Chapter 5

Bi$_{12}$SiO$_{20}$ and Bi$_{12}$SiO$_{20}$:Fe crystals

Optical limiting characteristics of Bi$_{12}$SiO$_{20}$ (BSO) and Bi$_{12}$SiO$_{20}$:Fe (BSO:Fe) crystals at different wavelengths in the visible region at 435, 532, 600 and 683 nm in the nanosecond regime are presented. Studies reveal the contributions of both two-photon absorption (TPA) and charge carrier absorption from the traps, leading to nonlinear absorption. Pump-probe studies with 25 ps pulses revealed ~60 ps relaxation of excited carriers. The effect of relaxation of excited charge carriers on the nonlinear absorption behavior is also discussed.

5.1 Photorefractive materials for NLO applications

Electro-optic photoconductive materials present many interesting phenomena, one among them is the photorefractive effect with a variety of potential applications in nonlinear optics and photonics which include phase conjugation, optical interconnections, optical spatial solitons, and optical signal processing [1]. The phenomenon of photorefraction arises on the nonuniform illumination of such materials and with the diffusion of the ensuing photogenerated carriers towards lesser-illuminated regions with the associated electric fields that, through the Pockels effect, cause localized changes in the refractive index. This photoionization occurs from relatively deep energy levels within the bandgap that are not normally thermally ionized. The light induced absorption due to the photoinduced charge transport has been studied widely in the field of photorefractive nonlinear optics because it plays an important role in the construction of passive optical limiters and optical threshold elements in optical processing systems [2].

In photorefractive materials, at higher input intensities, the mechanism of charge carrier generation and transport process involve impurity levels which leads to the greater possibility of the combined effect of trap assisted charge carrier absorption (TACCA) and TPA [3]. Here the former is an accumulative nonlinearity, which requires time for energy transfer from field to medium and hence depends on energy density deposited in the medium. This nonlinearity can
also be nonlocal due to the drift or diffusion of photogenerated charge carriers in the medium and hence can in principle only depend on the input fluence. The later is an instantaneous nonlinearity, which depends on the input light intensity, can be effective over broadband of the spectrum and for very short pulses. TPA can also act as a significant loss mechanism when a material is subjected to a strong beam of photons of energy \( \text{ft}_\omega \), with \( \text{fa}_\omega < E_g < 2\hbar \omega \), where \( E_g \) is the energy gap of the material. High sensitivity optical storage by the photorefractive process using multi-photon absorption was demonstrated in LiNbO₃ and in KTN \[4\]. Permanent and reversible changes of refractive index of pure and doped LiNbO₃ have been obtained by multi-photon absorption that results in increased sensitivity for optical storage and holography \[5\].

In this chapter, we compare the optical limiting behavior exhibited due to combined effect of TPA, free carrier absorption and trap assisted charge carrier absorption (TACCA) in photorefractive crystals of pure and iron doped BSO in the visible spectral range using nanosecond pulses at 435, 532, 600 and 683 nm. An excellent passive limiting behavior is demonstrated for the first time using these crystals in visible region. In our qualitative modeling of the effect, we account the absorptive changes due to combined effect of TACCA and TPA. Consequently, we present the precise role of the internal defects due to impurity centers present in the crystal lattice, to help in the understanding and obtaining optimum samples for enhanced optical limiting from these photorefractive materials.

5.2 \( \text{Bi}_{12}\text{SiO}_{20} \) and \( \text{Bi}_{12}\text{SiO}_{20}: \text{Fe} \)

The sillenite family crystals, in particular, BSO is considered attractive candidate for applications due to its strong photorefractive properties like high sensitivity, fast response time, comparable electro-optic coefficient with other crystals of the family and interesting piezoelectric, optically-active and many other interesting properties like beam deflection, switching, holography, phase conjugation and optical memories \[6\]. It has been reported that out of three non-zero electro-optic coefficients \( r_{41}, r_{52}, \) and \( r_{63} \), the element \( r_{41} \) is important for
device applications [7]. BSO has cubic symmetry, belonging to point group 23. In BSO the standard photorefractive effect is based on the absorption of photons by impurity levels. One can improve the performance by means of increasing the impurity levels by doping. In BSO, a large number of trap levels in the energy gap predicted from the spectral response of the photoconductivity [8] and the traps with high concentration were observed experimentally [9]. In addition to distinguishable shallow trap levels reported, there appears to be many overlapping levels that are not distinguishable at deep energy levels below the conduction band [10]. Attard [11] predicted the Fermi level shift in BSO via photon induced trap occupation. The shift of Fermi level is dependent on the density of trap sites in the bandgap, the radiation induced occupation density, and the energy levels of the traps. Investigations report that photorefractive materials doped with iron leads to favourable photorefractive properties such as small response time and high sensitivity [12]. It is also shown that optical properties and light induced absorption changes are affected due to iron doping [13]. Investigations on the possibilities for practical applications of sillenites have revealed that doping can conveniently be used to modify the absorption in a way suitable for the particular application. In BSO too, doping with various elements leads to significant changes in the electrical, photoelectrical and optical properties. Nagao and Minura [14] have investigated the influence of a large number of transition metals on the transmission and photoresponse of BSO. The general conclusion made about photoresponse is that the transition metal impurities in BSO crystals quench the photoconductivity. An intuitive explanation proposed for the quenching is the formation of recombination centers [15]. When the light intensities are strong enough, effects that are caused by TPA can become important [16] and can also be enhanced by the existence of intermediate energy levels inside the forbidden bandgap because of the impurities. It is found that addition of significant amount of Fe$^{3+}$ ions as impurities can easily change the valence state and may play a critical role in charge carrier mobility as well as intensity dependent absorption. Recent study of this effect [7] in pure BSO crystal examined the CW recording under applied electric field at low intensities of a CW laser. Optical limiting has been studied
in BaTiO$_3$ by using photorefractive nonlinearities [17] and by utilizing the photo induced lensing in BSO [18] at low intensities of a CW laser. Light controlled electro-optic power limiter has also been demonstrated in BSO crystal [7].

