Chapter 6

Non linear optical studies of BiFeO$_3$-NaNbO$_3$ composite powder, BiFeO$_3$-NaNbO$_3$ -PMMA composite film and Mn doped BiFeO$_3$-NaNbO$_3$ composite powder

Abstract

The (NLO) properties of various solid-state, inorganic and organic materials have been and are being extensively investigated for their use in photonic and opto-electronic applications. Ultrafast and large nonlinearity is needed to realize NLO devices. The magnitude and response of third-order nonlinear susceptibility are important parameters in characterizing and determining the applicability of any material as a nonlinear optical device. This chapter deals with studies on nonlinear optical properties of BiFeO$_3$-NaNbO$_3$ composites using Z-scan technique. Optical limiting efficiency of BiFeO$_3$-NaNbO$_3$ ceramic powder, Mn doped Nonlinear Optical BiFeO$_3$-NaNbO$_3$ ceramics and BiFeO$_3$-NaNbO$_3$ -PMMA film composites were studied.
6.1 Introduction

The Z-scan is the simplest and most sensitive technique amongst numerous techniques for measuring the nonlinear index of refraction and nonlinear absorption coefficient of materials.\textsuperscript{1,2} Z-scan studies give information about the nonlinear characteristics of a material and excitation of this study yields important information regarding the response time and the dynamics of the transient processes contributing to the nonlinear refractive index. In cases where nonlinear refraction is accompanied by nonlinear absorption, it is possible to separately evaluate the nonlinear refraction as well as the nonlinear absorption, by performing two Z scans, one with aperture and the other without an aperture. Materials with nonlinear optical property found applications in different fields including biomedical field.\textsuperscript{3-7}

Optical-power limiters are required to protect the eyes or photodetectors from damage caused by tunable laser pulses. Different phenomena are used for optical limiting, such as light scattering in carbon black suspensions,\textsuperscript{5,6} beam fanning in photorefractive materials\textsuperscript{7} and nonlinear absorption in absorbing materials (reverse saturable absorption RSA) and in transparent materials (two-photon absorption TPA). Phthalocyanines,\textsuperscript{8} porphyrins\textsuperscript{9} and carbon C\textsubscript{60} are efficient RSA materials.\textsuperscript{10} Their efficiency as optical-power limiters occurs for long pulse duration, but they have the drawback of being absorbing and highly colored.\textsuperscript{11} On the other hand, TPA materials are transparent in the visible region at low energy with an instantaneous response and no saturation. For nanosecond pulses, recent results have highlighted the interest of organic two photon absorbers.\textsuperscript{12-21}

Optical nonlinearities in ferrites are relatively unexplored and reports\textsuperscript{27-29} are rare compared to organics, semiconductors and metals. Modifications in optical nonlinearity caused by the inclusion of different transition metals into a spinel ferrite system would be of considerable interest owing to applications including optical limiting. Recent studies give evidence of a very promising nonlinear optical efficiency for BFO which is found to be superior to the standard oxide materials previously introduced.\textsuperscript{29,31}
6.2 Experimental

Basically, the Z-scan method consists in translating the nonlinear sample through the focal plane of a tightly focused Gaussian beam and monitoring the changes in the far field intensity pattern. For a purely refractive nonlinearity, the light field induces an intensity dependent nonlinear phase and as consequence of the transverse Gaussian intensity profile, the sample presents a lens-like behaviour. The induced self-phase modulation has the tendency of defocusing or re-collimating the incident beam, depending on its Z position with respect to the focal plane. By monitoring the transmittance change through a small circular aperture placed at the far field position, one is able to determine the nonlinear refractive index. Any nonlinear absorption present in the sample can be found in a measurement where the aperture is replaced by a lens (open aperture Z-scan).

