# Third order Nonlinearities in Scandium doped Zinc Oxide thin films

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***Abstract :*** The linear and nonlinear optical properties of semiconductors have garnered substantial interest in both theoretical and experimental realms. The pursuit of thin film nonlinear optical materials that can seamlessly integrate into optoelectronic devices has become a pressing demand. In this context, research endeavors have been dedicated to identifying a promising candidate for generation of third order nonlinearities. Utilizing the spin-coating sol-gel technique, an intricate exploration into the nonlinear optical attributes of thin films composed of Scandium doped Zinc Oxide (SZO) has been meticulously conducted, encompassing a range of Scandium (Sc) concentrations. This endeavor has yielded profound insights into the intriguing nonlinear behavior exhibited by these materials. Amidst the various Sc concentrations investigated, a notable standout is the SZO thin film containing 0.6 at.% Sc composition, showcasing the most remarkable coefficients of nonlinear refractive index. This distinction can be attributed to the notably superior crystalline quality inherent in the 0.6 at.% Sc composition when juxtaposed with its counterparts.

Specifically, the SZO thin film with a 0.6 at.% Sc doping concentration manifests a distinctive negative nonlinear index of refraction at a wavelength of 532 nm, a salient trait attributed to the manifestation of two-photon absorption The discernible peak-to-valley pattern observed in the measurements accentuates a self-defocusing tendency, further affirming the distinct and exceptional nonlinear characteristics inherent to this particular material composition.

.***IndexTerms*** **– Nonlinear index of Refraction,Thin Film,SZO,Self Defocussing.**

## I. Introduction

As the world continues to evolve, so do the demands and requirements of future conflicts. The landscape of warfare is projected to encompass radiation-based strategies, where various forms of radiation will serve as formidable ammunition to engage adversaries. In this new era of warfare, advanced sensors deployed across diverse terrains – land, air, space, and underwater – will take on a pivotal role in modern battlefield surveillance. Central to these advanced systems are electronic circuitry and an array of sensors that comprise crucial components of missile systems. However, in the exigencies of warfare, the need arises for robust materials that can shield and safeguard these sensors. Zinc Oxide (ZnO), renowned for its remarkable linear and nonlinear optical properties, emerges as a compelling choice. Its semiconducting characteristics have spurred significant theoretical and experimental interest.

A pressing demand exists for the development of thin film nonlinear optical materials that seamlessly integrate into optoelectronic devices. Among the diverse array of nonlinear optical materials investigated, ZnO, with its wide bandgap, stands out due to its exceptional nonlinear attributes. These properties position ZnO as an ideal candidate for nonlinear optical-based devices, holding promise for the future. The forefront of material innovation lies in nanosized ZnO, with its various forms such as nano wires, nano belts, and quantum dots. These forms have earned recognition as the vanguards of 21st-century materials. In the realm of nonlinear optical devices, the cornerstone often rests on the higher-order susceptibility of materials, represented by $\chi(3)$. Encouragingly, the exploration of ZnO has yielded significant milestones, including the reported second and third harmonic generation in ZnO microcrystalline thin films (1-4).

While bulk ZnO crystals have undergone scrutiny for their nonlinear optical properties through techniques like the Z-scan method, the exploration of nanosized doped ZnO has been relatively limited. Challenges arise from obtaining well-controlled semiconductor nanoparticles in solution, where factors like size, shape, and surface properties present hurdles. Consequently, the resulting nonlinear response is often modest due to the minuscule volume fraction of crystallites in the solution. Present endeavors delve into the augmentation of ZnO's properties through scandium doping, addressing both structural and nonlinear optical facets of SZO thin films. The Z-scan technique (Fig.1), utilizing the second harmonic of the Nd:YAG laser, serves as a reliable and precise means to probe these nonlinear optical properties(5).