![Absorption spectra of BSO and BSO: Fe.](image)

Figure 5.1: Absorption spectra of BSO and BSO: Fe.

Since the revelation of polymorphy of bismuth trioxide [19] various efforts were made for the growth and characterization of BSO single crystals [20]. An undoped BSO crystal bought from Fujian Castech Crystals Inc., China with dimensions of 10 mm x 10 mm x 5 mm, and a Fe-doped BSO crystal obtained from Alabama University, USA [21] with dimensions 5 mm x 4 mm x 4 mm, are cut to have thickness of 1 mm along c-axis are used for optical limiting and nonlinear absorption studies. The surfaces of the crystal were polished to minimize the scattering. Optical limiting studies are also done with 4 mm thick crystals. The amount of iron incorporation in the crystal is determined using Inductive Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES). The
result has shown that 150-ppm Fe is incorporated in the crystal as impurity. In principle, during the growth Fe can replace Bi as well as Si in BSO. But from ICP - AES study it is also found that the doped crystal grown from melt having no Si deficit. Hence it can be assumed that Fe atoms incorporated only on the Bi sites in our sample.

The absorption spectrum of the crystals used in this study is shown in Fig 5.1. The absorption spectrum shows a very large absorption above 3eV and matches well with that reported in literature [10,22]. As one can see from the absorption spectrum a long tail in the absorption edge goes all the way to 900 nm (1.38eV). This implies that the crystal possess large number of donor sites. The absorption centers/traps responsible for the absorption in the above region are reported as due to either silicon vacancy complex or bismuth substituting for silicon or Fe$^{3+}$ impurities. And these are raised to conduction band by optical excitation with photons in energy region 1.7eV to 3.5eV.[11] The change in the absorption spectrum with various metals as dopants and different growth conditions has been reported earlier in various photorefractives like BaTiO$_3$, LiNbO$_3$, and in PbBaNb$_2$O$_6$ [23] with major variation in the visible region. Doping of impurities like iron [10], cobalt [15] and transition metals [14] has been reported to change the optical absorption spectrum in the visible region. The crystal structures of both pure and iron doped BSO are studied using single crystal X-ray diffraction technique revealed body centered cubic structure with lattice constants of (10.0935 ± 0.003) Å and (10.0335 ± 0.006) Å respectively. The result shows that the lattice constants are slightly varied due to doping process without change in crystal structure and are in good agreement with earlier reports in the literature [20].

5.3 Energy levels due to iron impurity in BSO

The energy levels of iron are spread in the energy gap below the conduction band of BSO. This is a very important result for the understanding of the excitation (both thermal and light induced) and recombination processes and their influences on photorefractive measurements. In any case, it cannot be
assumed, as in the case of a semiconductor like silicon, that the dopant introduces a single, well-defined energy level in the band gap. An impurity atom with a certain valence can capture an electron and change its valence accordingly if the newly created state is stable. For example the Fe$^{4+}$ centre can capture an electron in the reaction Fe$^{4+} + e^- \rightarrow$ Fe$^{3+}$. On the other hand, an electron of Fe$^{3+}$ can be photoexcited leading to a Fe$^{4+}$ centre and an electron in the conduction band. The Fe$^{4+}$ centre has both empty and occupied levels near mid gap. The centre Fe cannot capture an electron because the Fe$^{2+}$ center appears to be unstable: its upper occupied energy level has energy higher than the energy of the lowest conduction band states. This centre becomes stable if the unit cell is slightly more distorted than assumed. It can also be stabilized by local charge compensation. The higher the ionicity of the impurity is, the lower are its energy levels. This is a general rule.

![Figure 5.2: Qualitative representation of the intra band-gap energy levels introduced by Fe impurity. Each level represents a photoionisation energy. The ability to trap an electron and to obtain a centre with such a photoionisation energy is indicated by a line. The presence of a photoexcitable electron is indicated with a grey dot. The levels are labelled with the photoionisation transition they represent.](image)

When the nominal ionicity of the impurity increases, the $d$ states of the transition metal (in the above example iron) move down in energy with respect to the valence band (oxygen 2$p$ orbitals). Under illumination the impurities with lower ionicity (e.g. Fe$^{2+}$) behave more as electron donors, and the impurities with
higher ionicity (e.g. Fe$^{4+}$) tend to be electron acceptors, or hole donors. Another general result valid for the Si ion as well as for the substituent Fe ion is that the environment of the metal atom (Si or Fe) has a strong influence on its energy levels: a low symmetry of the environment produces a splitting of degenerate energy levels and a general downward shift in energy. This effect can be produced by a phase transition to a phase with lower symmetry or by a modification of the local environment of the ion.