![Figure 6.1 Schematic representation of Z-scan experimental setup.](image)

The Z-scan works on the principle of moving the sample under investigation through the focus of a tightly focussed Gaussian beam. The interaction of the medium with the laser light changes as the sample is moved. This is because the sample experiences different intensities, dependent on the sample position (z) relative to the focus (z=0). By measuring the transmitted power (the transmittance) through the sample as a function of z-position of the sample, information about the light-matter interaction can be extracted. The two nonlinear interactions that can be determined in this fashion are the sample’s nonlinear index of refraction and nonlinear absorption coefficient. For the measurement of the nonlinear index of refraction, an aperture is placed in front
of the detector measuring the transmitted light. This makes the measurement sensitive to beam spreading or focusing and relates to a transformation of phase distortion into amplitude distortion. The basic setup of Z-scan technique is shown in Figure 6.1. In the Figure 6.1, BS is the beam splitter, D1 is the reference detector, D2 is the probe detector and $z$ represents position of the sample. An aperture is placed in front of the probe detector when measuring the nonlinear index of refraction. A sample displaying nonlinear refraction will act as a lens of variable focal length as it is moved along the $z$-axis. A maximum transmittance through the aperture will occur when the sample is just in front of the focus. This maximum transmittance (peak) will drop to minimum (valley) as the sample is moved further and the beam diverges as a result of the negative lensing by the sample. The transmittance through the aperture will again return to the linear value as the sample is moved further from the focus. The result of a scan such as transmittance versus position graph which has a peak followed by a valley. When the sample has a positive nonlinear index of refraction the graph is inverted.

The nonlinear optical measurements were carried out using the conventional open aperture Z-scan technique. The powder samples suspended in dimethyl formamide (DMF) by sonication were taken in a 1 mm cuvette. For excitation, 5 ns laser pulses were obtained from a frequency doubled Nd:YAG laser (Minilite Continuum, 532 nm) and 100 fs pulses were obtained from a regeneratively amplified mode-locked Ti-Sapphire laser (Spectra physics, 800 nm). In the Z-scan setup, the laser beam is focused using a lens and the sample is translated along the beam axis ($z$ axis) through the focus ($z=0$). At each position `$z$', the sample sees a different laser fluence and the transmission is measured using a pyroelectric laser energy probe which is placed after the sample. In order to monitor the pulse to pulse laser energy variation we have used a reference beam picked out from the main beam. All measurements were done in the single-shot mode and there is an interval of about more than one seconds between successive laser pulses. Using the data obtained from Z-scan measurements, nonlinear optical parameters could be calculated by numerically fitting the data points using the appropriate nonlinear transmission equations.
6.3 Results and discussion

6.3.1 Linear optical studies of BiFeO$_3$-NaNbO$_3$ composites powder

The UV-Visible absorption spectra of composites are shown in Figure 6 (a). The absorption cut-off wavelength of the as prepared composite samples lies between 500-600 nm which is close to the reported value for pure BFO (ie 560 nm), suggesting that the present material can absorb visible light in the wavelength range of 400–565 nm. The UV-Visible absorption spectroscopy is frequently used to determine the energy band gap of the powder samples from their absorption spectra. The optical band gap was determined using the Tauc’s formula, $\alpha h\nu = A(h\nu-E_g)^n$, where $\alpha$, $h\nu$, $E_g$ and $A$ are absorption coefficient, photon energy, band gap and a constant respectively. The exponent ‘n’ depends on the type of transition and it may have values 1/2, 2, 3/2 and 3 corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively. In the present case, the best fit of $(\alpha h\nu)^{1/n}$ versus the photon energy was obtained for $n = 1/2$. The energy band gap of nanoparticles could be estimated from the tangent line in the plot of $(E\alpha)^2$ against photon energy ($E$) as shown in Figure 3(b). The tangent line, which is extrapolated to $(E\alpha)^2 = 0$, gives the band gap ($E_g$).

![Figure 6.2](image)

Figure 6.2 (a) UV-VIS diffuse reflectance spectra of the BiFeO$_3$-NaNbO$_3$ nanoparticles, where the dotted line is the division between UV and visible light. (b) Plot of $(E\alpha)^2$ versus photon energy ($E$).
Table 6.1: Band gap energy of the samples

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Sample name</th>
<th>Band gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>X=0</td>
<td>1.7</td>
</tr>
<tr>
<td>2</td>
<td>X=0.1</td>
<td>1.9</td>
</tr>
<tr>
<td>3</td>
<td>X=0.5</td>
<td>2.3</td>
</tr>
<tr>
<td>4</td>
<td>X=0.7</td>
<td>2.8</td>
</tr>
</tbody>
</table>

The calculated band gap values for each composite is given in Table 6.1 which is in agreement with values from previous reports.\textsuperscript{33,36} Pure NaNbO\textsubscript{3} have reported \(E_g\) value of 3.3-3.4 eV.\textsuperscript{37} Incorporation of NaNbO\textsubscript{3} increases the band gap energy of the composite which is probably due to the interaction between BiFeO\textsubscript{3} and NaNbO\textsubscript{3}.

