CHAPTER 6

OPTICAL LIMITING STUDIES

6.1 INTRODUCTION

Research towards the nonlinear optical materials is gaining much interest for their application as passive optical limiters which can be used to strongly attenuate the optical beam to a threshold level at high intensity while exhibiting linear transmittance at low intensities. Such devices are used for protecting human eyes and optical sensors from damage due to exposure to intense radiation which may be used to protect human eyes and as optical sensors from highly intense laser beams. Nonlinear organic materials are more preferred for applications as optical sensors for the last ten years. Large nonlinearity, broadband spectral response and fast response time of the organic dye molecules are the important parameters that realize them for their applications in optical processing and optical limiting.

It was the thermal mechanism using a continuous wave (cw) laser which was the basis for the first optical limiter (Leite et al 1976). At low incident intensities, an optical limiter exhibits linear transmittance and is transparent and at high intensities, it becomes slightly opaque. Regardless of the magnitude of the input, an optical limiter is designed in such a way to keep the power, irradiance, energy or fluence transmitted by an optical system below some specified maximum value i.e. at low input powers, high transmittance is maintained. Apart from protection of sensitive optical sensors and components from laser damage, they can be used for other potential
applications such as laser power regulation, stabilization or restoration of signal levels in optical data transmission or logic systems.

There are many nonlinear optical mechanisms which may result in the optical limiting effect as reported in the literature for the fabrication of optical limiting devices. The various intensity dependent optical nonlinear processes that results in the optical limiting effect are (a) nonlinear refraction (NLR) (b) nonlinear absorption (NLA) (c) non linear scattering (NLS), (d) photo refraction (PR) and (e) optically induced phase transitions.

The origins of these nonlinearities are found to vary widely. The origin of nonlinear refraction may be due to molecular reorientation, the electronic Kerr effect, excitation of free carriers, photorefraction or optically-induced heating of the material. Nonlinear absorption may be associated with two-photon absorption, excited state absorption, or free carrier absorption. Induced scattering may arise due to optically-induced heating or plasma generation in the medium. The origin of optically-induced phase transitions is mainly of thermal.

Basically below a threshold value, an ideal optical limiter exhibits linear transmission and clamps the output to a constant above it, thus providing safety to sensors or eye. An effective optical limiter may be identified with the following minimum criteria such as

- High linear transmittance
- Fast response time (e.g. picoseconds or much faster).
- Low limiting threshold (the input corresponding to the breakpoint in the curve).
- Broadband response (e.g. the entire visible spectrum).
- Low optical scattering.
To achieve efficient optical limiting, study has been extensively done on a wide variety of organic and inorganic materials. Various approaches have been developed towards better optical limiting based on, e.g., electro-optical, magneto-optical, and all-optical mechanisms. The all-optical limiters rely on materials that exhibit one or more of the nonlinear optical mechanisms: nonlinear refraction such as self-focusing, self-defocusing, induced scattering, induced refraction, induced aberration, excited state absorption, two-photon absorption, photorefraction and free-carrier absorption in nonlinear optical media. Coupling two or more of these mechanisms has also achieved enhancement in optical limiting, like self-defocusing in conjunction with TPA, TPA in one molecule with ESA in another molecule. Different experimental geometries like cascaded limiters are also studied to achieve large figure of merit and dynamic range.

6.2 PROCESSES LEADING TO OPTICAL LIMITING

The first optical power limiter was reported by Leite et al (1967). The experimental demonstration of it is based on the laser induced thermal lens effect using 488 nm cw Ar ion laser beam as incident light and nitrobenzene as the linearly absorbing medium with an aperture in front of the detector. Though the change of power through the aperture was only 3% of the total input power change at high input levels, the original idea and set-up are still the basis of most popular optical limiting designs using organic dye solutions, semiconductors and other materials as linearly absorbing media. The two categories in which optical limiting devices are classified are energy-spreading type of devices and the energy-absorbing type of devices.