Fig. 5.2 is a schematic representation of the level structure of an impurity Fe atom in different valence states. Here Fe$^{2+}$ is assumed to be stable and to have two occupied energy levels with different energies inside the band gap. For this band diagram, we adopted a simplified notation that is useful in the context of a thermodynamic discussion. The energy levels that correspond to a certain ionization process (e.g. Fe$^{2+} \rightarrow$ Fe$^{3+} + e^-$) are identified by a series of horizontal bars (labeled Fe$^{2+}$/Fe$^{3+}$). The energy difference between a level and the lower edge of the conduction band represents the minimum energy that is necessary to photoexcite an electron from the impurity state to the conduction band. A solid dot is present if an electron exists with such ionisation energy. Absence of a solid dot means that the level is able to bind an electron and act as an electron trap. There are two levels labelled Fe$^{2+}$/Fe$^{3+}$ in Fig. 5.2 because there are two electron states with different ionisation energies. An electron can be photoexcited from both states to create a centre Fe$^{3+}$. A solid dot in the upper Fe$^{2+}$/Fe$^{3+}$ level represents the centre Fe$^{2+}$, with the ionization energy of the upper electron given by the position of the level in the energy diagram. An empty line in the upper Fe$^{2+}$/Fe$^{3+}$ level represents a Fe$^{3+}$ centre which is able to trap an electron to become the centre Fe$^{2+}$. The centre Fe$^{2+}$ has two occupied energy levels with different energies inside the band gap and has therefore two ionisation energies. The level corresponding to the electron with higher photoionisation energy is also drawn in Fig. 5.2. Photoexcitation of an electron from one of this two levels leads always, after thermalisation, to the formation of the centre Fe$^{3+}$. In Fig. 5.2, when empty levels are drawn, they can always capture an electron; their energy corresponds to the photoionisation energy of the captured electron. The levels that correspond to excited states of an impurity that
are present inside the conduction band are not drawn. The method used to draw
energy levels concentrates more on the photoionisation and recombination
process, that are of primary importance to the photorefractive effect rather than
on the possible electronic states in the band gap.

Note that the centre Fe$^{3+}$, which represents an empty site in the Fe$^{2+}$/Fe$^{3+}$
level, is shown as a full site in the Fe$^{3+}$/Fe$^{4+}$ level. In the band diagram of Fig.
5.2, empty levels appear to have the same energy as the filled ones, but at the
same time they can be interpreted as donors at a lower energy in the band
diagram (with a higher photoionisation energy). The occupation of the ionisation
levels (i.e. the valence state of the impurity atom) is connected with the
difference between the Fermi energy and the energy of the particular ionisation
level. When the Fermi level is below one particular level, that level will be
essentially empty and when the Fermi level is higher, the level will be primarily
filled. For a level to be partially full (that is, for an impurity atom to appear at the
same time in two valence states that act as donor and acceptors), the energy of the
Fermi level must be close to the energy of the impurity level. An important
conclusion, which is valid, also if there are many different impurities, is that in
thermal equilibrium there can be only one partially filled level for any particular
value of the Fermi energy (the distance between different levels is generally
greater than k_BT). This means that in thermal equilibrium a certain impurity
centre is expected to appear in the host crystal in at most two valence states.

Above we have described only the photoexcitation of electrons to the
conduction band. The symmetric case of photoexcitation of an electron in the
valence band to an empty level like Fe$^{3+}$ is also possible. This transition is often
described as photoexcitation of holes and Fe$^{3+}$ acts as a "hole donor". The
changes in level occupation induced by this transition are analogous to what was
described above in the case of transitions to the conduction band and we do not
describe them any further. In Fig. 5.2 three possible electron photoexcitation
transitions are drawn. Which transition will be favoured under illumination
depends on the photoionisation cross section of the impurities and on the
wavelength of the light. As an example, photoexcitation of Fe$^{3+}$ in Fig. 5.2 (Fe$^{3+}$
/ Fe$^{4+}$ level) requires light with a shorter wavelength than photoexcitation of Fe$^{2+}$. 
Thus, the concentrations of active photorefractive acceptors or donors are determined by the extent to which each level is filled or empty and by the wavelength of the light. The number of filled centres that can be photoexcited using a certain wavelength gives the number of active donors. The empty levels give the number of active traps. In the example shown in the diagram of Fig. 5.2 the centre Fe$^+$ (in the upper Fe$^{2+}$ / Fe$^{3+}$ level) acts as a trap with small ionisation energy. This trap disappears if Fe$^{3+}$ is photoionised to produce Fe$^{4+}$. The centre Fe$^{4+}$ (in the lower Fe$^{+}$ / Fe$^{4+}$ level) is an electron trap with much larger photoionisation energy. (One can also say that photoionisation of Fe$^{3+}$ transforms a trap with small ionization energy into a trap with higher ionisation energy.) The total number of trap levels available for electron recombination increases with the ionicity of the impurity (in the example of Fig. 5.2 the centre Fe$^{4+}$ can trap two electrons: Fe$^{4+}$ + 2 e$^- \rightarrow$ Fe$^+$. Since the ionicity of the impurity atoms is connected with the position of the Fermi level, the number of electron donors and traps also depends on the Fermi energy. We assume all donor impurities are identical and have exactly the same energy and lie in the middle of the bandgap. Absorbing photons ionizes these donor impurities and as a result ionization electrons are generated in the conduction band leaving empty trap states behind, which are capable of capturing electrons. The impurities due to the presence of Fe atoms may be in the form of Fe$^{3+}$ or Fe$^{2+}$ states.

5.4 **Optical limiting and Nonlinear absorption**

Optical limiting and nonlinear absorption measurements are performed with <110> direction of the crystal coinciding with the Z-axis of the beam propagation. Open aperture Z-scan studies are done with 1 mm thick crystals and OL curves are recorded with both 1 and 4 mm thick crystals. The sample satisfied the "thin" sample condition L < n$_0$z$_0$, where L is the sample thickness, n$_0$ the linear refractive index and z$_0$ the diffraction length of the focused beam for Z-scan studies. No external electric field is applied across the crystal. Beam fanning is observed in the far field from BSO:Fe while performing Z-scan and OL measurements. Proper precautions are taken to collect all the transmitted
light by bringing the collecting lens closer to sample and by using large diameter lens for collecting the output. Beam fanning is well known phenomenon in Fe doped photorefractive crystals arising from scattering due to the impurities within the crystal [24]. At room temperature BSO behaves as a two-photon absorber at 532, 600 and 683 nm as the band gap obey \( \hbar \omega < E_g < 2 \hbar \omega \). We find, from the theoretical modeling, that the nonlinear absorption is due to TPA assisted by free carrier absorption and trap assisted charge carrier absorption from TL to \( CB_L \). Absorption from trap levels has been discussed earlier for \( BaTiO_3 \) [25] and BSO [26]. The excitation of charges from shallow traps to the conduction band is also reported [27]. The domination of photogenerated carrier absorption with nanosecond pulsed lasers is reported earlier [28] in direct band gap semiconductors.

