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Wavelength Dependent Nonlinear Spectroscopic Study of Third Harmonic Generation Probed by Rotational Maker Fringes Method

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Abstract

Efficient third-order nonlinearities of the Zinc Oxide and Al-doped Zinc Oxide were studied by Third Harmonic Generation (Third Harmonic Generation) Maker fringes to establish the effect Aluminum of Aluminum doping (Al-doping) on the cubic nonlinearities. Adding the Al-dopant to the Zinc Oxide crystal structure results in changes that affect the optical and nonlinear characteristics. Presented results indicate that the magnitude of $\chi^{(3)}$ was enhanced at single experimental wavelengths; however, across the broadband experimental spectrum, the effect of Al-doping remained relatively constant. The observed enhancement of third-order nonlinearity was purely from the bound electronic response. The observation is attributed to increased charge carriers and spontaneous polarization in the Zinc Oxide and Al-doped Zinc Oxide crystal structure.

Keywords

Nonlinear Optics, Harmonic Generation, Maker Fringes, Zinc Oxide

1. Introduction

Zinc oxide (ZnO) is a thoroughly studied wide-bandgap semiconductor possessing excellent optical and electronic properties at room temperature. Nonlinear optical (NLO) properties of ZnO have been well researched; however, existing results are primarily available at single wavelengths or limited ranges; thus this work seeks to investigate Third harmonic generation over broadband wavelength far beyond existing experimental ranges and provide sufficient informa-

tion and data which aid in understanding the application of ZnO and Aluminum doped Zinc. The renewed interest in this material has been generated by doping with various impurities to enhance versatile optoelectronic responses for practical applications. Specifically, Al-doped ZnO (AZO) is an emerging transparent conducting oxide for photovoltaic applications [1] [2]. The material has a direct and wide bandgap in the near-ultraviolet (near-UV) spectral region (E_g = 3.3 eV) [3], making it ideal for various applications e.g. light-emitting diodes (LED's). Exciton binding energy in Zinc Oxide and Al-dopes Zinc Oxide is in the order of 60 meV; this large excitonic energy allows for emission to occur even at room temperature [1] [4] [5]. Under ambient conditions, Zinc Oxide and Al-doped Zinc Oxide typically crystallize in the wurtzite structure and are available as large bulk single crystals [6] [7]. Al-doped Zinc Oxide material properties have been extensively studied [3] [7] [8]. From the existing materials, the nonlinear optical (nonlinear optical) properties of zinc oxide have been well researched; however, existing results are mostly available at single wavelengths or limited ranges. However, the relevant Nonlinear Optical dispersions, *i.e.*, wavelength-dependences, are not fully studied especially at longer wavelengths, far below the bandgap, because doping can induce a drastic change in the Nonlinear Optical responses at this broad range of wavelengths via doping-induced subgap-state contributions. Moreover, there are only a few reports on the Nonlinear Optical Properties of Al-doped at the single wavelength of 1064 nm. In this paper, we explore the impact of Al doping on the third-order Nonlinear Optical properties of Al-doped prepared into thin films by atomic layer deposition (ALD) and systematically study whether Al doping can enhance Nonlinear Optical responses as a function of doping level. We explain our results by considering the existing theories and adequately referencing the available literature.

2. Motivation for Third Harmonic Generation Study

Third Harmonic Generation is of great use in ever-evolving technology. First, THG is useful in frequency conversions in photonic devices of, which are widely applicable in communications. Nonlinear optical Microscopy uses the THG, including imaging and analysis of the three-dimensional imaging. THG's Optical and nonlinear properties can be used to characterize materials and understand their properties for industrial applications. Many state-of-the-art NLO devices utilize third-order nonlinear properties involving optical switching and amplification. Wavelength division multiplexing uses the THG for coherent beam sources used in optical telecommunication.

3. Sample Preparation

ZnO and AZO films were grown by atomic layer deposition (ALD). A commercial ALD system from Sundew Technologies was used. This system employs sequential self-limiting surface reactions between the precursors to achieve atomic layer-controlled conformal thin film growth. The precursors used to grow the

sample were dimethyl zinc (DMZ), trimethylaluminum (TMA), and water. DMZ, water, and TMA pulse cycles were carefully chosen to achieve the desired thickness and composition. Detailed deposition procedure and reactions are explained in Ref (29) and references therein. ALD technique has many advantages over the commonly used sputtering due to; 1) it allows for the precise thickness control at Angstrom or monolayer. 2) ALD self-limiting aspect enables excellent step coverage and conformal deposition on high aspect ratio structures. 3) ALD produces a smooth and conformal film to the original substrate since the reactants are driven out entirely during the cycle, resulting in accurate thickness over large areas. 4) ALD growth is stable, and the thickness increase is constant in each cycle 5) It is easy to grow different multilayers on the same substrate; full details on sample preparation are detailed in and other references therein [9].