In the framework of the z-scan technique, the material undergoes exposure to a concentrated and intense radiation. This interaction precipitates a profound transformation in the material's absorption properties. This change in absorption manifests as a dynamic alteration in transmittance, wherein the material's behavior becomes contingent on the intensity of the incident radiation. This intricate phenomenon, aptly termed nonlinear absorption, constitutes the bedrock of the z-scan method .By leveraging the z-scan technique, this study effectively unveils the enigmatic interplay between scandium doping and the ensuing structural and nonlinear optical traits of SZO thin films. This nuanced exploration, made possible through the precise manipulation of intense radiation, not only advances our comprehension of material behavior under distinct conditions but also contributes to the arsenal of techniques employed for the meticulous analysis of nonlinear optical properties. As we navigate the complexities of material science, the z-scan technique stands as an invaluable tool, offering profound insights into the intricate world of nonlinear optical phenomena and paving the way for innovative applications across the technological landscape.

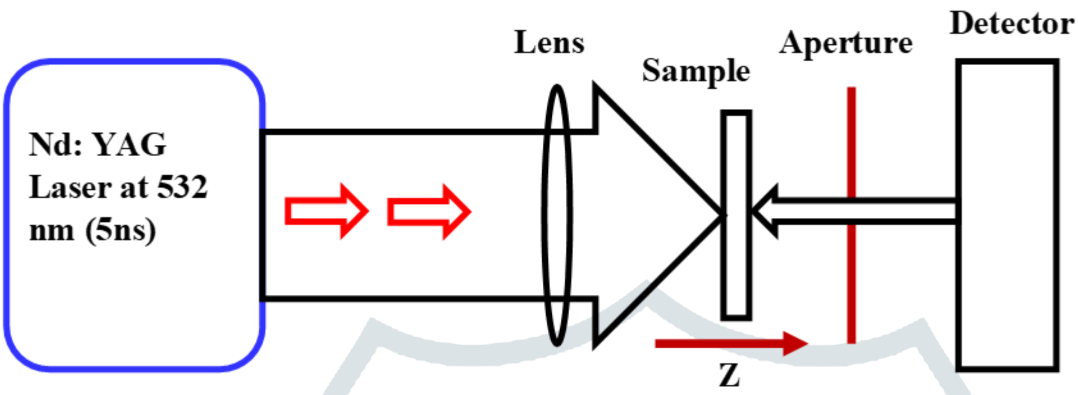


**Fig. 1:** Experimental setups of Z- scan method

## 2 RESULTS AND DISCUSSIONS

### 2.1 SURFACE MORPHOLOGY (SEM)

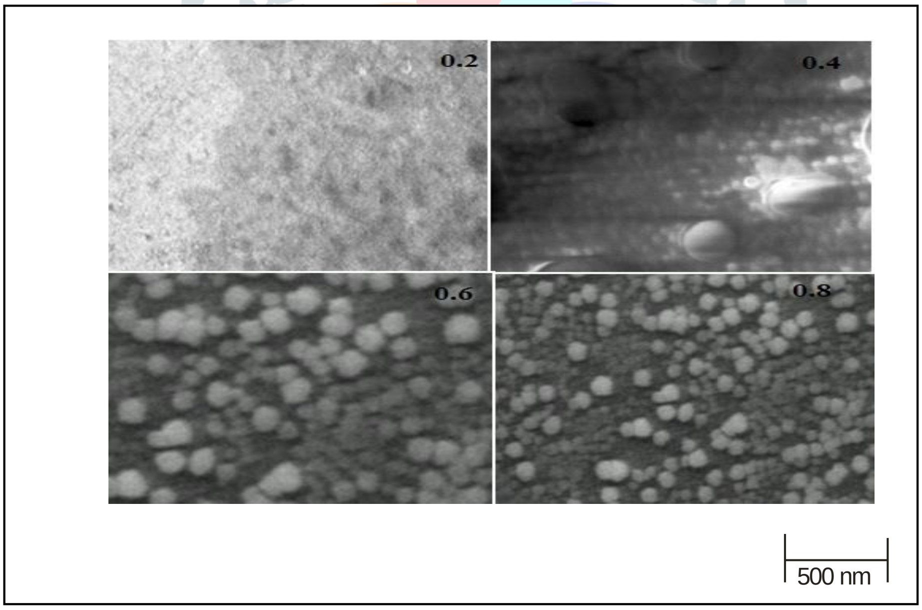


**Fig. 2: SEM Image of SZO films annealed at 450 °C as a function of Scandium concentration**

Fig 2 showcases scanning electron microscope (SEM) micrographs of SZO films that underwent annealing at 450ºC, demonstrating the evolution as a function of scandium concentration, spanning from 0.2 to 0.8 at.% (6). A careful examination of these micrographs reveals intriguing insights into the impact of doping on the film morphology.

The SEM micrograph of SZO with 0.2 at.% scandium content vividly illustrates the consequence of doping – a distinct shift characterized by the emergence of nano-sized particles. Moving along the scandium concentration gradient, at 0.4 at.%, a notable transformation unfolds as nanoparticles take on a more pronounced growth pattern. This progression is further magnified with an escalation in scandium concentration to 0.6 at.