Chapter 2

MATERIALS AND METHODS

2.1. Section 1. Preparation techniques
2.2. Section 2. Experimental tool and techniques used for characterization of ChG
2.3. Conclusions
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This chapter is divided into two sections namely the preparation techniques and the experimental tools and techniques used for the characterization of ChG in the present work.
2.1. Section 1. Preparation techniques

The techniques used for the preparation of bulk ChG, thin films, nano colloid solutions, ChG/Polyvinyl Alcohol nano composite film, stacked hybrid films of ChG and polymer and nano colloid ChG doped polymer fiber are discussed in this section.

2.1.1. Chalcogenide bulk glass preparation

Bulk glasses were prepared using melt quenching method. Melt quenching technique was the only method used for the preparation of bulk glasses before the development of chemical vapour deposition and sol gel technique\(^1,2\). One of the important features of the melt quenching technique is the high flexibility of geometry and composition and the advantage of obtaining materials of large size in comparison to other methods. The doping or codoping of active ions or transition metals are quiet easy using this method. This method can be used for the preparation of silicate, borate, phosphate, oxide or non oxide systems\(^1\). One of the main disadvantages of this method is the lack of ultra high purity as compared to other chemical methods. In order to avoid contamination, the crucibles made of noble metals can be used.

Melt quenching method applied for chalcogenide glass preparation is as follows. This method is based on the fusion of raw materials in to a viscous solid, followed by forming in to a shape and quenching to a glass. The electronic grade (5N purity) constituent elements are weighed in proportion to their atomic weight
percentages. The raw materials used in the present study are Ge, Se, Sb, Ga and Er which are all purchased from Alfa Aesar having a grade of 5N purity. For each composition approximately around 4gm of material is transferred to clean quartz ampoules of 8 mm diameter and 8cm length.

The ampoule is then evacuated at a pressure of $10^{-3}$ m bar for half an hour and then flame sealed at this vacuum using oxygen-indane flame torch. Precleaning and evacuating helps to avoid the presence of impurities. The ampoule is then placed in a rocking and rotating furnace as shown in Figure 2.1.

![Rocking and rotating furnace used for the preparation of ChG glasses.](image)

**Figure 2.1:** Rocking and rotating furnace used for the preparation of ChG glasses.

The furnace can attain a maximum temperature of 1100°C. The temperature controller in this unit is C961 Blind Temperature Controller with single thermocouple or RTD input and one relay output with user specific control action and relay logic. Before keeping the ampoule, the furnace can be programmed to the desired temperature. The samples presented in this thesis are prepared at a temperature of 1050°C. In order to homogenize the melt continuous rotation and rocking in an interval of
1 hour is given. The melt is then rapidly quenched to ice cold water. The samples are then taken out from the sealed ampoules by dipping it in Hydrofluoric acid (HF) solution. HF solution etches the quartz ampoule leaving the bulk glass.

2.1.2. Thin film preparation

Thin film preparation can be based on physical deposition or chemical deposition method\textsuperscript{3,4}. Depositions that happen because of a chemical reaction are Chemical Vapour Deposition (CVD), Electro deposition, Epitaxy, Thermal oxidation etc and depositions that happen because of a physical reaction are Physical Vapour Deposition, Evaporation, Sputtering and Casting. The vapour deposition methods such as thermal evaporation, sputtering and chemical vapour deposition methods can yield amorphous thin films deposited on a substrate.

2.1.2. a) Thermal evaporation technique

It is perhaps the simplest vapour deposition technique which involves resistive or electron beam heating in vacuum of a reservoir containing the material to be evaporated. The melt so produced then evaporates and the vapour is condensed on to a substrate, forming a thin film. In chalcogenide glass the deposition of the film at the oblique incidence may result to structural inhomogeneity which may lead to formation of columnar growth morphology for the films\textsuperscript{5}.

The making of an amorphous chalcogenide thin film by thermal evaporation in vacuum coating unit is done in the following
way. The unit used for coating is India High Vacuum pumps (12A4-D). Firstly, bulk sample is loaded in tungsten boat in the system as shown in Figure 2.2. After than the bell jar is closed and the system pumped down to around $2 \times 10^{-5}$ torr through a diffusion pump. At this level of air pressure, the entire environment inside the deposition chamber is free of impurities and the sample is ready for deposition. The chamber is evacuated by INDVAC Diffpak pump Model 114D abd backed by 250 liters per minute, doublestage, direct driven, Rotary vacuum pump, Model:IVP.

Figure 2.2: Schematic representation of the Bell jar in thermal evaporation unit.

With the shutter in the closed position, the temperature of the substrate is set to the desired level heated till the sample loaded starts to evaporate. The heating element in the system is conal sheated nichrome having a power rating of 500 watts, 120 V to 140V. Once the evaporation rate is stabilized and the substrate reaches its desired temperature, the vapour is allowed to come into contact with the substrate. The rate of evaporation is maintained to be $10 \text{A}^0/\text{s}$. The evaporation rate as well as the film thickness can be controlled using a quartz crystal in Digital thickness Monitor Model-CTM-200
attached to the bell jar. When the desired thickness is reached, the shutter is closed. The amorphous film is maintained at the substrate temperature until the boat and the chamber cooled down to a level suitable for the film to be removed from the system.

2.1.2 b) Spin coating and drop casting

Spin coating

SPIN 150-v3 was used for spin coating the films. Spin Coating involves the acceleration of a liquid puddle on a rotating substrate. In this technique the coating material is deposited in the center of the substrate either manually or by a robotic arm. The physics behind spin coating involve a balance between centrifugal forces controlled by spin speed and viscous forces which are determined by solvent viscosity. Some variable process parameters involved in spin coating are Solution viscosity, Solid content, Angular speed and Spin Time. The method of spin coating is given in Figure 2.3.

![Figure 2.3: Schematic diagram of spin coating.](image)

Drop casting

The drop casting technique is a simple method to deliver drops of liquid in the micromolar to millimolar range. The drops are deposited mostly by means of micropipettes onto solid surfaces. The
stirred solution is taken in a micro glass syringe and placed in a cleaned glass slide. The films were then allowed to dry and kept in dark in desiccators.

2.1.3. Chalcogenide Nano colloid preparation

Chalcogenide nano colloids were prepared by dissolving the bulk glasses in n-butylamine solution (Alfa Aesar). \( n \)-Butylamine is an organic compound (specifically, an amine) with the formula \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \). This colourless liquid is one of the four isomeric amines of butane, the others being sec-butylamine, tert-butylamine and isobutylamine. At standard temperature and pressure, \( n \)-butylamine is a liquid having the fishy, ammonia-like odor common to amines\(^{16} \).