Figure 5.3: Optical limiting response of BSO (o) and BSO: Fe (•) at (a) 532 nm and (b) 600 nm with 4mm thick crystals.
The transfer of the conduction electrons to trap levels and the recombination with the vb holes increases with the number density of excited electrons in the cb. this leads to more absorption of the electrons from the trap levels to the conduction band. however, for very short pulses (ps), transitions from lower conduction band to trap levels can be neglected. pure tpa is reported in another crystal of sillenite family $\text{Bi}_{12}\text{GeO}_{20}$ (BGO) at 532 nm using a 16 ps pulse width Nd: YAG laser [16]. optical limiting behavior of BSO and BSO: Fe at 532 nm and 600 nm with 4 mm crystal is shown in fig. 5.3.

The damage threshold is identified as the intensity at which a strong scattering appeared at the output followed by the darkening and then damage formed on the crystal. the optical limiting performance and the damage threshold have increased considerably with the presence of iron impurity. the limiting and damage thresholds of the crystals are given in table 5.1. fig 5.4 shows the open aperture Z-scan curves of BSO and BSO: Fe at 532 nm with different peak intensities. open aperture Z-scan curves of BSO: Fe appear slightly broader compared to that of BSO and nonlinear absorption has increased quite considerably even at lower intensities. at all the excitation wavelengths similar increase in nonlinear absorption is observed. open aperture Z-scan curves of both the crystals at 600 nm is shown in fig 5.5.

Figure 5.4: Open aperture Z-scan curve of (a) BSO and (b) BSO: Fe at 532 nm, 6ns pulses. Solid lines show the theoretical fits generated using the model explained in section 5.5.
Figure 5.5: Open aperture Z-scan curve of (a) BSO and (b) BSO: Fe at 600 nm, 6ns. The solid lines are theoretical fits generated using the model explained in section 5.5.

Table 5.1: Limiting and damage thresholds of BSO and BSO: Fe with 6 ns pulses with 1 mm crystal.

<table>
<thead>
<tr>
<th>$\lambda_{ex}$</th>
<th>Limiting Threshold (Jcm$^{-2}$)</th>
<th>Damage Threshold (Jcm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BSO</td>
<td>BSO: Fe</td>
</tr>
<tr>
<td>532 nm</td>
<td>3.38±0.4</td>
<td>1.29±0.2</td>
</tr>
<tr>
<td>600 nm</td>
<td>5.88±0.5</td>
<td>3.29±0.3</td>
</tr>
<tr>
<td>683 nm</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

Figure 5.6: Open aperture Z-scan curves of BSO and BSO: Fe at 683 nm.
Open aperture Z-scan curves of these crystals at Raman shifted wavelength of 683 nm are shown in Fig 5.6. As we move towards the red side of the spectrum, the nonlinear absorption has reduced slightly. But the overall contribution of TPA has remained almost same at the excitation wavelengths. It is the contribution from the trap levels and the FCA playing a very significant role in the nonlinear absorption. As one moves towards the longer wavelength region more contribution from the TPA can be expected.

The limiting threshold (I_{1/2}) is decreasing and the damage threshold increases with iron incorporation in these crystals. As one moves towards the longer wavelengths the I_{1/2} increases gradually and the damage threshold decreases. This may be due to the fact that at the longer wavelengths the contribution from the trap levels and free carrier absorption may be decreasing, where as the contribution of TPA remaining almost constant.

5.4.1 Open aperture Z-scan and Pump-probe and measurements with 25 ps pulses

Open aperture Z-scan experiment is performed with 25 ps pulses at 532 nm and a good nonlinear absorption is observed (Fig 5.7). Pump-probe measurements are done to find out the relaxation of the excited carriers at these timescales. The ratio of the intensity of the pump to probe beam is 1000:1. Pump energy is 300 µJ and the probe is kept at 0.3 µJ. At the probe energy used no nonlinear absorption is observed for BSO. Probe is delayed with respect to pump and its transmittance is monitored with delay. Probe transmittance has reduced considerably at the zero delay and as the probe moves away the transmittance starts to increase back to the linear transmittance (Fig. 5.8). In the pump-probe experiment, probe transmittance reduced in the presence of the pump pulse for a large range of delay times. The measurements showed that photoinduced absorption could occur even within a picosecond time scale. From the curve we can see that there is no original induced absorption before pump excitation (~ -300 ps). Also for a delay (~ 200 ps) there is saturation in the transmittance. We observed that the induced absorption reaches its maximum
within the first 70 ps and then decays slowly. And for longer delays the induced absorption is still present.

![Open aperture Z-scan curve of BSO at 532 nm, 25 ps pulse width. Circles represent experimental data the theoretical fit is shown by solid line obtained using the model explained in section 5.5.](image)

**Figure 5.7:** Open aperture Z-scan curve of BSO at 532 nm, 25 ps pulse width. Circles represent experimental data the theoretical fit is shown by solid line obtained using the model explained in section 5.5.

The inset in fig 5.8 shows the decay of probe absorption ~ 60 ps, which gives the relaxation of the excited charge carriers. Similar photoinduced absorption has been observed in BaTiO₃ which gives the hole recombination time of ~ 60 ps with secondary centers [29]. Measurements done with 1 ps pulse excitation at 596 nm [30] revealed two distinct features, first one is a pronounced rapidly recovering induced absorption at zero delay with a width indistinguishable from the width of the pulse duration consistent with an absorption process that depends on the instantaneous irradiance in the crystal which is attributed to TPA and the second is a long-lived induced absorption at positive delays. There are two processes that can contribute to the long-lived induced absorption: free-carrier absorption and redistribution of charge among the impurity levels. Although the relative contributions of these two processes
cannot be determined uniquely, long decay time of the induced absorption suggests that charge redistribution plays a significant role.