%, where particles exhibit a substantial increase in size. These SEM micrographs serve as a visual narrative, unraveling the intricate interplay between scandium doping and the resulting film structure. The evolution from scattered nano particles to a more defined and sizeable nanoparticle assembly underscores the nuanced effects of doping on the film's microstructure. This comprehensive exploration not only sheds light on the material's response to doping but also hints at the potential for tailoring film properties through controlled manipulation of scandium concentration. In an era where materials engineering play a pivotal role in shaping advanced technologies, these micrographs capture a snapshot of the dynamic relationship between dopant concentration and film morphology. As researchers venture deeper into the realm of nanoscale materials, such visual representations guide the path toward harnessing tailored properties for applications ranging from optoelectronic devices to advanced sensor systems.

### 3 NONLINEAR OPTICAL PROPERTIES-CLOSED APERTURE Z-SCAN

The closed aperture Z-scan measurements are plotted in Fig.3. The distinctive peak-valley arrangement observed in the configuration signifies the presence of negative nonlinearity within the sample. This observation aligns harmoniously with the outcomes computed by Sheik–Bahae and colleagues, who employed a two-band, effective-mass model (7-9) to arrive at analogous conclusions. In scenarios characterized by elevated values of refractive and absorptive nonlinearities, closed-aperture measurements encompass contributions stemming from both the intensity-dependent modifications in transmission and alterations in the refractive index (10).

The value of the nonlinear refractive index, denoted as $n_2$, is deduced from the alteration in peak-to-valley transmittance within a closed-aperture Z-scan. A comprehensive compilation of these calculated $n_2$ values are presented in Table 1. The graphical representation unmistakably portrays a distinct pinnacle succeeded by a trough, indicative of a negative (-ve) coefficient of nonlinear refraction, denoting a propensity for self-defocusing behavior. This intriguing phenomenon finds its primary origin in the realm of two-photon absorption, where ZnO exhibits conspicuous negative nonlinear refractive indices, particularly at a wavelength of 532nm.

For the SZO sample with a scandium concentration of 0.6 at.%, the determined value of the nonlinear refractive index, $n_2$, has been quantified at $-16.3\times10^{-6}$ esu. This measurement stands out as the most pronounced among all other SZO samples examined. The discerned magnitude of negative nonlinear refractive index not only provides a valuable metric for characterizing the material's optical properties but also underscores the distinctive self-defocusing traits intrinsic to SZO at this specific composition.