The bulk glasses were grounded to fine powders and weighed. After that solutions of different concentrations were made by dissolving the ChG in n-butylamine in a sealed bottle. The solutions were given continuous stirring at an ambient temperature (35°C) for expediting the dissolution mechanism. The solutions were then kept in refrigerator.

Chern and Luck\(^{9-11} \) has described the dissolution of the bulk glass in amine solvents as follows, the dissolution of the continuous network of the bulk glass chalcogenide glass in butylamine leads the bulk glass to get fragmented possibly along the weakly bonded interlayer planes in the form of clusters. The surface of these clusters react with the solvent to form amine salts. It is interesting to point out that the chalcogenide glasses are found to be both stable in neutral and acidic (non-oxidizing) solutions, but begin to dissolve quite
rapidly in basic solutions. The dissolution mechanism of the chalcogenide glass in solvents primarily centers on general acid-base chemistry. Amines are usually considered to be bases.

According to the Brønstead-Lowry (B-L)\textsuperscript{12} concept an acid is defined as a substance which is able to donate a proton while a base as a proton acceptor; whereas the Lewis concept\textsuperscript{12} defines acids as capable of accepting a lone pair in order to form a coordinate covalent bond and bases are the lone pair donors. This concept is equivalent in aqueous solutions but in nonaqueous solutions and particularly when the acid does not possess hydrogen atoms, the B-L concept becomes awkward\textsuperscript{13}.

In our case the glass is considered as the acid. Another important thing is nucleophilicity, which is distinct from basicity. Nucleophilicity is the focus of the Pearson hard-soft acid base (HSAB) concept\textsuperscript{13-15}. This concept defines the chemical hardness ($\eta$) as equal to one half of the derivative of the chemical potential of a system with respect to the total number of electrons. In other words it relates to the difference between the ionization potential and electron affinity\textsuperscript{14}. Hardness is therefore a measure of the energy needed to alter the electron cloud through addition or removal of an electron. Here species with extreme electronegativities or high charge densities would be considered hard while those with intermediate electronegativities and high polarizabilities would be considered soft. Thus hard-hard interactions will tend to be ionic in nature while soft-soft interactions are covalent, making soft bases generally better nucleophiles\textsuperscript{15}.
2.1.4. Composite film preparation

Chalcogenide/Polymer composite films were prepared by drop casting method. The prepared nano colloid solutions of different glasses and the polymer are mixed together. The polymer used for making films is polyvinyl alcohol\(^{16}\). Polyvinyl alcohol (PVOH, PVA, or PVAl) is a water-soluble synthetic polymer. Unlike many vinyl polymers, PVA is not prepared by polymerization of the corresponding monomer. The monomer, vinyl alcohol, almost exclusively exists as the tautomeric form, acetaldehyde. PVA instead is prepared by partial or complete hydrolysis of polyvinyl acetate to remove acetate groups. The chemical formula for PVA is,

\[
\begin{array}{c}
\text{CH}_2 \\
\text{O} \\
\text{CH} \\
\end{array}
\begin{array}{c}
\text{CH}_2 \\
\text{O} \\
\text{CH} \\
\end{array}
\begin{array}{c}
\text{CH}_2 \\
\text{O} \\
\end{array}
\begin{array}{c}
\text{CH} \\
\end{array}
\]

The nano colloid solutions of chalcogenide glass and poly Vinyl Alcohol were mixed in different proportions using a magnetic stirrer. The mixture was then carefully drop casted on to a cleaned glass slide. The films were then allowed to dry by keeping in desiccators.

2.1.5. Multilayers of chalcogenide glass

Multilayers of chalcogenide glass were prepared by coating the bulk chalcogenide glass by thermal evaporation on to composite films of chalcogenide glass and polymer prepared by drop casting method. The composite films are also coated on to the thermally evaporated films.
2.1.6. Fiber fabrication

Drawing of fiber directly from melts of material in crucibles or fiber drawing by Vapor phase oxidation are the basic techniques used in the fabrication of Polymer Optical fibers (POF).

2.1.6.1. Continuous extrusion method

Plastic optical fibers are produced in a simple extrusion process, which is similar to the double crucible method used for fabricating glass fibers. The disadvantage of this method is the possibility of introducing contaminants during the melting process. The most economical method for making polymer optical fiber that is also amenable to high-volume processing is the extrusion process. In this method, a purified monomer (methyl methacrylate), an initiator and a chain transfer agent are fed into a reaction chamber where the monomer is polymerized. The material is partially polymerized into a thick fluid, which is typically 80% polymer and 20% monomer. The temperature of the reactor chamber is typically 180°C. This concentrated solution is directed to the screw extruder, which pushes the material through a nozzle that creates the fiber. Remaining monomer is evaporated in the core extruder and recovered for further use. Subsequently, the core of the fiber runs into a second chamber and then through a nozzle where the cladding is coated onto the fiber—also using an extrusion process. This leads to the formation of a continuous fiber. Effectively, then, material is fed into one end and the fiber comes out the other end. The most important advantage of continuous extrusion is high production rate.
2.1.6.2. Vapor phase oxidation

With direct drawing, it is difficult to get pure and homogeneous fibers; therefore this method is not commonly used\textsuperscript{19,20}. The vapor phase oxidation processes have proven to be more successful. These processes are usually done in two steps:

- The first being the preparation of the Preform.
- The second being the drawing of the fiber.

This method is used for the preparation of nano colloid ChG doped polymer fiber.

\textbf{Preform method}

The preform drawing process can be used for making single mode step index fiber, multimode fiber and graded index fiber\textsuperscript{20}. So this method is very advantageous compared to other fiber fabricating methods. Fabrication of POFs by preform method involves two stages. In the first stage, a cylindrical preform of required diameter and length is made. In the second stage, the preform is drawn into fiber by the heat-drawing process.

Preform making is the most important part of making a POF because it decides the optical quality of the fiber. The fiber drawing process relies on the smooth flow of softened polymer. Since thermoplastics are polymers that flow at an elevated temperature, they are well suited as fiber materials. An important property of the polymer is its molecular weight, which is a measure of the average chain length. If the molecular weight is too high, the chains are too
long to permit them to slip and flow\(^{21}\). The result is that the polymer remains rubbery even at temperatures that are high enough to cause the material to decompose. The ideal molecular weight allows the material to flow without dripping. In making the polymer, a chain transfer agent is used to control the molecular weight.

