two-photon absorption.
When we tune the OPA further to access even longer excitation wavelengths, ranging from 820 nm to 980 nm ($E_{\text{photon}}/E_{\text{gap}}$ is from 0.39 to 0.46), we observe that two-photon absorption fitting of the Z-scan curves is inappropriate. Instead, we use three-photon absorption fitting of the Z-scan measurements, and plot the three-photon absorption coefficient as a function of $E_{\text{photon}}/E_{\text{gap}}$ in Fig. 2(b). The theoretical model is a good fit to the measured data up to about $E_{\text{photon}}/E_{\text{gap}} = 0.46$, where the three-photon absorption fit is no longer sufficient to describe the measured data. The reason is that near $E_{\text{photon}}/E_{\text{gap}} = 0.46$, there is a mixture of two- and three-photon absorption. It is important to mention that in the theoretical fitting with Brandi and Araujo [15] theory, represented by the solid lines in Fig. 2, the effective mass of conduction band, the reduced effective mass and the refractive index of ZnO used are those reported in the literature [9].

The 2PA coefficient we determined are in good agreement with the ones reported in Ref [9]. However, our 3PA data are about four times smaller than the ones reported in the literature [9] because in our results there is no spurious contribution from thermal effects since a low repetition rate laser was used.

To confirm the observed regions of nonlinear absorption processes and to verify the excitation energy positions of mixed absorption behaviour, we used photoluminescence data obtained from the same sample. The photoluminescence data, plotted on a log-log plot as a function of excitation intensity, is in agreement with previously reported data [18] and Z-scan results. Other photoluminescence [7,18] and Z-scan [8,9] data have observed multi-photon processes (two, three and mixture) in slightly distinct regions, probably due to differences on the sample quality as well as the distinct laser irradiance employed. Wang et al. claim that the observed mixture of two- and three-photon absorption at 800 nm results from a two-photon absorption followed by an additional one-photon absorption [18]. From our data the predominant mechanism observed through Z-scan and photoluminescence in range of 820-980 nm is a three-photon absorption. However, our measurement do not confirm nor exclude the potential for stepwise three-photon absorption due impurities present in ZnO. However, the probability of such event to occur is much lower than that of simultaneous three-photon absorption because the deep donor level concentration is low [22].

5. Conclusion

We demonstrated that under femtosecond laser excitation, ZnO presents distinct nonlinear absorption process, depending on the excitation wavelength. Simultaneous absorption of two- and three-photons were observed in the ranges of 540-760 nm and 820-980 nm, respectively. The multiphoton absorption processes were modeled by a theory developed by Brandi and Araujo [15], which properly describe the experimental results. In the region of 460-500 nm we observed a reverse saturable absorption due to one-photon excitation of deep levels in ZnO. Such process was described using a three-energy-level diagram and modeled by a rate equation system. For excitation around 530 nm and 800 nm we observed a mixture of one and two, and two and three-photon absorption. Such mixture of nonlinear processes was corroborated by fluorescence measurement.

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