6.3.2 Nonlinear optical studies of BiFeO\textsubscript{3}-NaNbO\textsubscript{3} composites powder

The open-aperture Z-scan technique was used for measuring the nonlinear optical properties of the samples. A frequency-doubled Nd:YAG laser (MiniLite, Continuum) emitting 5 ns laser pulses at 532 nm, operating in the single-shot mode, was used for excitation. A plano-convex lens of 10.75 cm focal length was used to focus the laser beam to provide a focal spot radius of about 18 \(\mu\)m. Uniform dispersions of the samples in DMF were obtained by ultra-sonication taken in 1 mm path length glass cuvettes were used for the measurements. Concentrations were adjusted such that all samples had a linear transmission of 70% at the excitation wavelength. Samples were mounted on an automated translation stage to control and facilitate their movement along the z-direction through the beam focus \((z=0)\). A plot of sample transmission against sample position (with respect to \(z=0)\) gives the Z-scan curve, from which the nature of the optical nonlinearity can be determined. The experiment was automated using a LabVIEW program. The open aperture Z-scan curves (inset) and the corresponding intensity dependent transmissions calculated from the Z-scan curves, measured for ultrafast laser pulse excitation (800 nm, 100 fs) in the BiFeO\textsubscript{3}-NaNbO\textsubscript{3} composites (for x=0, 0.1, 0.5, 0.7) are shown in Figure 6.8,
whereas those for short pulse excitation (532 nm, 5 ns) are shown in Figure 5.9. The linear transmission is adjusted to be about 70% at both excitation wavelengths, and experiments were carried out at an average energy of 40 µJ for nanosecond and 11 µJ for femtosecond excitations. The open aperture Z-scan curves obtained in both cases exhibit a smooth valley indicating typical reverse saturable absorption behaviour. In order to find the nature and strength of nonlinear absorption, numerically fitting of the measured data to different nonlinear transmission equations has been performed. The best fit was obtained for a model in which 2PA (for fs excitation) or effective 2PA (for ns excitation) occurred along with SA.\textsuperscript{22-26,38}

In such a case the nonlinear absorption coefficient can be written as

\[ \alpha(I) = \left[ \frac{\alpha_0}{1+(I/I_s)} \right] + \beta I \]  \hspace{1cm} (2)

and the corresponding transmission equation is given by

\[ \frac{dI}{dz} = -\left[ \alpha_0 + \frac{(I/I_s)} + \beta I \right] I \]  \hspace{1cm} (3)

This equation can be numerically solved to obtain the best fit values of saturation intensity (I_s) and two photon absorption coefficient (\beta). The calculated nonlinear parameters for short-pulse and ultrafast laser pulse excitations are presented in Table 6.2. The optical limiting performance is quantified using the optical limiting threshold value, which is defined as the input fluence at which the sample transmission drops to 50% of its linear transmission. The optical limiting threshold (OLT) value is an important parameter to determine the optical limiting efficiency of the material. A lower OLT value indicates higher limiting efficiency. Compared to other recent reports, this material is found to have higher optical limiting property.\textsuperscript{39-41}
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Figure 6.3 Open aperture Z-scan curves (inset) and the corresponding intensity dependent normalized transmission obtained in BiFeO$_3$-NaNbO$_3$ (for $x=0, 0.1, 0.5$ and $0.7$) for ultrafast (100 fs) pulse excitation. Open circles represents experimental data while the solid line represents numerical fit to Equation 3.

Table 6.2: Calculated values of nonlinear optical parameters of BiFeO$_3$-NaNbO$_3$ composites