![Temporal response of excited carriers from Pump-probe experiment for BSO at 532 nm, with 25 ps pulses. Inset shows the fit to get the relaxation of the excited carriers.](image)

**Figure 5.8:** Temporal response of excited carriers from Pump-probe experiment for BSO at 532 nm, with 25 ps pulses. Inset shows the fit to get the relaxation of the excited carriers.

### 5.5 Model for optical limiting

The early model of photorefractive effect, i.e., the single level deep-trap model [31], assumes that only one donor level in which the charge carriers can be excited and trapped by both donor and acceptor levels in a crystal. The model predicts that the optical absorption, beam coupling gain coefficient, and the effective Debye screening length are intensity independent. According to this model, the response time increases linearly with intensity if the dark conductivity is small compared with the photoconductivity, and the magnitude of the two-beam coupling coefficient is the same whether a beam is depleted or amplified.
However, many anomalous behaviors have been observed in photorefractive crystals. For example, a sublinear relationship between the response time and the optical intensity has been found [32,33]. The intensity dependence of the photorefractive beam-coupling gain coefficient and the effective Debye screening length [34], and the intensity dependence of the absorption coefficient [25,35] are inconsistent with the single-trap model. An asymmetry in the two-beam coupling strength when the weak beam was amplified or depleted has also been observed [36]. Subsequently, several photorefractive models were proposed. Strohendl et al. [37] and Valley [38] proposed a model involving electron-hole competition from a single level. This model explained the change of sign in the two-beam coupling gain coefficient observed in \( \text{BaTiO}_3 \) at 442 nm by Klein and Valley [39]. Motes and Kim [35] showed that part of the asymmetry between gain and depletion in the two-beam coupling is caused by the bulk light-induced absorption in the crystal. Brost et al. [25] showed that light-induced absorption requires more than one active level in the crystal. The sublinear dependence of the photoconductivity of \( \text{BaTiO}_3 \) was explained using a model that included an additional trap level [33]. Tayebati and Mahgerefteh [27] analytically solved the charge-transport equations for a photorefractive crystal with shallow and deep traps. They theoretically explained the light induced absorption, the sublinear dependence of photoconductivity on optical intensity, and the intensity dependence of the two-beam coupling strength and the effective Debye screening length in photorefractive crystals. Cudney et al. [in Ref. 34] theoretically solved for more general cases, in which multiple levels [40] are involved in charge distribution process in a photorefractive crystal. They obtained an analytical solution for absorption gratings from the band transport equations [31], taking the trap gratings into account [41] assuming that the polarizability of a filled trap differs from that of an empty one, i.e., the trapping sites themselves alter the susceptibility of the crystal. In all these models explaining different photorefractive properties two beams are applied, whereas in our case we used only a single beam to study the optical limiting properties.

The photoionization occurs from relatively deep energy levels within the band gap that are not thermally ionized. A variety of techniques such as
photoluminescence or thermally stimulated conductivity (TSC) are used to establish the presence of deep energy levels and their position inside the bandgap. Many TSC measurements have shown that deep trap levels are invariably present in sillenites such as BSO [42]. The deep energy/defect levels are attributed to arise from the specific crystalline defect or from a particular residual impurity that is introduced during the growth process. Various experimental studies have been performed on sillenite crystals to exactly find out the origin and position of the defect levels leading to photorefractive and photoionization process. Even with occasional variations in the growth parameters, such as deviating from the exact stoichiometric melt composition, provided remarkably similar TSC spectra and photoconductive properties [43]. The role of traps has been widely used for restoration of holographic images in BSO [44]. Considerable redistribution of impurity level populations, leading to varying lifetimes of mobile carriers, thus changing the dynamics of holographic recording with irradiation at different wavelengths in BSO has been reported [45]. Observations done on the decay dynamics of laser-induced phase gratings have been reported to be consistent with the assumption of multiple shallow and deep trap levels. From these studies three major types of trapping centers, one electron trapping center with a very short decay constant, a second electron trapping center with a longer decay time constant and a hole trapping center with a still longer time constant are found to be present [46]. Further photoconductive properties investigated revealed different mechanisms out of which hopping mechanisms appear to be important [8]. Evidence for the existence of multiple traps and the trapping mechanisms in BSO is described in detail in literature [46,47]. The electron mobility has been modulated 3-4 orders of magnitude due to trapping [48], where the filling of traps increased the mobility. Comparison of the photorefractive and photoconductive effects demonstrated that charge transport processes could not be explained by the effective-mass approximation to the "nearly free electron in the conduction band" model. The calculated drift length for the electron based on the photorefractive and conductivity measurements is inconsistent with the drift length required to explain the photoconductive measurements and charge transport via phonon-assisted tunneling (hopping model) is suggested as a major
contributor. Krainak and Davidson [49] investigated two-wave mixing in BSO with applied alternating electric fields and presented evidence that supports the hopping model for charge transport. All these earlier reported theoretical and experimental investigations provides a base for the band model used to explain the optical limiting behavior in BSO and BSO: Fe.

Figure 5.9: (a) Band model and (b) the equivalent five level diagram used for the modeling.

The energy band structure [8, 50] and the equivalent five level energy diagram used to explain the nonlinear absorption arc shown in Fig. 5.9 (a) and (b) respectively. The following assumptions are made to explain the observed optical limiting and nonlinear absorption behavior explaining various properties of in these crystals:

- Extrinsic silicon-vacancy center is taken as donor level
- All the shallow and deep trap levels from which light induced absorption is possible are considered to be originating from a single trap level (TL).
- Recombination rate with valance-holes from the deep level of the crystal is exceptionally small [51].
- Thermal excitation/decay effects are neglected in the modeling as they are of the time scale of few ms to sec.
- Two paths of TPA are taken into consideration; one from VB to CB and the other from donor level to CB.