6.2.1 Energy-Spreading Type Optical Limiters

The basic requirement for energy-spreading type of optical limiting device is to place an aperture or pinhole in front of a detector. The limiting of
the detected laser beam is based on the fact that, after passing through a nonlinear medium, the spatial energy distribution of the transmitted laser beams changes. When the input laser intensity (or fluence) increases, there will be more portions of the incident laser energy spreading to a wider solid-angle range. As a result, the portion passing through the aperture will decrease accordingly.

In these cases the observed limiting behaviour depends not only on the input laser intensity (or fluence) and the nonlinear medium, but also on the pinhole size and the geometric configuration of the optical system for a given device. For most of these type of devices, thermally induced refractive index change plays a major role. Typical designs for the energy-spreading type of optical limiting devices are schematically shown in Figure 6.1.

![Figure 6.1 Schematic illustration of energy-spreading type of optical limiters](image-url)
In all these cases the opening size of the aperture is chosen such that for a very low input fluence (or intensity) level, the transmitted laser beam after passing through the medium can just totally pass through the aperture without blocking.

Figures 6.1 (a) and (b) shows the optical limiter based on self-focusing and self-defocusing. In both the cases, due to spreading of energy in the aperture plane at high input levels, the detected energy portions are significantly reduced. In Figure 6.1 (c), the design is based on laser-induced and intensity dependent scattering. A system of linearly absorbing particles randomly distributed in a transparent host material will act as the limiting medium. In the case of a weak input light beam, the changes in the temperature and refractive index due to the particles absorption in the system are negligible, while in the case of a strong laser beam, the absorption-induced temperature change of the particles is no longer negligible and each particle forms an individual heating center. As a result of this local heating effect, the medium becomes highly inhomogenous and considerable portions of the energy will spread out into a wider spatial range and the portion of the light passed through the aperture will be limited. In Figure 6.1 (d), the medium is a mixed system composed of two microscopic components that have the same static refractive index but are in different phase states, e.g. one in liquid and the other is solid. If one component is transparent and the other is linearly absorptive to the incident laser beam, as a result of selective opto-heating process, the whole system becomes inhomogeneous in the boundary between the two components. In Figure 6.1 (e), the mechanism is based on induced aberration. Here, the induced refractive index change is a function of the local intensity distribution of the laser beam inside the medium. An irregular spatial distribution of local light intensity may lead to a random refractive index change at higher intensity levels, which may cause severe aberration influences on the wavefront of the transmitted laser beam. By
keeping a small pinhole in the focal plane of a focusing lens, the portion of the laser energy passed through the pinhole will decrease as the induced aberration becomes greater. Although, all optical limiting devices of energy spreading type are based on the laser induced refractive index change and featured by using an aperture, in some experimental devices no aperture is used. The limited sensitive area of the detector still plays the role of aperture. Even though opto-thermal effect induced refractive index change has a slower temporal response; it is considered to be important when compared to all other nonlinear optical effects related to refractive index changes.

The following are the origins that can cause thermally induced refractive index changes:

I. Non-zero residual linear absorption in transparent and non-resonantly absorptive medium may arise in the presence of small amount of impurities or external particles. The small residual linear absorption might be strong enough to create a remarkable thermally induced refractive index change at high input laser intensity (or fluence).

II. Thermally induced refractive index change will be significant for a resonant and linearly absorbing media such as dye solution or semiconductor crystal, even for a weaker cw laser beam or low fluence pulsed laser beam.

III. The contribution from the thermal effect will be largely responsible for the observed optical limiting behavior than the contribution from pure nonlinear absorption when an aperture is placed in front of a detector, while working with a nonlinear absorbing material in RSA or TPA mechanism.
6.2.2 Energy-Absorbing Type Optical Limiters

Another type of mechanism that may be employed for optical limiting is nonlinear absorption. The optical limiting relies on the fact that the transmission of nonlinear absorbing media decreases when the input laser intensity (or fluence) increases. Aperture or pinhole arrangement is not necessary. The optical limiting devices based on this mechanism can be called the energy-absorbing type of optical limiters and Figure 6.2 shows the common design for optical limiting devices for this type of limiters. The various processes that may lead to this type of optical limiting are Two-Photon Absorption (TPA), Excited State Absorption (ESA) and Free-Carrier Absorption (FCA). ESA is the process leading to nonlinear absorption in organic molecules and a similar process in semiconductors, metals and metal nanoparticles is called FCA.