A cylindrical tube, which serves as the cladding layer, is made by polymerizing a cladding material inside a rotating cylindrical reactor. Materials that can be polymerized by the radical polymerization reaction are used and the reaction is induced thermally or by UV radiation using photoinitiator\(^{22}\). Due to the fast rotational speed of the reactor about its axis, a tube of uniform thickness is formed once the reaction is complete. This tube is then removed from the reactor and filled with a core material mixed with an initiator and a chain transfer agent. The core material is then polymerized to make a preform that is drawn to a fiber by heat-drawing process.

There are two other commonly used methods for preform fabrication. First is the rod-in-tube method, in which a pre-fabricated polymer core rod is inserted into a pre-fabricated polymer cladding tube with a tight-fitting\(^{23}\). The disadvantage of this method is that the rod diameter is usually too large for the drawn fiber to achieve a single-mode operation. Also bubbles may be trapped at the core-cladding interface. The second method is the hole-in-rod technique\(^{23,24}\) where a hole is drilled into a cladding polymer rod followed by pouring in core monomer. A polymerization process is then initiated.
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to obtain a composite core-cladding polymer preform. The core-cladding interface of this preform may not be smooth because of drilling. This could lead to excessive loss.

The most successful technique that can be used for the fabrication of the preform is “Teflon technique”\textsuperscript{24}. In this technique a thin teflon string is properly fixed in the center of a glass tube. The thermal polymerization of the filled tube is carried out in a temperature controlled oil bath. After the monomers are fully polymerized and heat treated, the teflon string is removed and we obtain a polymer tube (polymer rod with a small hole in its center). The bottom side of the core is sealed and the hole is then filled with the initiated monomers for the core. Again it is kept in an oil bath for further polymerization.

\begin{itemize}
  \item \textbf{Heat drawing process}
\end{itemize}

The heat drawing process is shown schematically in Figure 2.4. The solid preform is then drawn or pulled into an optical fiber by a process called fiber drawing.

The fiber drawing process begins by feeding the preform into the drawing furnace. The drawing furnace softens the end of the preform to the melting point. The preform is positioned vertically in the middle of the furnace (or oven) where its lower portion is heated locally to the drawing temperature \textsuperscript{20,25}. Both convective and radiative heat transfer mechanisms are important in heating the preform in the furnace. When the lower part of the preform reaches a temperature beyond its softening point, it necks downward by its own weight due
to gravity. Once this initiation of the drawing process is achieved, tension is applied to the fiber by drawing rollers and the fiber is drawn continuously while the preform is fed at a predetermined rate.

The fiber diameter is continuously measured and the desired value is maintained by controlling the preform feed speed and the drawing roller speed. Another design of the fiber drawing system is the horizontal drawing rig. The only difference in this case from the conventional drawing system is that the whole drawing procedure is horizontal. GD Peng et al.\textsuperscript{25} have widely used this type of configuration and have observed no fiber sagging during drawing and the fiber diameter was kept at an acceptable tolerance. The horizontal machine offers an additional advantage of convenience of saving the need of climbing up and down the ladder during the draw initiation phase.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig24.png}
\caption{Schematic diagram of heat drawing process of polymer optical fiber.}
\end{figure}
2.2. Section 2. Experimental tool and techniques used for characterization of ChG

In this section the structural, thermal and optical characterization and the tools used for characterizing chalcogenide based materials are included.

2.2.1. Structural Characterization

The structural characterization of the investigated samples of chalcogenide glass was done using X-Ray diffraction technique, Scanning electron microscopy, Atomic force Microscopy, NMR Spectroscopy and Confocal microscopy.

2.2.1. a) X-Ray diffraction (XRD)

Macroscopically, the distinction between crystalline solids and non-crystalline solids can be made just by observation. The crystals have definite shapes which reflect the regular atomic arrangement in the atomic scales for example the cubic faces of common salt and glasses on the other hand have curved surfaces. Microscopically, the distinction can be made using X-ray diffraction (XRD). It is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined. Hence it is also called the powder diffraction method. Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a
crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg’s Law \( n\lambda = 2d \sin \theta \). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2\( \theta \) angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. If a material does not show this diffraction peaks it proves that the material is not a crystal and must be non crystalline. We have used the Bruker AXS D8 Advance diffractometer whose source of X rays is Cu, Wavelength 1.5406 A°.

2.2.1 b) Scanning electron microscopy (SEM)

Surface imaging of the chalcogenide nano clusters in the spin coated thin films are studied using Scanning electron microscope (JEOL Model JSM - 6390LV) equipped with EDS (JEOL Model JED - 2300) for the qualitative elemental analysis.

2.2.1. c) Atomic force microscopy (AFM)

The atomic force microscopy (AFM) include in the family of scanning probe microscopes which has grown steadily since the
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invention of the scanning tunneling microscope. Veeco, Nanoscope III, made by Digital Instruments Inc., USA base-style atomic force microscopes (AFMs) which uses the basic software element NanoScope is used in the present work to study the distribution of nano clusters in the composite films. The AFM can work either in contact mode or in Tapping Mode. In contact AFM, the tip— that part which directly interacts with the sample—is usually mounted on the end of a support (the cantilever) to create a unified probe. The cantilever provides a support for the tip and is deflected by pressure upon the tip. By monitoring how the cantilever is deflected, the tip’s travel over surface features is interpreted, and then rendered into an electronic image. In tapping mode the tip does not interact directly with the sample. The composite films prepared are studied in tapping mode.

2.2.1 d) Bruker Avance III 400MHz NMR spectrometer

Bruker Avance III 400MHz NMR spectrometer includes a inverse broadband probe fitted with a Z-axis gradient and with automatic tuning and matching. The inner coil is optimized for 1H and the outer coil can be tuned from $^{31}$P to $^{97}$Mo (and others in between). So X-frequencies are ranging from 162 to 27 MHz. The whole system is controlled by Bruker’s Topspin software. A B-ACS 60 sample changer is present to be flexible in non-working hours.

2.2.1. e) Confocal microscope

Leica TCS SP5 II laser scanning confocal microscope is used for the imaging of emission from nano clusters in the nano colloids of
ChG. The system is a Leica TCS SP5, a point scanning spectral confocal with five channels. The system runs on a Windows XP platform with Leica LAS AF system software. The microscope is enclosed in a Ludin environmental chamber with temperature, humidity, and CO₂ control. It has the following lasers: Blue diode 50 mW 405 nm, Multiline argon: 5 mW 458 nm, 5 mW 476 nm, 20 mW 488 nm, 5 mW 496 nm, 20 mW 514 nm, He-Ne 1 mW 543 nm, He-Ne 2 mW 594 nm, He-Ne 10 mW 633 nm.