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Sample Name</th>
<th>5 ns excitation</th>
<th>100 fs excitation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\beta$ ($\times 10^{-10}$ m/w)</td>
<td>$I_s$ ($\times 10^{11}$ w/m$^2$)</td>
</tr>
<tr>
<td>1</td>
<td>X=0</td>
<td>1.8</td>
<td>7.99</td>
</tr>
<tr>
<td>2</td>
<td>X=0.1</td>
<td>1.2</td>
<td>5.499</td>
</tr>
<tr>
<td>3</td>
<td>X=0.5</td>
<td>1.0</td>
<td>2.499</td>
</tr>
<tr>
<td>4</td>
<td>X=0.7</td>
<td>0.9</td>
<td>2.499</td>
</tr>
</tbody>
</table>
Z-scan experiments with relatively long (5 ns) laser pulses allow for multiple absorption from the same laser pulse, which greatly enhances excited state absorption (ESA). While the incorporation of NaNbO₃ into BiFeO₃ provides no significant modification to the ultrafast optical nonlinearity of BiFeO₃, it obviously affects the nanosecond optical nonlinearity (Figure 6.4). In this case, nonlinear absorption is found to decrease with increase in the NaNbO₃ concentration. This quenching of nonlinear optical absorption in the composite originates from factors associated with size reduction such as increase in grain boundaries and increase in the energy gap by increasing the NaNbO₃ content. Pure BiFeO₃ has an Eg of 1.702 eV, but the incorporation of NaNbO₃ into BiFeO₃ results in an increase in band gap energy to 2.53 eV when x=0.7. From exciting the samples using nanosecond and femtosecond laser pulses, it may be concluded that 2PA and effective 2PA are the dominant absorptive
nonlinearities in the present set of samples. These samples exhibit efficient optical limiting and can have potential applications in photonic devices.

6.3.3 Nonlinear optical studies of Mn doped BiFeO$_3$-NaNbO$_3$ composites powder

The measured open-aperture Z-scan curves and the corresponding optical limiting curves calculated from the Z-scan data for the Mn doped BiFeO$_3$-NaNbO$_3$ powder samples are plotted in Figure 6.5.

![Figure 6.5](image)

(a) Open aperture Z-scan curves obtained in Mn0, Mn0.05 and Mn0.1 compositions for 5 ns pulse excitation, (b) Intensity dependent normalized transmission in Mn0, Mn0.05 and Mn0.1 compositions for 5 ns pulse excitation at 532 nm.
It is found that the nonlinear transmission of the samples given in Figure 6.5 (a) and Figure 6.5 (b) can be best modelled numerically by a propagation equation which involves excited state absorption and relatively weak absorption saturation, given by\(^{42,43}\)

\[
\frac{dF}{dZ} = -\alpha F - \left( \frac{\alpha \sigma}{2h\nu} \right) F^2
\]

where \(\sigma\) is the excited state absorption cross section, \(F\) is the input laser fluence, \(x\) is the sample path length, \(h\) is the Planck's constant and \(\nu\) is the laser frequency. \(\alpha\) is the absorption coefficient which is given by

\[
\alpha(F) = \frac{\alpha_0}{1 + (F/F_s)}
\]

where \(F_s\) is the saturation fluence. Since \(F_s\) is given by \(h\nu/2\sigma_0\), it is possible to calculate \(\sigma_0\), the ground state absorption cross section, from the value of \(F_s\) (this is useful in the case of samples whose molar concentrations are not directly known). The nonlinear transmission behaviour will depend on the values of \(\sigma/\sigma_0\) and \(F_s\). Numerically calculated values of the excited state absorption cross section, saturation fluence and ground state absorption cross section are presented in Table 6.3.

**Table 6.3: Nonlinear optical parameters of Mn doped BiFeO\(_3\)-NaNbO\(_3\) ceramic powder**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Linear transmission at 532 nm (%)</th>
<th>Laser pulse energy ((\mu)J)</th>
<th>Excited state absorption cross section, (\sigma) (cm(^2))</th>
<th>Saturation fluence, (F_s) (J/cm(^2))</th>
<th>Ground state absorption cross section, (\sigma_0) (cm(^2))</th>
<th>(\sigma/\sigma_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn 0</td>
<td>70</td>
<td>40</td>
<td>1.65 (\times) 10(^{-19})</td>
<td>10</td>
<td>1.86 (\times) 10(^{-20})</td>
<td>8.8</td>
</tr>
<tr>
<td>Mn 0.01</td>
<td>70</td>
<td>40</td>
<td>1.8 (\times) 10(^{-19})</td>
<td>10</td>
<td>1.86 (\times) 10(^{-20})</td>
<td>9.6</td>
</tr>
<tr>
<td>Mn 0.1</td>
<td>70</td>
<td>40</td>
<td>2.2 (\times) 10(^{-19})</td>
<td>10.5</td>
<td>1.77 (\times) 10(^{-20})</td>
<td>12.3</td>
</tr>
</tbody>
</table>
The OLT values are found to be 4.5, 3.8 and 2.7 J/cm² for Mn0, Mn0.05 and Mn0.1 samples respectively. Comparing the OLT values of Mn0, Mn0.01 and Mn0.5, the Mn doping reduces the OLT values significantly which means the optical limiting property is enhanced by Mn doping.