![Diagram of Optical Limiting Device](image)

**Figure 6.2 Schematic illustration of Optical limiting device based on nonlinear absorption and optical bistability**

The nonlinear optical response can be exhibited when chromophores have strong excited-state absorption and weak ground-state absorption over some spectral range. A variety of materials and mechanisms are being explored for use in optical limiting. This type of optical limiting effects are more reliable and may be applied in fast (highly convergent)
optical systems as the optical energy is absorbed and converted to heat as opposed to being spread, as in nonlinear refractive or scattering media. The photophysical properties of chromophores may be systematically modified using rational changes in molecular structure which will enable molecular engineering approaches to the development of chromophores with enhanced limiting responses.

6.3 MATERIALS FOR OPTICAL LIMITING

Based on different nonlinear optical processes, large varieties of materials have been studied for optical limiting purposes. Improved nonlinear materials with more sensitivity and less linear loss are being developed to incorporate them into optical systems and their ability to protect real sensors. More attention is focused around pulsed lasers in the visible and near infrared bands, in view of the importance and vulnerability of the eye. Based on nonlinear absorption and nonlinear refraction, dyes may lead to optical limiting in selected portion of the visible band. The most extensively studied materials are the macrocyclics including phthalocyanines and naphthalocyanines, porphyrins and fullerenes and their derivatives in which long-lived triplet excited state can be produced copiously. Liquid crystals are another class of materials studied in the visible to mid IR region via refraction and TPA. Various materials like photorefractive materials, photonic band gap materials, nanomaterials and nanotubes, nonlinear absorbers doped in xerogels and solgel films, filters, organic/inorganic clusters, layered systems and bacteriorhodopsin are studied for their optical limiting properties. Among the various materials discussed in the literature, some of them show low limiting thresholds and low damage thresholds with continuous wave beams and ns/ps pulses. Some of the materials show very high damage thresholds with high limiting thresholds. Few metal and semiconductor nanoparticles are
found to exhibit excellent optical limiting responses toward nanosecond pulses. Also, nanomaterials emerge as new class of optical limiting materials.

The work aims at studying the organic materials to bring some of these in tandem to achieve eye-safe limiting thresholds using pulsed Nd:YAG laser and continuous wave He-Ne laser within the visible region of the spectrum. In pursuit of this, low limiting thresholds of the organic dyes are measured by varying the input fluence of the laser beam and the concentration of the dye.

6.4 EXPERIMENTAL SET-UP FOR OPTICAL LIMITING

Optical limiting studies were performed by focusing the input beam using convex lens of focal length 10 cm for ns excitation. The peak intensities used in experiments were in 0.05 - 50 MW/cm$^2$ range for ns pulse excitation. These studies were performed for different concentration of dyes. The input power is varied using the variable input control panel.

Initially, the laser beam was focused normally onto the sample by a convex lens of focal length of 10cm. The sample could be moved forth and back along the optic axis in order to change the position of the focal point of the lens with respect to the sample. The cuvette containing the nonlinear medium was placed after the focal point. For optical limiting of energy absorbing type, no aperture was placed in front of the photo detector. The beam after passing through the nonlinear medium was made to fall on a photodetector. The intensity of the input laser beam was varied systematically and the corresponding output intensity values were measured by the photodetector.

In order to study the optical limiting behavior of the dye samples, the sample was moved along the direction of the laser beam at various
position around the focus of the lens \((z = 0)\) forward and backward. The transmittance was recorded using a power meter connected to the photodetector. It is found that the limiting occurs when the sample was placed beyond the focus of the lens. Hence the sample is placed beyond the focus of the lens i.e. closer to the valley point (as determined from Z-scan graphs).