2.2.2. Thermal Characterization

Thermal characterization of the prepared bulk ChG’s was done using Differential scanning Calorimetry (DSC). A Mettler-Toledo DSC model 822e is used to follow the thermal behavior of the samples. The apparatus is equipped with a ceramic sensor FRS5 (heat-flux sensor with 56 thermocouples Au-Au/Pd). The differential scanning calorimeter was previously calibrated using indium and zinc standards for temperature and power calibration. The autosampler available on the Mettler-Toledo DSC 822e is used to automate the experimental procedure.

10 mg of the samples were sealed in a pierced aluminum crucible and heated under nitrogen flow (200 mL/min outside the oven, 100 mL/min inside the oven). Sample was then given temperature at heating rates of 10°C /min. This heating rate improves the calorimetric response (without a decrease of accuracy) and reduces the time of the analysis and, consequently, the risk of sample degradation.
2.2.3. Thickness measurement

Thickness is one of the most important thin film parameter to be characterized since it plays an important role in the film properties unlike a bulk material. Thickness measurement of the thin films prepared by thermal evaporation were carried out at the time of coating itself using a DTM thickness monitor attached in the vacuum system. After fabrication the thickness of the films were found using stylus profiler (Dektak 6M). The stylus profiler\textsuperscript{32} takes measurements electromechanically by moving the sample beneath a diamond tipped stylus. The high precision stage moves the sample according to a user defined scan length, speed and stylus force. The stylus is mechanically coupled to the core of a linear variable differential transformer (LVDT). The stylus moves over the sample surface. Surface variations cause the stylus to be translated vertically. Composite films of micrometer range were measured using a Mitutoyo digital outside micrometer, series 193 with a resolution ±0.001 mm.

2.2.4. Optical characterization

2.2.4 a) Absorption, reflection and transmission measurements

JASCO V-570 UV/VIS/NIR Spectrophotometer was used for the absorption, transmission and reflectance measurements of the samples. The spectrometer consist of Optical system\textsuperscript{33}: single monochromatic, UV/ VIS region 1200 lines/ mm plane grating, NIR region: 300 lines/ nm plane grating, Czenry -Turner mount double beam type Resolution: 0.1 nm (UV/ VIS region) 0.5 nm (NIR region).
Light source: 30 mW deuterium discharge tube in 190 nm to 350 nm region, 20 W tungsten iodine lamp in 330 to 2500 nm region. Wavelength range: 190 nm to 2500 nm. The beam from the light source is converged and enters the monochromator. It is dispersed by the grating in the monochromator and the light passes out through the exit slit. This light is split into two light paths by a sector mirror, one incident on the sample to be measured and the other on the reference sample such as solvent. The light that has passed through the sample or reference sample is incident on the photomultiplier tube and PbS photoconductive cell which are the detectors. In the reflectance measurement the set up has to be changed.

The Model SLM-468 single reflection attachment is designed to measure the relative reflectance of sample using the forward reflected light from the aluminum-deposited plane mirror as reference\textsuperscript{34}. It permits the measurement of the reflectance of metal deposited film, metal plating etc. The wavelength range is 220 nm to 2200 nm with a beam port diameter of 7 mm and angle of incidence approximately 5\(^\circ\).

2.2.4 \textit{b) Optical absorption spectroscopy of amorphous semiconductors}

Absorption spectroscopy of the materials investigated in this thesis was studied using Jasco V570 spectrophotometer. The typical absorption spectrum of chalcogenide glass is shown in Figure 2.5. In amorphous semiconductors, the optical absorption edge spectra generally contain three distinct region\textsuperscript{35}:

A) High absorption region (\(\alpha=10^4\) cm\(^{-1}\)), which involves the optical transition between valence band and conduction band
which determines the optical bandgap. The absorption coefficient in this region is given by

\[ \alpha h\nu = B(h\nu - E_g)^p \]  \[2.1\]

where \( E_g \) is the optical bandgap and \( B \) is a constant related to band tailing parameter. In the above equation, \( p=1/2 \) for a direct allowed transition=\( 3/2 \) for a direct forbidden transition, \( p=2 \) for an indirect allowed transition and \( p=3 \) for an indirect forbidden transition.

**Figure 2.5:** Regions A,B,C of a typical absorption curve of chalcogenide glass.

B) Spectral region with \( \alpha=10^2-10^4 \) cm\(^{-1}\) is called Urbach’s exponential tail region in which absorption depends exponentially on photon energy \(^{36}\) and is given by

\[ \alpha h\nu = \alpha_0 \exp(h\nu/E_e) \]  \[2.2\]

where \( \alpha_0 \) is a constant and \( E_e \) is interpreted as band tailing width of localized states, which generally represents the degree of
disorder in amorphous semiconductors. In this region most of the optical transitions take place between localized tail states and extended band states.

C) The region with $\alpha \geq 10^{2}$ cm$^{-1}$ involves low energy absorption and originates from defects and impurities.

2.2.4. c) Analysis of Transmission Spectra of thin films using Swanepoels method

Basically, the amount of light that gets transmitted through a thin film material depends on the amount of reflection and absorption that takes place along the light path. The transmission spectrum which depends on the material will have two distinctive features, it will either have interference fringes or it will not. The schematic representation of behaviour of light passing through the material is shown in Figure 2.6.

![Figure 2.6: Schematic sketch of the typical behaviour of light passing through a thin film on a substrate. On the left, oblique incidence is shown to demonstrate the multiple internal reflections. In most measurements, the incident beam is nearly normal to the film as shown on the right.](image-url)
The optical constants can be measured by examining the transmission through a thin film deposited on a transparent glass or other (e.g. sapphire) substrate. Figure 2.7 shows a spectrum taken from a thin film on glass substrate. Swanepoel\textsuperscript{37} has critically reviewed how a single transmission spectrum as shown in figure can be used to extract the optical constants of a thin film.