4. Third-Order Harmonic Nonlinear Optical Theory

This section briefly presents the basic theoretical description of the Third Harmonic Generation Nonlinear theory, and we follow from [10] [11]. The Macroscopic polarization P is the number of dipole moments per unit volume. In a linear regime, P is simply related to the electric field E of the incident light by

$$P(t) = \varepsilon_0 \chi^{(1)} E(t), \tag{1}$$

where $\chi^{(1)}$ is the linear susceptibility and ε_0 is the permittivity of free space. To fully describe the nonlinear polarization effect, Equation (1) can be expressed as a power series in E and given by

$$P(t) = \varepsilon_o \left[\chi^{(1)} E(t) + \chi^{(2)} E^2(t) + \chi^{(3)} E^3(t) + \cdots \right], \tag{2}$$

where the higher-order susceptibilities $\chi^{(n)}$ are tensors in general that relate the vector nature of P and E assuming that the nonlinear medium is lossless and dispersionless. The second and the third terms in Equation (2) are the second-and third-order nonlinear polarization, respectively. The second-order susceptibility $\chi^{(2)}$ can only occur in a material that has no inversion symmetry (noncentrosymmetric), whereas the third-order susceptibility $\chi^{(3)}$ can occur in any material including amorphous materials. The Nonlinear Optical response is described by a nonlinear wave equation that has time-varying nonlinear polarization acting as a source to the newly generated electric fields in the medium, and the wave equation can be readily obtained from Maxwell's equations as

$$\nabla^2 E - \frac{n^2}{c^2} \frac{\partial^2 E}{\partial t^2} = \frac{1}{\varepsilon_o c^2} \frac{\partial^2 P^{NL}}{\partial t^2} \tag{3}$$

where macroscopic polarization P has both the linear and the nonlinear terms that are written as $P = P^{(1)} + P^{NL}$, where $P^{(1)}$ is linear polarization and P^{NL} is nonlinear polarization. Third harmonic generation (Third Harmonic Generation), which is the focus of this study, can be represented by the third term in Equation (2). For an electric field of the form

$$E(t) = E \cos \omega t, \tag{4}$$

incident on a material, the third-order contribution is given by

$$P^{(3)}(t)=\frac{1}{4}\varepsilon_o\chi^{(3)}E^3\cos 3\omega t+\frac{3}{4}\varepsilon_o\chi^{(3)}E^3\cos\omega t, \tag{5}$$

the first term describes the response at 3ω which is responsible for the Third Harmonic Generation. The second term is the so-called optical Kerr effect. It is important to note that the Third Harmonic Generation arises from the interaction of three photons of the same frequency with a Nonlinear Optical medium, generating a single photon with thrice the frequency [10] [11]. To maximize the conversion efficiency, it is necessary to achieve the phase-matching condition. Third Harmonic Generation phase-matching in transparent materials is difficult because of a large index match between the fundamental and the Third Harmonic Generation beams. As a result, the Third Harmonic Generation study is used as a characterization tool. The wurtzite Zinc Oxide and Al-doped Zinc Oxide structures in this study had a preferential growth orientation along the (0001). The optical axis is therefore along the *c*-axis thereby presenting only two nonvanishing components of $\chi^{(3)}_{ijkl}$ namely; $\chi^{(3)}_{zzzz}$ and $\chi^{(3)}_{xxxx}$. With the known preferential growth direction of the samples, each nonvanishing component of $\chi^{(3)}_{ijkl}$ can be characterized with appropriate polarization choice [12] [13]. In this study only the $\chi^{(3)}_{xxxx}$ was characterized with p^{ω} and $p^{3\omega}$ polarization. For the film samples the absolute value of $\chi^{(3)}$ can be estimated from the relation

