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Review Article

Z-scan technique for nonlinear materials characterization: a review

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ABSTRACT
Nonlinear optical materials exhibiting large optical nonlinearities are in great demand owing to their potential applications in optical limiting, optical switching, optical data storage etc. To determine the third-order nonlinear optical properties of nonlinear optical materials, the well-known single Z-scan technique is employed. It is a simple experimental technique to measure intensity dependent third-order nonlinear susceptibility of nonlinear optical materials. It was originally introduced by Sheik Bahae et.al. In this technique, the sample is translated in the z-direction along the axis of a focused Gaussian beam, and the far field intensity is measured as function of sample position. Consequently, increases and decreases in the maximum intensity incident on the sample produce wavefront distortions created by nonlinear optical effects. This is a simple and sensitive single beam technique to measure the sign and magnitude of both real and imaginary part of the third order nonlinear susceptibility $\chi^{(3)}$ of nonlinear optical materials.

1. Introduction

When a nonlinear optical material is irradiated by an intense laser beam, the induced polarization may be expressed as:

$$P_i = \varepsilon_0\chi^{(1)}E + \varepsilon_0\chi^{(2)}E^2 + \varepsilon_0\chi^{(3)}E^3 + ... \\ = P^{(1)} + P^{(1)} + P^{(1)} + ... \quad (1.1)$$

Here, $\chi^{(1)}$, $\chi^{(2)}$ and $\chi^{(3)}$ are known as the first-, second- and third-order nonlinear optical susceptibilities, respectively. We shall refer to $P_{(i)}$ as induced polarization while $P^{(1)}$, $P^{(2)}$ and $P^{(3)}$ are the first-, second- and third-order nonlinear polarization, respectively. This term governs many nonlinear phenomena like third harmonic generation, optical Kerr effect, stimulated Raman scattering and stimulated Brillouin scattering. In general, $\chi^{(3)}$ couples together four frequency components: in other words, three fields interact to produce a fourth field

$$P(\omega_4) = \varepsilon_0\chi^{(1)}E(\omega_3)E(\omega_2)E(\omega_1) \quad (1.2)$$

in a lossless medium the susceptibility coefficients of $\chi^{(3)}$ are real. In this case, the primary nonlinear optical effects are the generation of new frequency components and the intensity dependent refractive index change (Kerr effect). In third-order interactions involving absorption, the imaginary part of χ (3) describes Raman and Brillouin scattering and two-photon absorption [1].

The development of photonic technology during the past decade has intensified research activities on searching for new materials that display unusual and interesting nonlinear optical (NLO) properties. New NLO materials are the key elements to future photonic technologies in which their functions can be integrated with other electrical, optical and magnetic components that have become important in the era of optical communication. Organic molecular and polymeric materials are relatively newcomers in the field of nonlinear optics compared with inorganic materials. The third-order optical nonlinearities of inorganic materials are large but their response time is relatively slow [2-3]. Large third order NLO susceptibilities have been measured in inorganic semiconductors using them as quantum wire and quantum dot materials.

Recently, research activities have been directed towards developing new organic molecular and polymeric materials. The superiority of organic materials has been realized because of their versatility and possibility of tailoring material properties by applying the techniques of molecular engineering to them for particular end-uses. In addition organic materials also exhibit large nonlinear figure of merit, high damage thresholds, and ultrafast response time.

The applications of NLO materials are widespread in the field of solid state technology that includes harmonic generators, optical computing, telecommunications, laser lithography, image processing and sensors, other optical systems. This shows that the study of NLO properties is truly an interdisciplinary area of research. The development of new materials can shed light on the theoretical understanding of the origin of NLO processes. Every year a wide variety of new NLO molecular and polymeric materials are discovered and the field continues to expand rapidly. Since the level of integration is also increasing rapidly in photonic technologies, organic polymers seem more promising compared with inorganic counterparts because of their compatibility with a variety of materials used in fabrication technology. Organic liquids, molecular solids, conjugated polymers and related model

compounds, NLO chromophore functionalized polymers, organometallic compounds, organic composites, liquid crystals, semiconductors, nanoparticles etc. are different types of nonlinear materials used for various applications in the photonic industry [4-8].