In fig 5.9(b) VB is the valence band, TL is the trap level, DL is the donor level, CB_L is the lower energy levels of the conduction band and CB_H is taken as the high energy levels of the conduction band. The extrinsic center (silicon-vacancy complex) is considered as \( N_i \) from where the photo absorption is possible. The shallow traps, deep traps and secondary photorefractive centers are taken as TL \( (N_d) \), CTI.H and \( \tau_1 \) represent the contributions of free-carrier absorption coefficient and recombination times respectively inside the levels of conduction band.

The rate equations for the five level model assumed to explain the observed nonlinear absorption are given below:

\[
\frac{dN_0}{dt} = - \frac{\beta_v I^2}{2h\omega} + \frac{N_2}{\tau_{cv}} \tag{5.1}
\]

\[
\frac{dN_1}{dt} = - \frac{\beta_d I^2}{2h\omega} + \frac{\sigma_0 I N_1}{h\omega} + \frac{N_2}{\tau_{cd}} \tag{5.2}
\]

\[
\frac{dN_2}{dt} = \beta_v I^2 + \frac{\sigma_0 I N_1}{h\omega} - \frac{N_2}{\tau_{cv}} \left( \frac{1}{\tau_{cv}} + \frac{1}{\tau_{cd}} + \frac{1}{\tau_{et}} \right) + \frac{N_3}{\tau_1} - \frac{\sigma_{LH} I N_2}{h\omega} - \frac{\sigma_{TL} I N_4}{h\omega} \tag{5.3}
\]

\[
\frac{dN_3}{dt} = \frac{\beta_d I^2}{2h\omega} + \frac{\sigma_{LH} I N_2}{h\omega} - \frac{N_3}{\tau_1} \tag{5.4}
\]

\[
\frac{dN_4}{dt} = - \frac{\sigma_{TL} I N_4}{\hbar\omega} + \frac{N_2}{\tau_{et}} \tag{5.5}
\]

Intensity transmitted through the sample is given by

\[
\frac{dI}{dz} = -\sigma_0 I N_1 - \sigma_{LH} I N_2 - \sigma_{TL} I N_4 - \beta I^2 \tag{5.6}
\]

with

\[
I = I_{00} \times \left( \frac{\omega_0^2}{\omega^2(z)} \right) \times \exp(-\frac{I^2}{\tau_p^2}) \times \exp\left(-\frac{2r^2}{\omega^2(z)}\right) \tag{5.7}
\]
where $\sigma_0$ is the absorption cross-section from the donor levels, $\beta_v$ is the two photon absorption coefficient from the valence band to the conduction band, $\beta_d$ is the two photon absorption coefficient from the donor levels to the higher conduction band leading to an effective two photon absorption coefficient, $\beta = \beta_v + \beta_d$. $\sigma_{TL}$ is the charge carrier absorption cross-section from the trap levels (TL) to the lower conduction band (CBL), $\sigma_{LH}$ is the free carrier absorption cross-section within the conduction band to the intraband absorption. Both these absorptions are effectively considered as $\sigma_{T, eff}$. $N_i$’s are the corresponding carrier densities in different states, $r_i$’s are the lifetimes of the states, and $1/\tau_{CTR}$ is the crossing rate to TL from conduction band, $1/\tau_{CV}$ is the crossing rate from CB$_L$ to VB, $\sqrt{TCPD}$ is the crossing rate from CB$_L$ to DL. Relaxation of the excited charge carriers obtained from the pump-probe experiment with 25 ps pulses is taken as $\tau_{CTR}$. The refractive index $n_0$ of BSO at 532, 600 and 683 nm and is taken as 2.6, 2.55, and 2.52 respectively [52]. The differential equations are solved numerically using Runge-Kutta fourth order method as explained in section 2.11. The carrier density [53] of the extrinsic absorption center $N_i$ is taken as $\sim 10^{19}$ cm$^{-3}$. Ground state absorption cross-section $\sigma_0$ is calculated from the absorption spectrum shown in Fig.5.1, and is given in table 5.2.

At higher intensities, BSO has shown nanosecond timescale relaxation rates [54]. Nanosecond and picosecond recombination rates were also reported for KNbO$_3$ [55] and BaTiO$_3$ [29,30] at higher intensities. Since the intensities used in the present study are very high ($>10^8$ Wcm$^{-2}$), the following relaxation (recombination) times, $\tau_l = 0.1$ psec, $\tau_{cd} = 10$ nsec, and $\tau_{cv} = 10$ nsec [56,57] are used for the theoretical modeling. The excited charge carrier relaxation $\tau_{cl}$ is taken as $\sim 60$ psec from the pump-probe measurements. The solid lines in the figures 5.4, 5.5, 5.6 and 5.7 are the theoretical curves generated using the above
mentioned relaxations and the values of $\beta_{\text{eff}}$ and $\sigma_{\text{eff}}$ are then estimated through least square fit of the experimental data and are given in the Table 5.3. The effect of $\tau_{\text{rel}} = 4$ nsec [58,59] and different $\beta_{\text{eff}}$ on the nonlinear absorption is shown in Figs 5.10 to 5.12.