$$I_{3\omega}=\frac{2304\pi^6}{A}\left(t^{\omega}_{af}\right)^6\left(t^{3\omega}_{fa}\right)^2\frac{\sin^2\Psi}{\left(n^2_{\omega}-n^2_{3\omega}\right)^2}\left|\chi^{(3)}\right|^2 I^3_{\omega}, \tag{6}$$

where t^k_{ij} are the field transmission coefficients at the input and output surface of the sample. n_{ω} and $n_{3\omega}$ are the refractive indices at the fundamental frequency and third-harmonic frequency, respectively. I_{ω} is the input fundamental beam, A is the beam area, and $I_{3\omega}$ is the Third Harmonic Generation intensity. In Equation 4.1 Ψ is the phase factor and is defined as

$$\Psi_{\text{Third Harmonic Generation}}=\frac{3\pi L}{\lambda_{\omega}}\left(n_{\omega}\cos\theta_{\omega}-n_{3\omega}\cos\theta_{3\omega}\right), \tag{7}$$

where L is the interaction length, *i.e.*, the sample thickness, λ_{ω} is the wavelength of the input beam. θ_{ω} and $\theta_{3\omega}$ are propagation angles at fundamental and third harmonic beam. The Third Harmonic Generation intensity depends on the phase-matching factor

$$\Delta k=\frac{6\pi}{\lambda}\left(n_{3\omega}-n_{\omega}\right), \tag{8}$$

Considering the thickness of these samples (L= 250 nm), the Spectral Maker fringes effect is not expected within the experimental wavelength range. **Figure 1** shows the absence of oscillations for L = 0.25 μm thin films used in the experiment. The advantage of characterizing nonlinearity by measuring Third Harmonic Generation is that it only accounts for the fast Nonlinear Optical response.

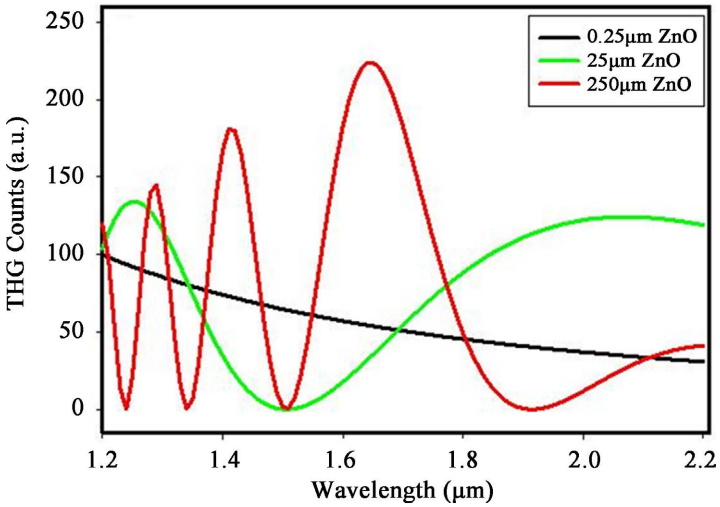

Figure 1. Spectral maker fringe for Zinc Oxide, the sample thickness is varied for comparison. There are no oscillations for the L = 0.25 μm (black line) over the experimental range.

Due to this, other contributions to Nonlinear Optical response, such as the thermal effects, orientation, and vibration effects, are excluded and cannot affect our results [12] [14].

5. Experimental Details

The THG properties of the ZnO and AZO were studied for between the wavelength 1.2 μm and 2.1 μm by Maker fringe. The excitation source was Nd: YAG picosecond laser (30 ps, 50 Hz). The polarization of the fundamental beam was adjusted using a polarizer placed before the sample. The THG signal was directed to a fiber optic bundle connected to the CCD camera using a collection lens. The polarization of the THG signal was adjusted using the analyzer. The measurement was done in transmission geometry with the sample placed in on a rotating stage to allow for continuous angular variations. The rotation axis of the sample was centered on the beam and perpendicular to it to get the fringe symmetry. Since the glass substrate, as well as other optical components, can generate THG, careful measurements and data processing were required to eliminate or minimize these background THG signals. First, a short-pass filter (50 transmittance in the visible region) was used just before the fiber-optic cable to suppress the remnant fundamental beam that can cause additional THG at the fiber input. Second, a THG Z-scan was conducted to locate an optimized sample position to maximize the THG counts from ZnO with minimal THG from the glass substrate, whereas another THG Z-scan determined the latter on a bare glass substrate with the same thickness. Finally, background THG signals from the substrate were measured at each wavelength and subtracted in the THG data to single out THG counts from ZnO only. A similar procedure was employed for THG measurements of all the AZO samples.