![Figure 2.7: Transmission spectra showing the interference fringes.](image)

The refractive index of the thin film with uniform thickness can be calculated from the two envelopes, $T_M(\lambda)$ and $T_m(\lambda)$, by considering the extremes of the interference fringes\textsuperscript{38}:

\[
\text{Maxima: } T_M = \frac{Ax}{B - Cx + Dx^2}, \quad 2.3
\]

\[
\text{Minima: } T_m = \frac{Ax}{B + Cx + Dx^2}, \quad 2.4
\]
Subtracting the reciprocal of above first equation 2.3 from second equation 2.4 yields an expression that is independent of the absorbance, \( x \),

\[
\frac{1}{T_m} - \frac{1}{T_M} = \frac{2C}{A}
\]  

Where \( A = 16n^2s \),

\[
C = 2\left(\alpha^2 - 1\right)\left(n^2 - s^2\right).
\]  

Rearranging it for \( n \),

\[
n = \sqrt{N + \sqrt{N^2 - s^2}}.
\]  

Where \( N = \left[\frac{2s}{T_M T_m} - \frac{s^2 + 1}{2}\right] \),

In this equation, \( s \) is the refractive index of glass substrate and its values are obtained from transmission spectra of substrate \( T_s \), using the relation.

\[
s = \frac{1}{T_s} + \left(\frac{1}{T_s} - 1\right)^{1/2}
\]  

In the region of weak and medium absorption, where \( \alpha \neq 0 \), transmittance decreases mainly due to the effect of absorption coefficient, \( \alpha \) and Eq.(2.9) modifies to

\[
N = 2s\left[\frac{T_M - T_m}{T_M T_m}\right] + \frac{s^2 + 1}{2}
\]
where \( T_M \) and \( T_m \) are the transmission maximum and corresponding minimum at a certain wavelength.

If \( n_1 \) and \( n_2 \) are refractive indices of two adjacent maxima or two adjacent minima at wavelengths \( \lambda_1 \) and \( \lambda_2 \), respectively, then the thickness \( d_1 \) of the film is given by\(^{36}\)

\[
d_1 = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_2)} \quad 2.12
\]

The accuracy of the above equation can also be increased by taking into consideration the basic interference equation,

\[2nd_1 = m\lambda, \quad \text{where } n \text{ is the order number, } m \text{ is an integer for maxima and half integer for minima.}\]

2.2.4. d) Refractive index of films without interference fringes

When light gets transmitted through a material at normal incident with multiple reflections at both surfaces of the material, the absorptivity, the reflectance and the transmittance can be expressed by the following relationships\(^{39}\)

\[
R = r + \frac{(1-r^2)e^{-2ad}}{1+r^2e^{-2ad}} \quad 2.13
\]

\[
A = (1-r)\frac{1-e^{-ad}}{1-re^{-ad}} \quad 2.14
\]

With:

\[
r = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad 2.15
\]
and
\[ \alpha = \frac{4\pi k}{\lambda} \]  
2.16

where \( r \) is the reflectivity in a single reflection, \( \alpha \) is the absorption coefficient, \( k \) is the extinction coefficient or also called the absorption constant, \( d \) is the thickness and \( n \) is the refractive index. By definition the absorptivity \( A = I_A / I_o \), the reflectance \( R = I_R / I_o \) and the transmittance \( T = I_T / I_o \), where \( I_A, I_R \) and \( I_T \) are the intensities of the respective absorption, reflection and transmission activities, and \( I_o \) is the original intensity of the light.

2.2.4 e) Dispersive analysis of the refractive index using Wemple-DiDomenico model

The spectral dependence of the refractive index has been analyzed in terms of Wemple-DiDomenico (WDD) model\textsuperscript{40}, which is based on the single effective oscillator approach having the expression, where \( h \nu \) is the photon energy, \( E_0 \) is the single oscillator energy (also called average energy gap) and \( E_d \) is the dispersion energy, which is a measure of average strength of the inter band optical transitions. The oscillator parameters are determined by plotting refractive index factor \( (n^2-1)^{-1} \) versus\((h\nu)^2 \) and by fitting a straight line to the points. Slope gives \((E_0/E_d)^{-1}\) and the intercept on vertical axis gives \((E_0/E_d)\).

The effective oscillator energy \( E_0 \), which can be directly correlated with optical energy gap by an empirical formulas proposed by Tanaka as\textsuperscript{41}
\[ E_0 \approx 2E_g \]  
2.17
The values for the static refractive index \( (n_0) \) have been calculated from WDD dispersion parameters \( E_0 \) and \( E_d \) by using the formula
\[
n_0 = \left(1 + \frac{E_d}{E_0}\right)^{1/2}
\]

The values of \( n_0 \) can be calculated by extrapolating the WDD dispersion equation with \( h \nu \to 0 \). The high frequency dielectric constant \( (\varepsilon_{\infty}) \) (static dielectric constant) has been calculated from the relation
\[
\varepsilon_{\infty} = (n_0)^2
\]

**2.2.4. f) Calculation of Nonlinear susceptibility and refractive index using Generalized Millers rule and WDD model**

Simple empirical relation based on generalized Miller’s rule\(^{43}\) can be used for the estimation of the non linear refractive index \( (n_2) \) and susceptibility \( (\chi^{(3)}) \). The non linear refractive index \( (n_2) \) and susceptibility \( (\chi^{(3)}) \) can be calculated by combining Miller’s generalized rule\(^{44}\) and low-frequency linear refractive index estimated from Wemple-DiDomenico\(^{40}\) single effective oscillator model. The linear optical susceptibility in the case of chalcogenide glasses is given by relation: \( \chi^{(1)} = (n_2 - 1)/4\pi \). Using generalized Miller’s rule we obtain
\[
\chi^{(3)} = A(\chi^{(1)})^4
\]

Estimated A value\(^{44}\) is \( 1.7 \times 10^{-10} \) (for \( \chi^{(3)} \) in (esu)).

The \( n_2 \) can be calculated from the relation,
\[
n_2 = \frac{12\pi\chi^{(3)}}{n_0}
\]
2.2.4. g) Absorption coefficient, extinction coefficient, dielectric constants and optical conductivity

The absorption coefficient ($\alpha$) of these materials strongly depends on optical transmission ($T$) and reflection ($R$) and is evaluated using the relation $^{38}$

$$\alpha = \frac{2.303}{d} \log \left( \frac{(1 - R)^2}{T} \right)$$  \hspace{1cm} 2.22

The optical energy gap ($E_g$) of the thin films has been determined from absorption coefficient data as a function of photon energy. Once the absorption coefficient is calculated the band gap and the width of localized states can be found using Eqs (2.1) and (2.2).

The extinction coefficient ($k$) and refractive index ($n$) are important parameters characterizing photonic materials. Values of $n$ and $k$ are calculated using the experimental data obtained for the samples under study has been calculated using the relation$^{39}$

$$k = \alpha \lambda / 4 \pi$$  \hspace{1cm} 2.23

The knowledge of real part and imaginary part of the dielectric constant provide information about the loss factor$^{37}$. The real part of the dielectric constant is associated with the term that shows how much it will slow down the speed of light in the material and the imaginary part shows how a dielectric absorbs energy from an electric field due to dipole motion.