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>$\sigma_0 \times 10^{20}$ cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BSO</td>
</tr>
<tr>
<td>532</td>
<td>9.15</td>
</tr>
<tr>
<td>600</td>
<td>3.30</td>
</tr>
<tr>
<td>683</td>
<td>2.49</td>
</tr>
</tbody>
</table>

Table 5.2: $\sigma_0$ calculated from the absorption spectrum for BSO and BSO: Fe

<table>
<thead>
<tr>
<th>$\lambda_{\text{ex}}$ (nm)</th>
<th>$\beta_{\text{eff}}$ (cm/GW)</th>
<th>Intensity (GWcm$^{-2}$)</th>
<th>$\sigma_{\text{eff}}$ ($10^{19}$ cm$^2$)</th>
<th>Intensity (GWcm$^{-2}$)</th>
<th>$\sigma_{\text{eff}}$ ($10^{19}$ cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>BSO</td>
<td></td>
<td>BSO:Fe</td>
</tr>
<tr>
<td>532</td>
<td>4.47</td>
<td>0.21</td>
<td>15</td>
<td>0.36</td>
<td>41</td>
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<tr>
<td></td>
<td></td>
<td>0.70</td>
<td>21</td>
<td>0.67</td>
<td>91.8</td>
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<tr>
<td></td>
<td></td>
<td><strong>1.23</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>5.02</td>
<td>0.54</td>
<td>16.8</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.98</td>
<td>39.4</td>
<td>0.94</td>
<td>54</td>
</tr>
<tr>
<td>683</td>
<td>4.36</td>
<td>0.31</td>
<td>8.0</td>
<td>0.26</td>
<td>10.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.52</td>
<td>11.0</td>
<td>0.41</td>
<td>16.5</td>
</tr>
</tbody>
</table>

Table 5.3: $\sigma_{\text{eff}}$ calculated at 532, 600 and 683 nm at different input intensities with 6 ns pulses for BSO and BSO:Fe.

From the pump-probe and open aperture Z-scan curves with 25 ps pulses the relaxation of the excited charge carriers and TPA coefficient are evaluated. These values are used to find out the contribution of TACCA in these crystals with ns pulse excitation. With ns pulse excitation various processes will come into picture and the data can be fitted using all the effects TPA, FCA, and TACCA or any one of them and with the relaxation times of the excited carriers. The effective TPA coefficient, which is a sum of the effects from valence bands and donor levels; is 4.47 cm/GW. From the theoretical considerations given by earlier reports [66] the TPA value is nearly around $K \sim 1940$ cm/GW (eV)$^{5/2}$, value given assuming the two level band model. Ratio of $\sigma_{\text{eff}} / \sigma_{\text{th}}$, which is considered as one of the figures of merit for optical limiters is found to increase
with increasing input intensity as can be seen from table 5.3. In iron doped crystal the contribution from the trap levels is found to be more, which increases with increasing intensity. Intensity dependent absorption is observed in PR crystals with low-intensity CW beams [25,35]. The effect is attributed to the photoinduced shift of the carriers from a primary trap with a lower absorption cross-section to a secondary trap with a higher absorption cross-section. Motes et al. [35] showed that this is not a photorefractive effect. It exists in unpoled crystals, can be induced at one wavelength and observed at a second wavelength, and has a rise time of the induced absorption that is an order of magnitude faster than the grating formation time. The contribution of the thermal effects is also ruled out as the absorption decreases with increasing temperature [60]. Similar induced absorption due to resonant TPA occurring in steps and free carrier absorption due to the trap levels is also reported in BSO [26]. Intensity dependent absorption and light induced absorption (LIA) have been studied in various doped and undoped photorefractive crystals like BaTiO₃ [61], LiNbO₃ [62], KNbO₃ [63] and in sillenites Bi₂TiO₂O [64]. In all these crystals, LIA and intensity dependent absorption are explained using the contributions from shallow and deep trap levels. In the doped crystals the contribution of the shallow levels is reported to be more.

Out of the two major phenomenon contributing to nonlinear absorption in these materials, TPA plays a decisive role in these materials with ultrashort pulses. There have been two basic approaches to the calculation of degenerate TPA coefficients in a crystalline solid. First, second order perturbation theory can be used to calculate the transition rate from valence band to conduction band (resulting from the absorption of two photons). Second, first-order perturbation theory can be used with electronic wavefunctions that have been dressed to include the acceleration of the electrons as a result of the ac light field developed by Keldysh and is often termed as tunneling theory [65]. Fermi’s golden rule derived from the second-order time dependent perturbation theory provides the form of the two-photon transition rate:
\[ W_2 = \frac{2\pi}{\hbar} \sum_{\omega} \left| \sum_{\psi_i} \langle \psi_i | \hat{H}_{\text{opt}} | \psi_i \rangle \langle \psi_i | \hat{H}_{\text{opt}} | \psi_i \rangle \right|^* \delta \left( E_{cv}(k) - 2\hbar \omega \right) \] \tag{5.8}

\[ \hat{H}_{\text{opt}} = \left( \frac{e}{mc} \right) \hat{A} \cdot \vec{p} \] \tag{5.9}

\( \hat{H}_{\text{opt}} \) is the optical interaction Hamiltonian applicable to solids; \( \psi_c (\psi_v) \) is the Bloch wave function for the conduction (valence band) and \( E_{cv} \) is the energy difference between the bands. The sum over all possible intermediate states \( \psi_i \) and over all possible transitions starting from a filled and ending at an empty state (usually valence band to conduction band for an intrinsic semiconductor), i.e., a sum over bands and the electronic wave vector.