The Third Harmonic Generation properties of the Zinc Oxide and Al-doped

Zinc Oxide films were studied for the wavelength ranging from 1.3 μm to 2.1 μm by the Maker fringe. The excitation wavelengths were from a tunable Optical Parametric Oscillator. The polarization of the fundamental beam was adjusted using a polarizer placed before the sample. The Third Harmonic Generation signal was directed to a fiber optic bundle connected to the CCD camera using a collection lens. The polarization of the Third Harmonic Generation signal was adjusted using the analyzer after the sample. The measurements were done in transmission geometry, with the sample placed on a rotation stage to allow for continuous angular variation. The rotation axis of the sample was centered on the beam and perpendicular to it to generate symmetric fringe patterns [15] [16]. Since the glass substrate, as well as other optical components, can generate Third Harmonic Generation, careful measurements and data processing were required to eliminate or minimize these background Third Harmonic Generation signals. First, we used a short-pass filter (~50% transmittance in the visible region) just before the fiber-optic cable to suppress the remnant fundamental beam that can cause additional Third Harmonic Generation at the fiber input. Secondly, we conducted Third Harmonic Generation Z-scan to locate an optimized sample position to maximize the Third Harmonic Generation counts from Zinc Oxide with minimal Third Harmonic Generation from the glass substrate, where the latter was determined by another Third Harmonic Generation Z-scan on a bare glass substrate with the same thickness. Finally, background Third Harmonic Generation signals from the substrate were measured at each wavelength and subtracted in the Third Harmonic Generation data accordingly to single out Third Harmonic Generation counts from Zinc Oxide only. A similar procedure was employed for Third Harmonic Generation measurements of Al-doped Zinc Oxide samples.

6. Results and Discussions

Zinc Oxide and Al-doped exhibited strong angular dependent Third Harmonic Generation Maker fringe when the fundamental wavelength was varied between 1.3 μm and 2.1 μm. The corresponding Third Harmonic Generation wavelengths ranged from.433 μm to.7 μm. Representative graphs for experimental Third Harmonic Generation Maker fringes for the Zinc Oxide and Al-doped Zinc Oxide samples at λ = 1.907 μm is shown in **Figures 2(a)-(d)**. The experimental data were fit according to Equations 4.1 and 4.2. Experimental $\chi^{(3)}$ values were determined using fused silica as a reference, the $\chi^{(3)}$ of fused silica is ~ 1.99 × 10^{-22} m^2/V^2 at λ = 1.907 μm [17] [18]. Fused silica was chosen as a reference material since it is well-studied, and its third-order nonlinearity has been determined with high accuracy.

Since fused silica is centrosymmetric, using it as a reference improves the accuracy of our results, given its Third Harmonic Generation cannot be affected by any cascade effect. The results indicate that the Third Harmonic Generation depends on the concentration of the dopant atoms Al^{3+} at specific experimental