The dielectric constant ($\varepsilon_r$) and dielectric loss ($\varepsilon_i$) have been determined from$^{39}$
\[ \varepsilon_r = n^2 - k^2 \quad 2.24 \]
\[ \varepsilon_i = 2 \, nk \quad 2.25 \]

The optical response of a material is most conveniently studied in terms of the optical conductivity. It has dimensions of frequency which are valid only in a Gaussian system of units. The optical conductivity \( (\sigma) \) has been determined from the relation \(^{39}\)

\[ \sigma = \alpha nc / 4\pi \quad 2.26 \]

where \( \alpha \) is the absorption coefficient, \( n \) is the refractive index and \( c \) is the velocity of light.

2.2.4. h) Photodarkening experiment

Photoinduced darkening experiments were done on the thin films using the experimental set up \(^{42}\) as shown in Figure 2.8.

![Experimental setup for photodarkening experiment](image)

**Figure 2.8:** Experimental setup used for photodarkening experiment.

Photoinduced studies were carried out using above band gap and near band gap laser sources. We have used 4 mW, 10 mW and 20 mW He–Ne laser (1.96 eV) and Sacher Semiconductor laser (1.53 eV) to study the photosensitivity of the unannealed films. The laser power was made stable during exposure to avoid significant
uncertainty in the total supplied energy. The laser beam was expanded from an initial beam waist of 1.0 mm (FWHM) using a plano-concave lens and collimated with a second plano-convex lens. At the sample stage an aperture (1 cm$^2$) was used to admit only the central maximum of the laser beam, so as to assure irradiating the sample with a fairly uniform intensity.

The transmittance and reflectance spectra of the films at normal incident condition in the spectral range 250–2500 nm were recorded by a double beam UV–VIS–NIR spectrophotometer (Jasco V 570) after and before exposure. All the measurements were executed at room temperature and the samples were kept in the dark between experiments.

2.2.4. i) Photoluminescence spectroscopy

Photoluminescence studies on nano colloid chalcogenide glasses were carried out using Varian Spectro fluorometer. The fluorescence excitation and emission spectrum of the samples were taken using Cary Eclipse Fluorescence spectrophotometer of VARIAN$^{45}$. It has a single cell holder for liquid sample analysis and a solid sample holder accessory to perform fluorescence measurements on solid samples. The solid sample holder accessory provides both rotational and translational adjustment of the sample. The angle of incidence of the excitation may be varied from 20º- 35º. This is the angle between the exciting light and a line perpendicular to the surface of the sample mounting slide. The source of excitation is xenon lamp.
Laser induced photoluminescence

Laser induced photoluminescence is spontaneous emission from atoms or molecules that have been excited by laser radiation. Two radiative transitions are involved in the Laser induced photoluminescence process. First, absorption takes place, followed by a photon-emission step. Laser induced photoluminescence has a large range of applications in spectroscopy. Laser induced photoluminescence is a dominant laser spectroscopic technique in the probing of unimolecular and bimolecular chemical reactions. This technique serves as a sensitive monitor for the absorption of laser photons in fluorescence excitation spectroscopy. It is well suited to gain information on molecular states if the fluorescence spectrum excited by a laser on a selected absorption transition is dispersed by a monochromator.

The pump beam is taken from a Quanta Ray Q-switched Nd:YAG laser which emits pulses of 7 ns duration at 532 nm and at a repetition rate of 10 Hz. A cylindrical lens is used to focus the pump beam in the shape of a stripe on the sample. In the present case it is adjusted to a pump beam width of 7 mm. The output is collected from the edge of the front surface of the cuvette using an optical fiber in a direction normal to the pump beam. The emission spectra are recorded with Acton monochromator attached with a CCD camera (Figure 2.9). Princeton Instruments NTE/CCD air cooled detectors have three distinct sections. The front vacuum enclosure contains the CCD array seated on a cold finger. This finger is in turn seated on a four-stage Peltier thermoelectric cooler. The back enclosure contains the heat exchanger. An internal fan cools the heat.
exchanger and the heat exits the unit through openings in the housing. The CCD array used is Roper Scientific NTE/CCD-1340/100-EM. The electronics enclosure contains the preamplifier and array driver board. This keeps all signal leads to the preamplifier as short as possible, and also provides RF shielding SPEC-10 controller of Princeton Instruments controls the CCD.

SpectraPro-500i is a 500 mm focal length monochromator/spectrograph. It features an astigmatism-corrected optical system, triple indexable gratings and triple grating turret. The SpectraPro-500i includes a direct digital grating scan mechanism with full wavelength scanning capabilities, plus built-in RS232 and IEEE488 computer interfaces. The 1200 grooves/mm grating has an aperture ratio f/6.5. The scan range is 0 to 1400 nm (mechanical range) and an operating range of 185 nm to the far IR and a resolution of 0.05 nm at 435.8 nm. WinSpec, the spectroscopic software, of Princeton Instruments® is used for collecting, storing and processing data from the Roper Scientific system.

Figure 2.9: Laser induced luminescence experimental set up.
Luminescence studies on the fibers are also carried out using the above setup. Instead of the sample in the cuvette the fiber is inserted axially in a fiber holder and studied.

Luminescence studies on fiber are also carried out transversely in the prepared fiber using the set up as shown in Figure 2.10. More information regarding the experiment is given in chapter 7. Studies are made on excitation with LED as excitation source also.

![Figure 2.10: Experimental set up for luminescence studies on fiber.](image)

### 2.2.5. Thermal lens technique for diffusivity measurement

Thermal lens technique is based on the optical measurement of the thermal energy released by a sample subsequently to light absorption and nonradiative relaxation of the excited species. In this method, sample is illuminated using a gaussian beam. A part of the incident radiation is absorbed by the sample and subsequent nonradiative decay of excited state population results in local heating of the medium. The temperature distribution in the medium mimics the beam profile of the excitation beam and hence a refractive index gradient is created in the medium. Due to this modification in
refractive index, the medium act as a lens, called thermal lens (TL). The thermal lens generally has a negative focal length since most materials expand upon heating and hence have negative temperature coefficient of refractive index. The formation of the thermal lens causes the probe beam to expand and is detected as a time dependent decrease in power at the centre of the beam at far field. Most of the currently employed techniques for thermal parameter evaluation are mainly depending upon the heat exchange mechanism or on temperature gradients. However, the thermal lens technique depends upon change in refractive index due to nonradiative deexcitation of sample following the optical excitation which can offer accurate results. The experimental set up used for the studies is given in Figure 2.11. This method offers certain advantage such as its response to even small absorption coefficient as well as accurate measurement of thermal parameters.