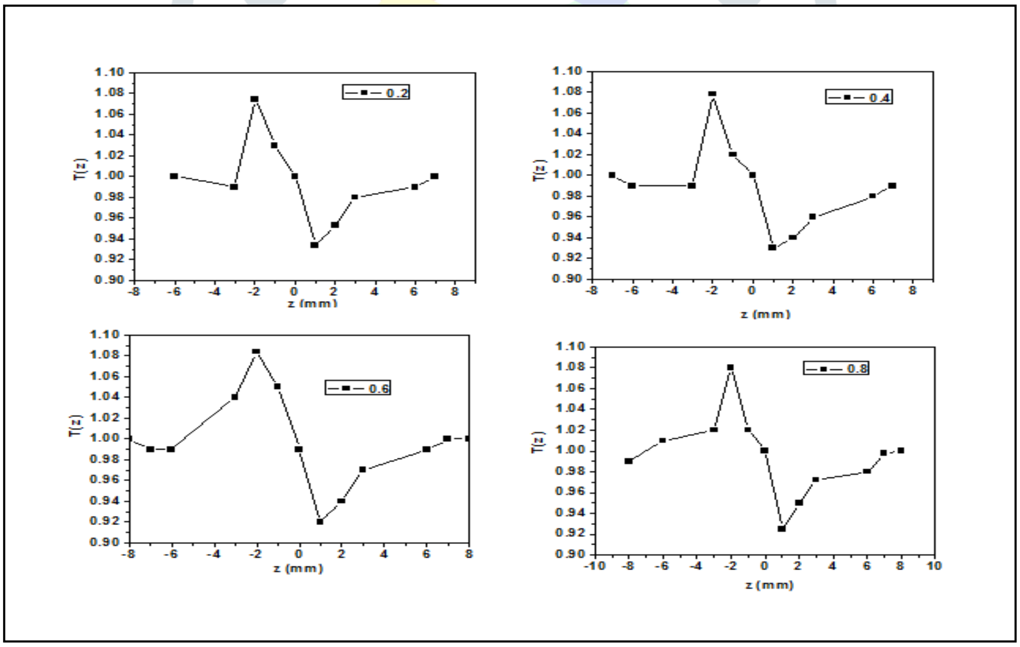


**Fig..3. Normalised transmittance with closed-aperture as a function of the position for SZO films of different doping concentration at 532 nm**