### 6.5 LIMITING CHARACTERISTICS OF ORGANIC DYES

#### 6.5.1 Limiting Characteristics of Xylidine Ponceau Dye

The optical limiting experiment was performed for Xylidine Ponceau dye belonging to Azo family. The solvent used was ethanol. The dye solution was taken in a dye cuvette and was placed at the valley position behind the focal point. The pulsed Nd:YAG laser of second harmonic wavelength 532 nm was used as the excitation source. In order to study the contribution of the solvent towards optical limiting property, the experiment was first done for the solvent alone (without dye). But no limiting property was observed. The experiment was then performed for the dye in ethanol solvent with three different dye concentrations of 0.01 mM, 0.02 mM and 0.03 mM using a 1 mm quartz cuvette.

The input power of the laser beam was varied systematically and the corresponding output power through the aperture was detected by a photodetector connected to the power meter. The characteristics curve of the output intensity as a function of the input intensity was obtained. A graph was drawn between the input intensity along the x-axis and the corresponding output intensity along the y-axis. The optical limiting curve of the dye is shown in Figure 6.3. The transmitted output intensity was found to vary linearly with the incident input intensity at low input intensities, but starts to deviate at high incident intensities. With further increase of the input intensity, the transmitted intensity reached a plateau and was saturated at a
point defined as the limiting amplitude (i.e.) the maximum output intensity, showing obvious limiting property.

A graph is plotted between the limiting amplitude and concentration for Xylidine Ponceau dye. Figure 6.4 shows the variation of limiting amplitude with concentration for the dye. The values of limiting amplitude for different dye concentration are given in Table 6.1.

**Table 6.1** Concentration dependence of limiting amplitude of Xylidine Ponceau dye

<table>
<thead>
<tr>
<th>Dye</th>
<th>Limiting Amplitude for the different Dye Concentration in MW/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.01 mM</td>
</tr>
<tr>
<td>Xylidine Ponceau</td>
<td>0.283</td>
</tr>
</tbody>
</table>

**Figure 6.3** Optical limiting curves of Xylidine Ponceau dye in liquid medium
Figure 6.4 Variation of limiting amplitude with concentration for Xylidine Ponceau dye

The mechanism responsible for optical limiting in Xylidine Ponceau dye was reverse saturable absorption and was mainly attributed to the stronger excited state absorption of the dye chromophores when compared to its weaker ground state. From the results, it was also found that optical power limiting threshold is inversely proportional to concentration. Highly concentrated dyes in solution exhibited stronger optical limiting behaviour when compared to its lower ones indicating that the number density of dye molecules was a main factor which affects the clamped level of the beam (Rekha & Ramalingam 2009). The limiting threshold for 0.03 mM concentration of the dye was found to be 0.212 MW/cm².

6.5.2 Limiting Characteristics of Azophloxine Dye

The optical limiting experiment was performed for Azophloxinedye belonging to Azo family. The solvent used was ethanol. The dye solution was taken in a dye cuvette and was placed at the valley position behind the focal point. Pulsed Nd:YAG laser of second harmonic wavelength 532 nm was
used as the excitation source. In order to study the contribution of the solvent towards optical limiting property, the experiment was first done for the solvent alone (without dye). But no limiting property was observed. The experiment was then performed for the dye in ethanol solvent with three different dye concentrations of 0.03 mM, 0.05 mM and 0.07 mM using a 1 mm quartz cuvette.