**Figure 2.11:** Schematic diagram of the experimental set up. BS1, BS2- Beam Splitters, C – Chopper, L1, L2 – Lenses, DM - Dichroic Mirror, S - Sample, F- Filter, OF- Optical fiber, DSO- Digital Storage Oscilloscope.
Laser radiation at 532 nm wavelength from a Diode Pumped Solid state laser (50mW) is used as the pump beam to generate the thermal lens in the medium. Micro DPSS laser model BWT-50 (B&W) at 532 nm was also used\(^{50}\). BWT series are miniature diode-pumped Nd: YVO4 lasers with integrated internal thermoelectric cooler. They can be operated over a temperature range of -10 to 50°C.

It has TEM\(_{00}\) mode with a spectral line width <0.1 nm and a beam size of 1 mm. JDS Uniphase He-Ne gas laser emitting at 633 nm with 4 mW power was used as the probe beam in studies. The pump beam is intensity modulated using a mechanical chopper. The probe beam is made to pass collinearly through the sample using a dichroic mirror. An optical fiber mounted on XYZ translator serves as the finite aperture. The other end of the fiber is coupled to a fast photodetector. The signal output from detector is processed using a digital storage oscilloscope. Mechanically chopped optical radiation from pump laser is focused using a lens L1 to the sample in a cuvette of 1cm length. The sample holder is placed in a micrometer translational stage and the position of the sample holder is adjusted along the optic axis to obtain the maximum intensity change of the probe beam (one confocal length away from the beam focus). When the chopper allows impinging of pump beam on the sample, it creates a thermal lens within the sample. The chopper used in the study for light beam modulation is HMS/ITHACO model 230 light beam chopper\(^{51}\) with a set of three interchangeable blades of slots 2, 10 or 30 providing three frequency ranges. The frequency ranges from 4 to
200 Hz, 20 to 1 kHz and 60 to 3 kHz for 2, 10 and 30 slotted blades respectively. The probe beam from the He-Ne laser which travel collinearly with pump beam experience a diverging lens and the beam shape expands in the presence of thermal lens. The change in intensity of the probe beam is measured using a fast photodetector using fiber which is fixed on the optic axis of the experimental set up. The TL signal is recorded from which the relative change in intensity and initial slope is measured. The value of $\theta$ and $t_c$ are determined. From these values, the thermal diffusivity of the sample under investigation is evaluated.

**Theory**

The magnitude of the effective thermal lens produced by propagation of a cw Gaussian laser beam of spot size $\omega$ is governed by the steady state balance between laser heating and solvent or matrix heat dissipation. If the beam is suddenly turned on at time $t=0$, the lens approach to steady state governed by

$$ f(t) = f_\infty \left( 1 + \frac{f_\infty}{2t} \right) $$

and the steady state focal length $f_\infty$ of such a lens is derived as

$$ f_\infty = \frac{\pi k \omega^2}{P_A (dn/dt)} $$

where $k$ is the thermal conductivity (W cm$^{-1}$ K$^{-1}$), $P$ is the laser power (W), $A$ is the sample absorbance, $dn/dt$ is the refractive index change with temperature and $t_c$ is the time response to attain the steady state focal length given by
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\[ t_c = \frac{\omega^2}{4T_D} \] 2.29

from which thermal diffusivity \((T_D)\) can be calculated. The thermal diffusivity in the sample is detected by its effect on the propagation of the probe laser beam aligned with the centre of the lens. The expression relating the intensity as a function of time is given as

\[
I(t) = I(0) \left[ 1 - \frac{\theta}{1 + t/2(t - t_0)} + \frac{\theta^2}{2 \left(1 + t/2(t - t_0)\right)^2} \right]^{-1} \]

2.30

The modified equation for continuous wave laser source is,

\[
I(t) = I(0) \left[ 1 - \frac{\theta}{1 + t_c/2(t - t_0)} + \frac{\theta^2}{2 \left(1 + t_c/2(t - t_0)\right)^2} \right]^{-1} \]

2.31

where \(t_0\) is the time at \(t=0\), \(\theta\) is directly proportional to \(P_{th}\) by the relation

\[ \theta = \frac{P_{th} (dn/dT)}{\lambda k} \] 2.33

where \(P_{th}\) is the laser power degraded to heat and \(\lambda\) is the laser wavelength. For a given solvent or matrix the experimental parameter of interest is \(\theta\), which may be obtained from the initial intensity \(I_0\) and the intensity after the steady state has been established, \(I_\infty\), so that
\[ \theta = 1 - (1 + 2I)^{1/2} \]

\[ I = \frac{I_0 - I_\infty}{I_\infty} \]

The initial slope of the decay curve, \( m = \frac{2\theta}{I_0 I_c} \) from which the value of \( t_c \) and hence \( T_D \) is calculated.

2.2.6. Z-scan technique for the analysis of nonlinear optical properties of the samples investigated

Z-scan technique introduced by Sheik Bahae\textsuperscript{53} is a single beam method for measuring the sign and magnitude of nonlinear refractive index that has a sensitivity compared to interferometric methods. It provides direct measurement of nonlinear absorption coefficient. Previous measurements of nonlinear refraction have used a variety of techniques\textsuperscript{54} including nonlinear interferometry, degenerate four wave mixing, nearly degenerate three wave mixing, ellipse rotation and beam distortion measurements. The first three methods namely nonlinear interferometry and wave mixing are potentially sensitive techniques, but all require complex experimental apparatus. The propagation of laser beam inside such a material and the ensuing self refraction can be studied using the z-scan technique. Thus it enables one to determine the third order nonlinear properties of solids, ordinary liquids, and liquid crystals. The experimental set up for single beam z-scan technique is given in Figure 2.12. In the ordinary single beam configuration, the transmittance of the sample is measured, as the sample is moved along the direction of the focussed
guassian beam. A laser beam propagating through a nonlinear medium will experience both amplitude and phase variation. If transmitted light is measured through an aperture placed in the far field with respect to focal region, the technique is called closed aperture z-scan. In this case, the transmitted light is sensitive to both nonlinear absorption and nonlinear refraction. In a closed aperture z-scan experiment, phase distortion suffered by the beam while propagating through the nonlinear medium is converted into corresponding amplitude variations. On the other hand, if transmitted light is measured without an aperture, the mode of measurement is referred to as open aperture z-scan. In this case, the output is sensitive only to nonlinear absorption. Closed and open aperture z-scan graphs are always normalized to linear transmittance i.e., transmittance at large values of $|z|$.

Closed and open aperture z-scan methods yield the real part and imaginary part of nonlinear susceptibility $\chi(3)$ respectively. Usually closed aperture z-scan data is divided by open aperture data to cancel the effect of nonlinear absorption contained in the closed aperture measurements. The new graph, called divided z-scan, contains information on nonlinear refraction alone.
Figure 2.12: Z Scan set up.