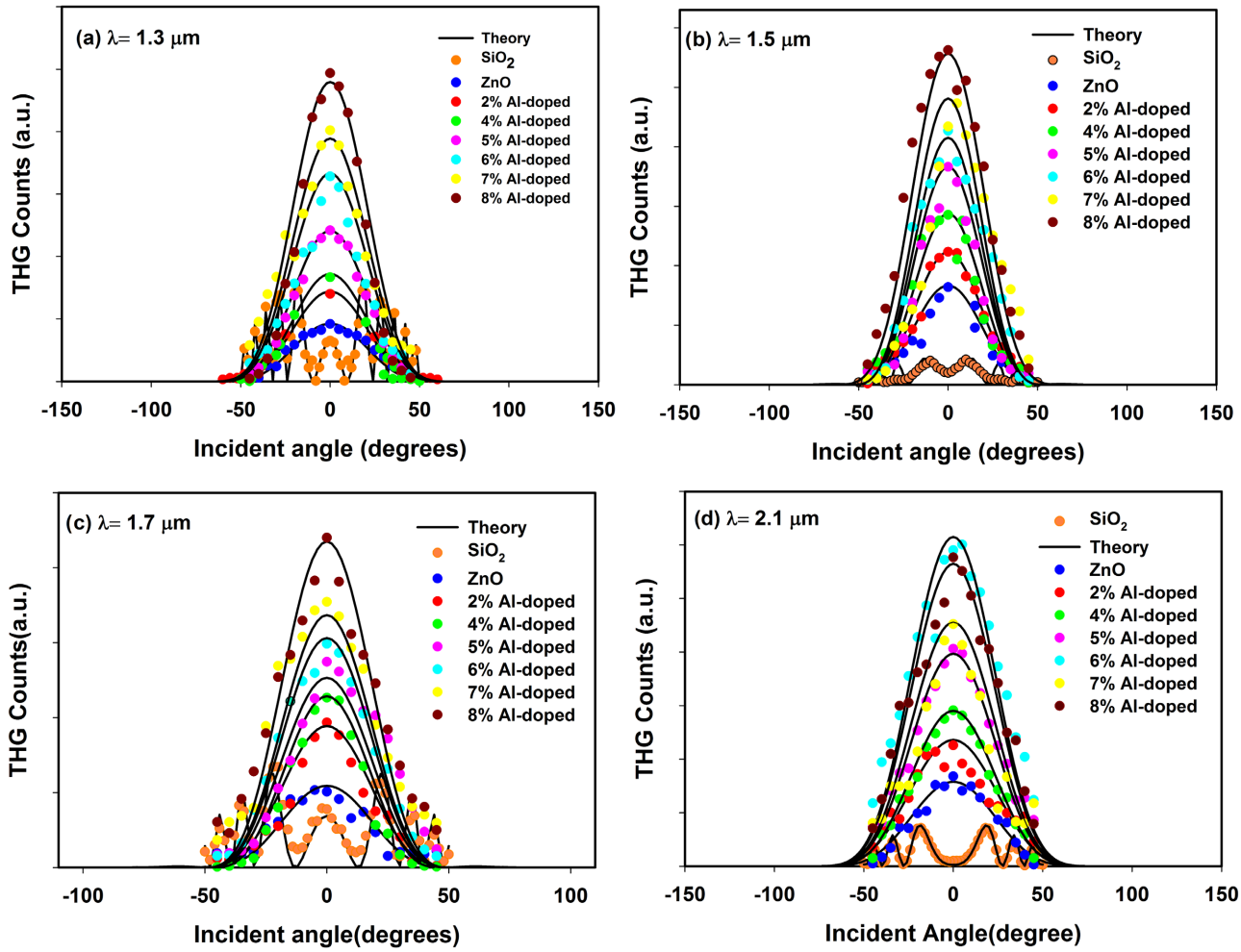

Figure 2. Spectral maker fringe for Zinc Oxide, the sample thickness is varied for comparison. There are no oscillations for the L = 0.25 μm (black line) over the experimental range.

wavelengths but largely remained constant across the observed spectrum. This observation is similar to the one reported by Sofiani *et al.* on Al-doped Zinc Oxide grown by spray pyralysis [19] [20] Abed *et al.* observed an enhanced Third Harmonic Generation in Nickel doped Zinc Oxide (Ni: Zinc Oxide) as compared to undoped Zinc Oxide [21]. The enhancement of the Third Harmonic Generation signal can be explained by considering the effects of Al^{3+} dopant atoms as follows. Increased concentration of Al^{3+} in Zinc Oxide crystal structures results in two effects: 1) Since Al^{3+} is a donor atom, more of it results in increased carrier density (more electrons). 2) Due to the difference in the ionic sizes of Al^{3+} and Zn^{3+}, a higher concentration of Al-dopant, the Al^{3+} occupies interstitial and grain boundary. This overall results in different in-plane orientation unit cells, causing the bonds in the neighboring cells to move from the mean position due to Coulomb interaction; this favors dangling bonds at the interface of different unit cells overall, resulting in increased change carrier [22].