2. Objectives

The main objective of this study is to review the z-scan technique for the nonlinear materials characterization.

3. Z- scan technique for material's characterization

The characterization of the nonlinear optical properties of various NLO materials for various applications like frequency mixing, optical short pulse generation and measurement, optical communication, optical switching, optical limiting etc. is a fascinating field in modern optics [9-12]. The magnitude and response of third order nonlinear susceptibility is one of the important parameters of this class of materials and several techniques are available for the measurement of such parameters. Degenerate Four Wave Mixing (DFWM), Third Harmonic Generation (THG), optical Kerr effect, Z-scan etc. [1] are some of the techniques used for this purpose. Degenerate four-wave mixing can give both the magnitude and response of the third order nonlinearity. Similarly THG is another technique used for the measurement of the magnitude of the third order susceptibility tensor. While optical Kerr effect is used for the photo physical processes determining the nonlinearity. Using z-scan technique, the sign and magnitude of the third order susceptibility tensor can be calculated.

The z-scan technique is a simple and popular experimental technique to measure intensity dependent nonlinear susceptibilities of materials and it was originally introduced by Sheik Bahae et.al [13-14]. In this method, the sample is translated in the z-direction along the axis of a focused Gaussian beam, and the far field intensity is measured as function of sample position. Consequently increases and decreases in the maximum intensity incident on the sample produce wavefront distortions created by nonlinear optical effects in the sample being observed. This is a simple and sensitive single beam technique to measure the sign and magnitude of both real and imaginary part of the third order nonlinear susceptibility $\chi^{(3)}$ of materials. The z-scan is obtained by moving the sample along a well-defined, focused laser beam, and thereby varying the light intensity in the sample. In the original single beam configuration, the Investigations of nonlinear transmittance of the sample is measured, as the sample is moved, along the propagation direction of a focused Gaussian laser beam. A laser beam propagating through a nonlinear medium will experience both amplitude and phase variations. If transmitted light is measured through an aperture, placed in the far field with respect to focal region, the technique is called closed aperture z-scan experiment [13-14]. By varying the aperture in front of the detector, one makes the z-scan transmittance more or less sensitive to either the real or imaginary parts of the nonlinear response of the material, i.e., nonlinear refractive index and nonlinear absorption, respectively.

In the closed aperture z-scan the transmitted light is sensitive to both nonlinear absorption and nonlinear refraction. In this case, phase distortion suffered by the beam while propagating through the nonlinear medium is converted into corresponding amplitude variations and the real part of the susceptibility tensor can be calculated. On the other hand, if transmitted light is measured without an aperture the z-scan obtained is known as open aperture z-scan and in this case entire light from the sample is collected [14]. In the open aperture z-scan the output intensity is sensitive only to the nonlinear absorption of the sample and the imaginary part of the susceptibility tensor can be calculated form the data obtained.

Z-scan technique is highly sensitive to the profile of the beam and also to the thickness of the samples [13-15]. Any deviation from the Gaussian profile of the beam and also from thin sample approximation will give rise to erroneous results. To enhance its sensitivity and applicability new extensions have been added. A two color Z-scan is used to perform the studies of non-degenerate optical nonlinearities [16]. A much more sensitive technique, EZ-scan (eclipsed Z-scan), has been developed which utilizes the fact that the wings of a circular Gaussian beam are much more sensitive to the far-field beam distortion [17]. A reflection z-scan technique was introduced to study the optical nonlinearities of surfaces [18]. Z-scan with top-hat, investigations of nonlinear beams and elliptical Gaussian beams has been performed resulting in better sensitivity [19]. The dual wavelength (two-color) extension of the standard z-scan technique has been used to measure the non-degenerate nonlinearities [16]. This has been further used to time resolve the dynamics of the nonlinear process by introducing a delay between the pump and probe beams [16]. Z-scan measurements can also been done with astigmatic Gaussian beams [20]. In the case of astigmatic Gaussian beam, a slit is used instead of a (circular) aperture. Z-scan measurement for non-Gaussian beams with arbitrary sample thickness [21] and arbitrary aperture [22] has also been suggested. In the case of the former, nonlinear parameters are measured in comparison with a standard sample, mostly carbon disulphide (CS_2) [23]. The Z-scan technique has been used extensively to study different materials like semiconductors, nano-crystals, semiconductor-doped glasses, liquid crystals, organic materials, biomaterials etc. [4-8, 24].