An important requirement in the z-scan measurement is that, it is assumed that the sample thickness is much less than Rayleigh’s range $z_0$ (diffraction length of the beam $[z_0=k \omega_0^2/2$, where $k$ is the wave vector and $\omega_0$ is the beam waist radius. The beam waist radius $\omega_0$ is given by $\omega_0=f\lambda/D$, where $f$ is the focal length of the lens used, $\lambda$ is the wavelength of the source and $D$ is the beam radius at the lens. This is essential to ensure that the beam profile does not vary appreciably inside the sample because z-scan technique is highly sensitive to the profile of the beam and also to the thickness of the sample. Any deviation from gaussian profile of the beam and also from thin sample approximation will give rise to erroneous results.

2.2.6.1. Open aperture z-Scan.

Non linear absorption of a sample is manifested in the open aperture z-Scan measurement. If the sample is having nonlinear absorption such as two photon absorption (TPA)\textsuperscript{55}, it is manifested in the measurement as a transmission minimum at the focal point. Otherwise if the sample is a saturable absorber, the transmission
increases with increase in incident intensity and results in transmission maximum at the focal region.

**Theory of open aperture z-scan technique**

In the case of an open aperture z-scan, the aperture as shown in Figure 2.12 is absent. In the absence of an aperture the transmitted light measured by the detector is sensitive only to intensity variations. Hence, phase variations of the beam are not taken into consideration. The intensity dependent nonlinear absorption coefficient $\alpha(I)$ can be written in terms of linear absorption coefficient $\alpha$ and TPA coefficient $\beta$ as

$$\alpha(I) = \alpha + \beta I$$  \hspace{1cm} 2.37

The irradiance distribution at the exit surface of the sample can be written as

$$I_r(z,r,t) = \frac{I(z,r,t)e^{-\alpha l}}{1 + q(z,r,t)}$$  \hspace{1cm} 2.38

Where $q(z,r,t) = \beta l(z,r,t)L_{\text{eff}}$. $L_{\text{eff}}$ is the effective length given in terms of sample length $l$ and $\alpha$ by the relation

$$L_{\text{eff}} = \frac{\left(1 - e^{-\alpha l}\right)}{\alpha}$$  \hspace{1cm} 2.39

The total transmitted power $P(z,t)$ is obtained by integrating Eq 2.38 over $z$ and $r$ and is given by

$$P(z,t) = P_0(t)e^{-\alpha l} \ln\left[1 + \frac{q_0(z,t)}{q_0(z,t)}\right]$$  \hspace{1cm} 2.40

$P_0(t)$ and $q_0(z,t)$ are given by the following equations respectively.

$$P_0(t) = \frac{\pi \omega_0^2 I_o(t)}{2}$$  \hspace{1cm} 2.41
For a pulse of guassian temporal profile, Eq 2.40 can be integrated to give the transmission as

\[
T(z) = \frac{C}{q_0 \sqrt{\pi}} \int_{-\infty}^{\infty} \ln \left( 1 + q_0 e^{-t^2} \right) dt
\]

Non linear absorption coefficient is obtained from fitting the experimental results to the Eq (2.43).

If \(|q_0|<1\), the Eq 2.42 can be simplified as

\[
T(z,S=1) = \sum_{m=0}^{\infty} \left[ -q_0(z,0) \right]^m (m+1)^{1/2}
\]

where m is an integer. Once an open aperture z-scan is performed, the parameter \(q_0\) can be obtained by fitting the experimental results to equation (2.42). Then the nonlinear absorption coefficient \(\beta\) can be unambiguously deduced using equation (2.43). The imaginary part of third order susceptibility \((\chi^{(3)})\) determines the strength of the nonlinear absorption. The TPA coefficient is related to \(\text{Im}(\chi^{(3)})\) by the relation \(^{56}\)

\[
\text{Im}(\chi^{(3)}) = \frac{\varepsilon_0 n_0^2 c^2 \beta}{\omega} (m2V-2) = \frac{n_0^2 c^2 \beta}{240\pi^2 \omega} \quad (\text{esu})
\]

where \(\lambda\) is the excitation wavelength, \(n_0\) is the linear refractive index, \(\varepsilon\) is the permittivity of free space and \(c\) the velocity of light in vacuum.
2.2.7. Two Photon absorption

Two-photon absorption (TPA) is the phenomenon in which two photons of identical or different frequencies are absorbed simultaneously such that a molecule from one state (usually the ground state) will be excited to a higher energy electronic state. Schematic representation of TPA is shown in Figure 2.13. Two-photon absorption can be broadly classified into two types, one is called the resonant TPA and the other one belongs to non resonant TPA. The non resonant TPA is the process in which two photons combine to bridge an energy gap larger than the energies of individual photons. When there exists an intermediate state in the gap, the transition happen through two separate one photon transitions and the process is now described as resonant TPA (sequential TPA).

![Figure 2.13: Schematic representation of TPA.](image)

In non resonant TPA there need not be an intermediate state for the atom to reach before arriving at the final excited state (as if it were moving up two stair steps by stepping one at a time). Instead,
the atom is excited to a “virtual state” which need not correspond to any electronic or vibrational energy eigen state. The nonlinear absorption in this case is proportional to the square of the instantaneous intensity and is given by\textsuperscript{57}

\[
\frac{dl}{dz} = -\alpha l - \beta l^2
\]

where \(\alpha\) is the linear absorption coefficient and \(\beta\) is the two photon absorption coefficient.

2.2.8. Optical limiting studies

The optical limiting behaviour of the samples and the threshold value of optical limiting are understood by keeping the sample in a fixed position and measuring the transmittance as a function of input fluence\textsuperscript{58}. The optical limiting properties of a material can also be estimated from its z-scan plots for various input fluence. For this, the nonlinear transmission has to be plotted as a function of input fluence and such plots can be generated from the z-scan measurements. From the value of fluence at the focus, fluence level at other sample positions can be calculated using the standard equation for Gaussian beam waist given by\textsuperscript{58},

\[
\omega(z) = \omega_0 \left(1 + \frac{z'}{z_0} \right)
\]

Generally it is found that the threshold value of optical limiting is not sharp for material\textsuperscript{58}. One will be able to find an exact value for threshold from the Z-scan plot for the transmission in terms of input fluence.
2.3. Conclusions

The preparation method used in the research work for bulk, thin film, nano colloid, composite film, stacked film and nano colloid doped polymer fiber from ChG are discussed in detail. The characterization tools and experimental set up along with theory used for the study of absorption spectroscopy, photoinduced darkening, photoluminescence mechanism, thermal diffusivity measurement and z-scan technique used for investigating ChG based samples are also discussed.

2.4. References


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