6.3.4 Nonlinear optical studies of BiFeO₃-NaNbO₃–PMMA film

![Figure 6.6](image_url)

**Figure 6.6** (a) Open aperture Z-scan curves obtained in PMMA, x=0 and x=0.1 compositions for 5 ns pulse excitation, (b) Intensity dependent normalized transmission in PMMA, x=0 and x=0.1 compositions for 5 ns pulse excitation

BiFeO₃-NaNbO₃-PMMA film samples for 5% ceramic particle in the polymer matrix were taken for the nonlinear optical study. The Z-scan and fluence
curves of the films using 5 ns laser pulses at 532 nm are shown in Figure 6.6. For 5 ns excitation, the input laser pulse energy was fixed to 25 µJ. The data obtained is plotted against sample position from which the nonlinear optical parameters can be calculated by numerically fitting them to the transmission equations (equation 1 & 2). The Z-scan traces show decreased transmittance at higher laser fluences indicating the occurrence of nonlinear absorption. The nonlinear optical coefficients were calculated by numerically fitting the obtained Z-scan data to standard nonlinear transmission equations. It is well known that the nonlinear optical transmission of a medium can have contributions from saturable absorption (SA) and/or reverse saturable absorption (RSA). Occurrence of RSA is material dependent and can happen due to phenomena such as excited state absorption, free carrier absorption, two-photon or three-photon absorption and nonlinear scattering.

As excited state absorption (ESA) is the main processes leading to nonlinear absorption in the current samples at an excitation pulse width of 5 ns, ESA will be a maximum resulting in strong RSA and the contribution of 2PA will be relatively small. The value of $\sigma/\sigma_0$ (shown in Table 6.4) gives the figure of merit for a nonlinear optical material. The calculated nonlinear optical parameters for the films are presented in Table 6.4.

<table>
<thead>
<tr>
<th>sample</th>
<th>linear transmission at 532 nm (%)</th>
<th>laser pulse energy (µJ)</th>
<th>excited state absorption cross section, $\sigma$ (cm$^2$)</th>
<th>saturation fluence, $F_s$ (J/cm$^2$)</th>
<th>ground state absorption cross section, $\sigma_0$ (cm$^2$)</th>
<th>$\sigma/\sigma_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>polymer</td>
<td>92</td>
<td>25</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>X=0</td>
<td>69</td>
<td>25</td>
<td>3.1 x 10^{-19}</td>
<td>10</td>
<td>1.86 x 10^{-20}</td>
<td>16.5</td>
</tr>
<tr>
<td>X=0.1</td>
<td>52</td>
<td>25</td>
<td>3.42 x 10^{-19}</td>
<td>12</td>
<td>1.55 x 10^{-20}</td>
<td>21.9</td>
</tr>
</tbody>
</table>

In the present case, the OLT values are found to be 3.38 and 5.1 J/cm$^2$ for x=0 and x=0.1 respectively. OLT of an optical limiter is the value of input fluence.
at which the transmittance falls to 50% of the linear transmittance. However, the optical limiting property of BiFeO$_3$-NaNbO$_3$ ceramic powder is much higher than the film composite.$^{24}$

6.4 Conclusion

BiFeO$_3$-NaNbO$_3$ nanocomposite samples with pure phase were successfully synthesized using Pechini method. The effect of Mn doping in the composite were also studied. The reduced size and absence of impurity were the remarkable achievement which alter the optical limiting properties of the samples. The reduced band gap and reduction in particle size were found as the reason for enhanced nonlinear optical properties of the present set of samples compared to their bulk form. From exciting the samples using nanosecond and femtosecond laser pulses, it may be concluded that 2PA and effective 2PA are the dominant absorptive nonlinearities in the present set of samples. These samples exhibit efficient optical limiting and can have potential applications in photonic devices. The Mn doped samples were also found to be efficient optical limiters. But the optical limiting property of Mn doped samples are less compared to undoped samples. The OLT values of film samples are higher than the powder samples which indicate the reduced optical limiting efficiency of the film compared to powder samples.
References


40. D. R. Vinayakumara, Manish Kumar, P. Sreekanth, Reji Philip, Sandeep Kumar, RSC Adv., 2015, 5, 26596.