The input power of the laser beam was varied systematically and the corresponding output power through the aperture was detected by a photodetector fed to the power meter. The characteristics curve of the output intensity as a function of the input intensity was obtained. A graph was drawn between the input intensity along the x-axis and the corresponding output intensity along the y-axis. The optical limiting curve of the dye was shown in Figure 6.5. The transmitted output intensity was found to vary linearly with the incident input intensity at low input intensities but with further increase of the input intensity, the transmitted intensity reaches a plateau and was saturated at a point defined as the limiting amplitude: (i.e.) the maximum output intensity, showing obvious limiting property. A graph is plotted between the limiting amplitude and concentration for Azophloxine. Figure 6.6 shows the variation of limiting amplitude with concentration for the dye. The values of limiting amplitude for different dye concentration are given in Table 6.2.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Limiting Amplitude for the different Dye Concentration in MW/cm²</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>0.03 mM</td>
</tr>
<tr>
<td>Azophloxine</td>
<td>8.3</td>
</tr>
</tbody>
</table>
Figure 6.5 Optical limiting curves of Azophloxine dye in liquid medium

Optical limiting in Azophloxine dye was due to the stronger absorption in the excited state of the dye when compared to its weaker ground state and the mechanism responsible for the optical limiting was reverse saturable absorption.

Figure 6.6 Variation of limiting amplitude with concentration for Azophloxine dye
From the Figure 6.6, it can be seen that 0.07 mM dye concentration had lesser optical power limiting threshold indicating that the highly concentrated dyes in solution exhibited stronger optical limiting behaviour when compared to its lower ones. The main factor which affects the clamped level was the number density of dye molecules in the laser beam.

### 6.5.3 Limiting Characteristics of Purpurin Dye

The optical limiting experiment was performed for Purpurin dye belonging to anthaquinone family. The solvent used was ethanol. The dye solution was taken in a dye cuvette and was placed at the valley position behind the focal point. Here, the optical limiting was of energy-spreading type and an aperture was placed in front of a detector. An aperture of 2 mm diameter fixed in front of the photodetector is used to collect the beam coming through the sample cuvette. The pulsed Nd:YAG laser of second harmonic wavelength 532 nm was used as the excitation source. In order to study the contribution of the solvent towards optical limiting property, the experiment was first done for the solvent alone (without dye). But no limiting property was observed. The experiment was then performed for the dye in ethanol solvent with three different dye concentrations of 0.03 mM, 0.05 mM and 0.07 mM using a 1 mm quartz cuvette.

The input intensity of the laser beam was varied systematically and the corresponding output intensity through the aperture was detected by a photodetector fed to the power meter. The characteristics curve of the output intensity as a function of the input intensity was obtained. A graph was drawn between the input intensity along the x-axis and the corresponding output intensity along the y-axis. The optical limiting curve of the dye is shown in Figure 6.7. At low input intensities, the transmitted output intensity was found to vary linearly but at larger input intensities, the transmitted intensity reached a plateau and was saturated at a point defined as the limiting amplitude: (i.e.)
the maximum output intensity, showing obvious limiting property. A graph is plotted between the limiting amplitude and concentration for Purpurin dye. Figure 6.8 shows the variation of limiting amplitude with concentration for the dye. The values of limiting amplitude for different dye concentration are given in Table 6.3.

Table 6.3 Concentration dependence of limiting amplitude of Purpurin dye

<table>
<thead>
<tr>
<th>Dye</th>
<th>Limiting Amplitude for the different Dye Concentration in MW/cm^2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.03 mM</td>
</tr>
<tr>
<td>Purpurin</td>
<td>6.1</td>
</tr>
</tbody>
</table>

The mechanism responsible for optical limiting in Purpurin dye is nonlinear refraction (self-defocusing). The observed limiting behaviour depends not only on the input laser intensity (or fluence) and the nonlinear medium, but also on the aperture. The optical limiting effect was attributed to the thermally induced refractive index.

Figure 6.7 Optical limiting curves of Purpurin dye in liquid medium
Figure 6.8 Variation of limiting amplitude with concentration for Purpurin dye

From the results obtained, it was found that 0.07 mM dye concentration has lesser optical power limiting threshold (4.8 MW/cm$^2$) when compared to the other lower dye concentrations namely 0.03 mM and 0.05 mM as shown in Figure 6.8 indicating that the highly concentrated dyes in solution exhibit stronger optical limiting behaviour.