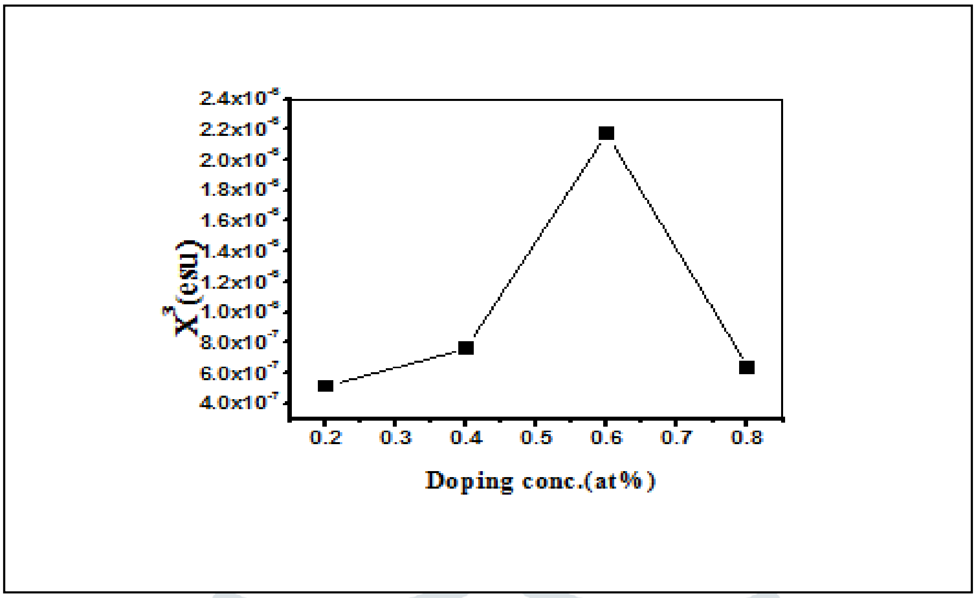


**Fig 4: variation of $\chi^{(3)}$ with different doping conc. of SZO samples**

In unraveling the intricate interplay of nonlinear optical phenomena, these findings contribute to our understanding of material behavior under intense radiation. Such insights hold promise for diverse applications, ranging from optical signal processing to the development of advanced optical devices, ushering in new avenues for harnessing nonlinear optical effects in modern technology. The value of $n_2$ and $\chi^3$are comparable to the already reported values by various researchers [11-13].The value of $n_2$ are directly related to the value of imaginary ($Im\chi^{(3)}$) and real ($Re\ \chi^{(3)}$) part of nonlinear susceptibility. The absolute value of $\chi^{(3)}$have been obtained and are mentioned in table 1.Fig.4 shows that the SZO(0.6 at.%) thin film has the highest value of $\chi^{(3)}$ Among all other samples due to better crystallinity.

| **Thin film Sample** | **Nonlinear refractive Index ($n_2$)(esu)** | **$\chi^{(3)}$esu** |
|---|---|---|
| **SZO (0.2at.%)** | $-5.2 \times 10^{-6}$ | $7.1 \times 10^{-7}$ |
| **SZO (0.4at.%)** | $-11.7 \times 10^{-6}$ | $18.6 \times 10^{-7}$ |
| **SZO (0.6at.%)** | $-16.3 \times 10^{-6}$ | $26.7 \times 10^{-7}$ |
| **SZO (0.8at.%)** | $-8.9 \times 10^{-6}$ | $14.3 \times 10^{-7}$ |

**Table 1 -Measured values of nonlinear refractive index($n_2$), third order nonlinear susceptibility($\chi^{(3)}$)of SZO films of different Sc concentration at 532 nm**

## 4 CONCLUSION

Employing the spin-coating sol-gel technique, an intricate exploration into the nonlinear optical attributes of SZO thin films encompassing diverse Scandium (Sc) concentrations has been undertaken. The consequential discoveries have illuminated intriguing insights into the nonlinear behavior exhibited by these materials. Among the varied Sc concentrations studied, the SZO sample featuring a 0.6 at.% Sc composition emerged as a standout performer, boasting the highest coefficients of nonlinear refractive index and nonlinear absorption. This achievement is underpinned by the superior crystalline quality inherent to the 0.6 at.% composition when compared to its counterparts. the SZO sample at 0.6 at.% Sc doping concentration showcases a distinctive negative nonlinear index of refraction at a wavelength of 532 nm, a characteristic attribute attributed to the manifestation of two-photon absorption.

Delving into the intricacies of the nonlinear behaviour, the SZO films doped at 0.6 at.% Sc concentration exhibit a remarkable nonlinear response. This is vividly reflected in the elevated values of the third-order nonlinear susceptibility ($\chi(3) = 26.7 \times 10^{-7}$ esu) and nonlinear coefficient of refraction ($n^2$ = -16.3 $\times 10^{-6}$esu). The distinctive peak-to-valley pattern observed underscores a self-defocusing inclination, further substantiating the unique nonlinear characteristics inherent to this material.

The substantial magnitude of the third-order nonlinear susceptibility $\chi^{(3)}$ unveils the material's exceptional nonlinear optical behavior. These findings position the SZO samples, particularly those with 0.6 at.% Sc doping, as promising candidates for generating third harmonic signals. In essence, this comprehensive investigation lays the foundation for SZO thin films to emerge as formidable contenders in the realm of nonlinear optics. The prowess of the SZO (0.6 at.%) composition in exhibiting exceptional nonlinear behavior, coupled with its promising attributes for third harmonic generation , augments its status as a compelling candidate for advanced optical applications.

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