We have compared our experimental results and the fits with simple two-parabolic band model describing both semiconductors and dielectric materials. The energy-gap dependence of the TPA coefficient was determined by measurements on a variety of materials with gaps ranging from 1.4 to 3.7 eV \[28,66,67\] predicting a scaling relation for the degenerate TPA coefficient given by

\[ \beta(\omega) = K_{\text{ph}} \left( \frac{E_p}{E_g} \right)^{1/2} F_2 \left( \frac{\hbar \omega}{E_g} \right) \] \tag{5.10}

Where

\[ F_2 = \left( 2x - 1 \right)^{3/2} / \left( 2x \right)^5 \quad \text{for} \ 2x > 1 \] \tag{5.11}

is the dispersion function for the TPA, and is only a function of the ratio of the photon energy to \( E_g \) i.e., optically coupled states. \( E_g \) being the bandgap of the material and \( E_p \) is the Kane momentum parameter

\[ E_p = 2 \frac{\left| p_{vc} \right|^2}{m_0} \approx 21 \text{ eV} \] \tag{5.12}

\( p_{vc} \) is the interband momentum matrix element given by

\[ p_{vc} = \frac{i}{\hbar} \int d^3 r \psi_c^* (\vec{k}, r) \nabla \psi_v (\vec{k}, r) \] \tag{5.13}
$K_{pb}$ is a material independent constant:

$$K_{pb} = \frac{2^9 \pi}{5} \frac{e^4}{\sqrt{m_0 c^2}}$$  \hspace{1cm} (5.14)

which has a value of 1940 in units cm/GW (eV)$^{5/2}$ such that $\beta$ is in cm/GW and $E_s$ and $E_p$ are in eV. A wealth of experimental and theoretical work regarding TPA in semiconductors and crystalline materials exists. The best fit to the data [28] using equations (10), (11) and (13) gave $K_{pb} = 3100$ cm/GW (eV)$^{5/2}$. While second-order perturbation calculation for a four-band model gave $K_{pb} = 5200$ cm/GW (eV)$^{5/2}$ for parabolic bands neglecting any coulomb interaction [68]. The value of $\beta_{eff}$ obtained from the open aperture Z-scan curve with 25 ps pulses and at 532 nm is in close agreement with the value obtained using $E_p = 21$ eV, and $K_{pb} = 1940$ cm (eV)$^{5/2}$/GW. These values are used to estimate the absorption from the trap levels and the free carriers.

The energy gaps are taken as 3.25 eV and 2.65 eV for the calculation of $\beta_v$ and $\beta_d$ respectively. The values of the estimated TPA values for $\beta_v$ and $\beta_d$ and the effective theoretical TPA coefficient $\beta_{th}$ is given in table 5.4.

<table>
<thead>
<tr>
<th>$\lambda_{ex}$ (nm)</th>
<th>$\beta_v$</th>
<th>$\beta_d$</th>
<th>$\beta_{eff}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>532</td>
<td>1.801</td>
<td>2.766</td>
<td>4.567</td>
</tr>
<tr>
<td>600</td>
<td>1.701</td>
<td>3.328</td>
<td>5.029</td>
</tr>
<tr>
<td>683</td>
<td>0.956</td>
<td>3.510</td>
<td>4.466</td>
</tr>
</tbody>
</table>

Table 5.4: Estimated values of $\beta_{eff}$ different wavelength excitations used with $E_p = 21$ eV and $K_{pb} = 1940$ cm (eV)$^{5/2}$/GW. $\beta$ has units of cm/GW.

From table 5.3, it is clear that TPA plays a dominant role and the intraband processes inside the conduction band and the excitation of the carriers from the trap levels to the CB assist TPA for reverse saturable absorption. TPA coefficient is evaluated in various photorefractive crystals like BGO [16], BaTiO$_3$ [30] and LiNbO$_3$ [68], at different wavelengths and pulse widths. In all these reports a large deviation from the value calculated using equations (5.10) - (5.14) has been reported. Boggess et al. [30], with 1 ps excitation in BaTiO$_3$ found that the estimated value is an order of magnitude higher than the measured value and Adinolfi et al. [68], found almost 50% variation in LiNbO$_3$. With ps and shorter
pulses only TPA is playing a major role. Though pump-probe studies show approximately 50-60 ps decay of the excited carriers, the contribution from the traps is negligible compared to TPA. With ns pulses TPA as well as TACCA comes into picture.

![Figure 5.10: Effect of $\tau_{CT}$ on nonlinear absorption at constant $\beta_{eff} = 12.24$ cm/GW (corresponding to $K_{ph} = 5200$) and $\sigma_{eff} = 8 \times 10^{-18}$ cm$^2$]

By considering ($I$ with $K_{pb} = 5200$ cm/GW (eV)$^{5/2}$) we are able to fit with high TPA only at higher intensities and at lower intensities more contribution coming from TACCA; which is not matching with the earlier reported theoretical and experimental observations in literature. Whereas with low TPA in the ns regime (with $K_{pb} = 1900$ cm eV$^{5/2}$/GW); with increasing intensity TACCA increases, which matches well with the earlier secondary center models. Theoretical fits with two different $\tau_{ct}$ (4 ns and 60 ps) and different values of $\beta$ (with $K_{pb} = 1940$ and 5200 cm (eV)$^{5/2}$/GW) are shown in Fig 5.10 to Fig 5.12 to give an idea of the effect of these factors on nonlinear absorption in these crystals.
Figure 5.11: Effect of $\tau_{CT}$ on nonlinear absorption at constant $\beta_{eff} = 4.43$ cm/GW (corresponding to $K_{ph} = 1900$ from the ps data) and $\sigma_{eff} = 21 \times 10^{-6}$ cm$^2$.

Figure 5.12: Effect of TPA coefficient $\beta$ nonlinear absorption at constant $\tau_{CT}$ ($= 60$ ps) and $\sigma_{eff} (= 43 \times 10^{-19}$ cm$^2$).
5.6 Conclusions

- Broadband response in the visible wavelength region
- The crystals are found to have a very strong nonlinear absorption with major contribution from TPA assisted by intraband carrier absorption and charge carrier absorption from trap levels.
- In the ps regime TPA plays a dominant role and in the ns regime absorption from the trap levels and free carrier absorption also come into play.
- Low limiting thresholds and high damage threshold with iron doping makes the material suitable for limiting purposes even for short pulse duration and high energy sources over broadband region.
- Relaxations of the excited carriers in the timescales of ~ 60 ps and TPA make these crystals very good materials for ultrashort pulse applications.

5.7 References

1. P. Yeh, "Introduction to photorefractive nonlinear optics", John-Wiley, (1993);