The enhancement in the Third Harmonic Generation observed is thus attributed to the higher carrier densities [22] [23] [24]. The input field will induce

perturbation change on the Al^{3+} causing nonlinear polarization in the media [25] [26]. Kulyk *et al.* have also advanced a similar argument in thin microcrystalline films of Zinc Oxide [20] [27]. The results for broadband dispersion of $\chi^{(3)}_{zzzz}$ are presented in **Figure 3**. The spectral dispersion did not show any significant variation over the experimental range; after all, the wavelength was varied far from the band gap, so no resonance effect was expected. The efficient broadband Third Harmonic Generation with suppressed SHG has earlier been observed in Zinc Oxide nanorods prepared by hydrothermal deposition [28]. The authors attributed the Third Harmonic Generation response to be bound by the electronic response and suppressed SHG to the micron-size film thickness. For further comparison, we looked at the results of Zappettini *et al.* [12] who studied the dispersion of $\chi^{(3)}_{zzzz}$ and $\chi^{(3)}_{zzzz}$ of Zinc Oxide single crystals in the transparency wavelength range 0.344 - 0.540 μm, and presented results showing significantly high values attributed to exciton enhancement. In this section, we present a comparative study of the reported $\chi^{(3)}$ of Zinc Oxide and X: Zinc Oxide (X: Al, Ce, Ga, Sn, F, N, Ag, Cu) at λ = 1.604 μm with our study. The $\chi^{(3)}$ reported in the literature, and can be seen from **Figure 3**, the $\chi^{(3)}$ values were found to depend on several factors including; 1) concentration of the dopant atoms used, 2) thickness of the sample, 3) sample preparation techniques and growth kinetics 4) excitation source and the wavelength of study. Results of several authors who have studied (Zinc Oxide and Al-doped Zinc Oxide) similar to ours and reported varied results, a few discussed here include; Sofiani *et al.* studied the dependence of $\chi^{(3)}$ on different types of dopants (Cu, Er, Sn, and Al) [19] reported the highest $\chi^{(3)}$ from Sn-doped Zinc Oxide sample ~ 3.2×10^{-19} m^2/V^2 (see **Figure 3**). Castaneda studied F-doped Zinc Oxide and obtained $\chi^{(3)} \sim 1.2\times10^{-22}\ m^2/V^2$ more comparison are in **Figure 3** below for $\chi^{(3)}$ studied at 1064 nm. The units are all in MKS and converted according to [29].

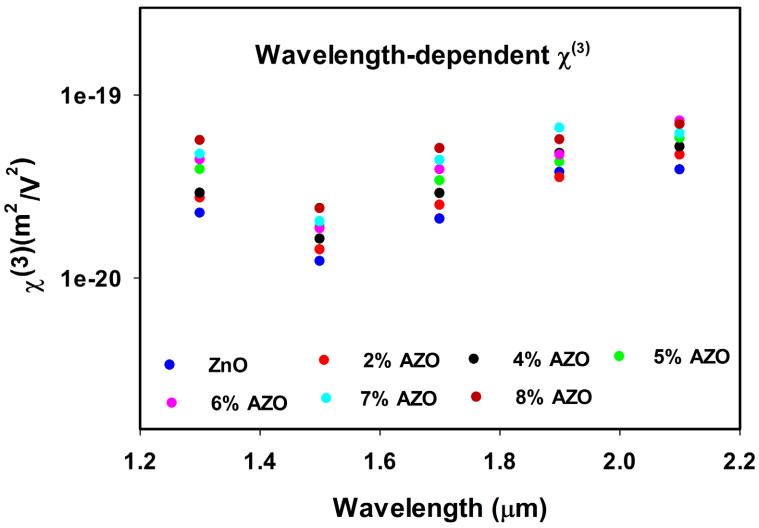

Figure 3. Spectral maker fringe for Zinc Oxide, the sample thickness is varied for comparison. There are no oscillations for the L = 0.25 μm (black line) over the experimental range.

7. Conclusion

Efficient third-order nonlinearities of Zinc Oxide and Al-doped Zinc Oxide were studied by Third Harmonic Generation Maker fringes beyond the existing ranges to establish the effect of doping on the cubic nonlinearities. The addition of the Al-dopant to the Zinc Oxide crystal structure results in changes that affect the optical and nonlinear characteristics of Zinc Oxide. Our results indicate a slight enhancement of the Third Harmonic Generation at experimental wavelengths. Third Harmonic Generation remains constant over the entire observed range. We discussed the possible causes of these observations based on the available models, and we concluded that the slight enhancement is due to the increased charge carried with increased Al-doping. We provided unique results as a function of wavelength and doping. Further study is proposed for different dopants to present an opportunity and guideline on choosing the best dopant for the highest Third Harmonic Generation conversion. The results will go a long way in adding to the existing literature and material applications. The author declares no conflict of interest and no funding for this research.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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