3.1 Closed aperture Z-scan

In order to measure the nonlinear refraction or the real part of $\chi^{(3)}$ a sample is moved using a translation stage along the propagation direction of the tightly focused beam and the transmitted light is collected through an aperture placed in front of a detector as shown in Figure 1.

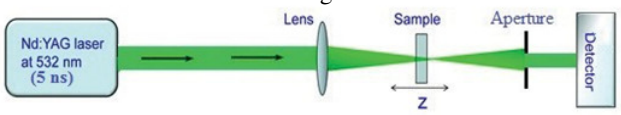

Figure 1: Closed aperture z-scan setup for nonlinear refraction measurements.

For a positive refractive index change it would act as converging lens and for a negative refractive index change it would act as a diverging lens. The normalized transmittance through the aperture is shown in Figure 3 for both positive and negative refractive index changes. The graph obtained by dividing the closed aperture z-scan data by the open aperture z-scan data measured simultaneously is known as "divided z-

scan graph" [14]. In the "divided zscan" the effect of nonlinear absorption is cancelled out and the measured nonlinear effect is due to the nonlinear refraction alone.

When the Gaussian beam propagates through the sample, due to the nonlinear refractive index change in the transverse direction the sample acts as converging or diverging lens as displayed in Figure 2.

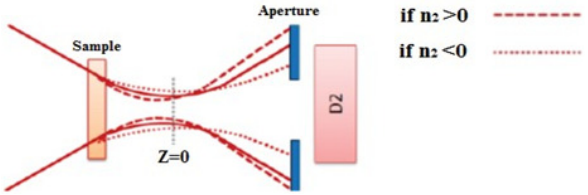

Figure 2: Depending on the sign of the change of the nonlinear refractive index, the sample may act as a converging or diverging lens.

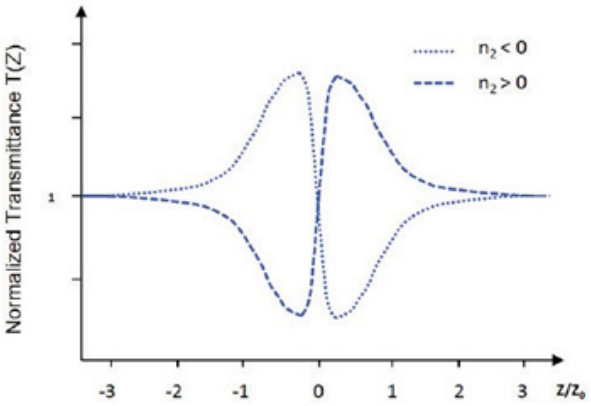

Figure 3: Z-scan traces for the transmission through the aperture for negative and positive nonlinear refractive index change.

Thus the curve for Z versus transmittance has a peak followed by a valley for a negative refractive nonlinearity. The curve for a positive refractive nonlinearity will give rise to the opposite effect, i.e. a valley followed by a peak [13-14]. The former is called self-defocusing and the latter is called self-focusing. Figure 3 shows a typical closed aperture z-scan curve of samples having negative and positive nonlinearities respectively.

One of the mechanisms of self-focusing is optical Kerr effect [25] which has instantaneous response. In this case the electric field of a light beam exerts a torque on anisotropic molecules by coupling to oscillating dipole induced in the molecule by the field itself. Resulting light induced molecular reorientation is the main mechanism for optical nonlinearity in a transparent liquid. Nonlinear refractive index depends linearly on light intensity. Other mechanism of optical Kerr effect includes off resonant excitation of narrow band absorbers and consequent distortion of electronic distribution among energy levels in the materials. The resultant intensity dependent refractive index is responsible for self-focusing or self-defocusing. In self-focusing beam collapses upon itself spatially. Kerr like nonlinearity has very fast response time of the order of picoseconds.