6.5.4 Limiting Characteristics of Methyl Blue Dye

The optical limiting experiment was performed for Methyl Blue dye belonging to Triarylmethane family. The solvent used was ethanol. The dye solution was taken in a dye cuvette and was placed at the valley position behind the focal point. An aperture of 2 mm diameter fixed in front of the photo detector was used to collect the beam coming through the sample cuvette. The pulsed Nd:YAG laser of second harmonic wavelength 532 nm was used as the excitation source. In order to study the contribution of the solvent towards optical limiting property, the experiment was first done for the solvent alone (without dye). But no limiting property was observed. The
experiment was then performed for the dye in ethanol solvent with three different dye concentrations of 0.03 mM, 0.05 mM and 0.07 mM using a 1 mm quartz cuvette.

The input intensity of the laser beam was varied systematically and the corresponding output intensity through the aperture is detected by a photodetector fed to the power meter. The characteristics curve of the output intensity as a function of the input intensity was obtained. A graph is drawn between the input intensity along the x-axis and the corresponding output intensity along the y-axis. The optical limiting curve of the dye is shown in Figure 6.9. The transmitted output intensity was found to vary linearly with the incident input intensity at low input intensities, but started to deviate at high incident intensities. With further increase of the input power, the transmitted intensity reached a plateau and was saturated at a point defined as the limiting amplitude: (i.e.) the maximum output intensity, showing obvious limiting property. A graph is plotted between the limiting amplitude and concentration for Methyl Blue. Figure 6.10 shows the variation of limiting amplitude with concentration for the dye. The values of limiting amplitude for different dye concentration are given in Table 6.4.

Table 6.4  Concentration dependence of limiting amplitude of Methyl Blue dye

<table>
<thead>
<tr>
<th>Dye</th>
<th>Limiting Amplitude for the different Dye Concentration in MW/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.03 mM</td>
</tr>
<tr>
<td>Methyl blue</td>
<td>2.12</td>
</tr>
</tbody>
</table>
The mechanism responsible for optical limiting in Methyl Blue dye was nonlinear refraction (self-defocusing). The observed limiting behaviour depends not only on the input laser intensity (or fluence) and the nonlinear medium, but also on the aperture. The optical limiting effect was attributed to the thermally induced refractive index. From the results obtained, it was
found that optical power limiting threshold started decreasing with increase of concentration which indicated that the highly concentrated dyes in solution exhibit stronger optical limiting behaviour.

6.6 CONCLUSION

Optical limiting behavior for dyes under pulsed Nd:YAG laser excitation for different dye concentrations are studied. The mechanism responsible for optical limiting is mainly attributed to the thermally induced nonlinear refraction and nonlinear absorption. The defocusing effect and reverse saturable absorption observed in these samples under pulsed illumination is utilized to demonstrate their optical limiting action. From the values of the limiting amplitude, it is found that all the dyes have good optical limiting effect even at low powers. These results are quite encouraging for possible applications in nonlinear optical devices.

At the valley positions, the optical limiter works at very low powers as the self-defocusing effect is enhanced by the thermal effect which is closely related to the absorptive properties of the samples used. Thus it can be suggested that the best position for a sample when used for optical limiting based on self-defocusing is at the valley of the Z-scan curve of the medium. The optical limiting responses of the low concentration solutions are generally much weaker than those of high concentrated solutions, while high concentrated solution exhibits strong optical limiting. This indicates that the number density of dye molecules in the laser beam is the main factor affecting the clamped level. From the threshold intensity for optical limiting for each sample, it can be seen that the optical power limiting threshold is inversely proportional to the concentration. The data shows that as the concentration increases, a reduction in linear transmittance as well as the clamping level are observed. Xylidine Ponceau, Azophloxine, Purpurin and Methyl Blue all show better optical limiting response under Nd:YAG laser excitation.