3.2 Open aperture z-scan

In order to determine the nonlinear absorption of a material, the aperture in front of the light collection photodiode is fully opened or removed as shown in Figure 4. When the normalized transmittance vs. the sample position is recorded then it will be a symmetric curve around the focus as shown in Figure 5.

Nonlinear absorption of the sample is manifested in the open aperture z-scan measurements. For example, if nonlinear absorption like two-photon absorption (TPA) is present, it is manifested in the measurements as a transmission minimum at the focal point [14]. On the other hand, if the sample is a saturable absorber, transmission increases with increase in incident intensity and results in a transmission maximum at the focal region. A straightline z-scan graph is obtained in the case of samples with linear absorption. In the case of reverse saturable absorption (RSA), the sample experiences the strongest intensity and fluence at focus; therefore it absorbs the most energy and allows least transmittance.

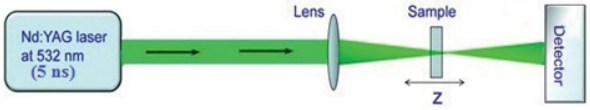

Figure 4: Open aperture z-scan setup for nonlinear absorption measurements. In order to measure the nonlinear absorption, all the transmitted light is collected by a detector.

Away from the focus in the direction of both increasing and decreasing z transmittance increases evenly because the irradiance decreases symmetrically about the focus. These features are shown in Figure 5.

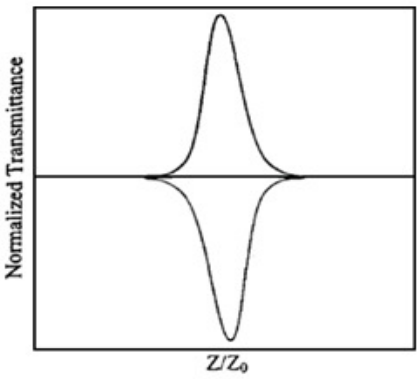

Figure 5: Open aperture z-scan curves.

3.3 Advantages and disadvantages of Z-scan technique

The Z-scan has several advantages. Among these is its simplicity. As a single beam technique, the alignment of beam is not difficult although it is to be kept centered on the aperture. It can be used to determine both the magnitude and the sign of n_2. The sign is obvious from the shape of the transmittance curve. Generally, data analysis is quick and simple, making it a good method for screening new nonlinear materials. Under certain conditions, it is possible to isolate the nonlinear refractive and nonlinear absorptive contributions to the far-field transmittance. Thus, unlike most DFWM methods, the z-scan can determine both the real and the imaginary parts of $\chi^{(3)}$. The technique is also highly sensitive, capable of resolving a phase distortion of $\lambda/300$ in samples of high optical quality. Finally, the Z-scan can also be modified to study nonlinearities on different time scales as well as higher order contributions.

Disadvantages of the technique include the fact that it requires a high quality Gaussian TEM_{00} beam for absolute measurements. The analysis must be different if the beam is non-Gaussian. Sample distortions or wedges, or a tilting of the sample during translation, can cause the beam to walk off the-field aperture. This produces unwanted fluctuations in the detected signal. The technique cannot be used to measure off-diagonal elements of the susceptibility tensor except when a second non-degenerate frequency beam is employed. Such a technique is useful for measuring the time dependence of nonlinearities but this detracts from the simplicity and elegance of the method. The introduction of a second beam of a different frequency requires careful alignment of the two beams, taking into account difference in spot sizes and focal positions due to chromatic aberration, and physical separation and filtering of the beams prior to detection.

4. Conclusions

Nonlinear optics (NLO) is a broad field of research and technology that encompasses subject matter in the fields of Physics, Chemistry, Biology and Engineering. The z-scan technique is a simple and popular experimental technique to measure intensity dependent nonlinear susceptibilities of materials. In this method, the sample is translated in the z-direction along the axis of a focused Gaussian beam, and the far field intensity is measured as function of sample position.

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