CHAPTER 2

Experimental techniques

2.1 Introduction

This chapter deals with the details of the various experimental techniques used for the investigations of different physical properties of the selected chalcogenide glass samples. Photoacoustic and photopyroelectric techniques have been used to determine various thermal parameters viz., thermal diffusivity ($\alpha$), thermal effusivity ($\varepsilon$), thermal conductivity ($k$) and heat capacity ($c_p$) of the samples. Photoconductivity studies are done on selected systems. Variations of thermal parameters during electrical switching are studied on In-Te system. UV-Vis-NIR spectrophotometer is used to study the optical absorption of the samples. Details of these techniques are described in the following sections of this chapter. The results presented in chapters 3, 4, 5, 6 and 7 have been obtained by carrying out measurements using the above techniques.

2.2. Photoacoustic spectroscopy

Optical spectroscopy is one of the most powerful and effective techniques to study the physical properties of matter. It is based on the interaction of light with matter at atomic or molecular levels. Conventional optical spectroscopic methods are either transmission type or reflection type. In transmission type, the intensity of the transmitted light beam through the medium is measured, while the reflection type
involves the measurement of intensity of radiation reflected or scattered from the sample. However, these techniques fail in the case of weakly absorbing samples, highly light scattering samples like powders, amorphous materials etc. or opaque materials. Several techniques have been developed to overcome these difficulties and the most common of these are diffuse reflectance [1], attenuated total reflection (ATR) and internal reflection spectroscopies [2] and Raman scattering [3]. Even though such techniques have been very useful, they suffer from several limitations. Each method is applicable only to a limited category of materials, each is useful only over a limited wavelength range, and the data obtained are often difficult to interpret.

The photoacoustic spectroscopy has evolved over the past two-three decades as a powerful method to study those materials that are unsuitable for study by conventional spectroscopic techniques [4-7]. This technique is based on the photoacoustic effect, originally detected by Alexander Graham Bell in 1880 [8, 9]. It possesses some unique features, mainly due to the fact that, even though the incident energy is in the form of photons, the interaction of these photons with the sample is studied not through the subsequent detection and analysis of some of the photons, but through a direct measurement of the energy absorbed by the material as a result of its interaction with the incident photon beam.

The photoacoustic (PA) effect is the generation of an acoustic signal when the sample under investigation, placed inside an enclosed chamber, is irradiated by an intensity modulated beam of light. In case of gaseous or liquid samples, the sample fills the entire volume of the cell and acoustic signals are detected by a microphone or a piezoelectric transducer. In the case of solids, the samples fill only
a portion of the cell and the remaining volume of the cell is filled with a non-absorbing gas like air. The PA signal is detected using a sensitive microphone suitably placed inside the cell. The absorption of the incident radiation will excite the internal energy levels of the sample and upon subsequent deexcitation, all or part of the absorbed photon energy is converted into heat through non-radiative deexcitation processes. In the case of gas and liquid samples, which fill the entire volume of the sample chamber, this internal heating causes pressure fluctuations having the same frequency as that of the modulation frequency of the incident radiation and can be detected using an acoustic transducer kept in intimate contact with the sample. In the case of solid samples which fill only a portion of the sample chamber, the periodic heating of the sample results in a periodic heat flow from the interior of the sample to the surrounding non-absorbing gas medium, which in turn produces pressure fluctuations in the gas and are detected as acoustic signal by a microphone suitably placed in the chamber. It is also possible to measure the heat generated in a bulk solid sample through the subsequent pressure or stress variations in the sample itself by means of a piezoelectric detector in intimate contact with the sample. Even though the sensitivity in this case is better, it is not always possible to employ a piezoelectric detector due to the limitations imposed by the nature of the sample. Also, the use of piezoelectric transducers is very difficult for PA measurements that involve variations of the sample temperature over a wide range.

Photoacoustics is essentially a combination of optical absorption spectroscopy and calorimetry. From the calorimetric viewpoint, the heat input into the sample is supplied indirectly by the incident beam of light and the rise in temperature is detected by another indirect method using an acoustic transducer.
instead of a thermal detector. For a typical solid sample, using gas-microphone detection system, temperature rise of the order of $10^{-6}$ °C can be detected. This acoustic detection has several advantages over conventional thermal detection using temperature sensors such as thermistors or thermopiles in terms of sensitivity, detector rise time and the speed at which measurements can be made. The advantages of photoacoustics as a form of spectroscopy are evident from the very nature of the technique. Since absorption of optical or electromagnetic radiation is essential for the generation of the PA signal, light that is transmitted or elastically scattered by the sample does not interfere with the inherently absorptive PA measurements. This enables one to work with essentially transparent media or highly light scattering materials such as powders, amorphous solids, gels and colloids. On the other hand, since the technique does not depend upon the detection of photons, it is possible to obtain optical absorption spectra of materials that are completely opaque to transmitted light. Thus, the advantages offered by photoacoustics over other conventional spectroscopic techniques are due to the following two basic aspects viz., the insensitivity to the non-absorbed light and the non-dependence on the detection of photons.

Spectroscopy is however, only one of the several applications of PA effect. In the spectroscopic regime itself, photoacoustics can be used to measure the absorption and excitation spectra, the life time of excited states and the quantum yield of radiative processes. In addition to this, the calorimetric or thermal aspects associated with the PA effect offers a wide range of applications to study the thermal and elastic properties of materials. In such studies, the calorimetric or acoustic aspect of photoacoustics plays the dominant role, while the optical part is simply a
convenient mechanism for heat generation. Such applications include measurement of thermal parameters, thermal wave imaging and study of phase transitions in solids.

2.2.1 Theory of Photoacoustic effect in solids

A number of theoretical explanations of PA effect have been put forward in the 19th century itself. But the present understanding of the PA effect in solids is based on modern theories developed during 1970's. The first attempt to develop a proper theory of PA effect in solids was carried out by Parker [10] in 1973 in order to give a quantitative explanation for the PA signal emanating from cell windows while performing PA measurements on gases. The general theory of PA effect in solids formulated by Rosencwaig and Gersho [11, 12] has been found to be very successful in interpreting most of the experimental observations. The Rosencwaig-Gersho theory states that in a gas-microphone PA cell, the signal depends on the generation of an acoustic pressure disturbance at the sample-gas interface and is caused by the periodic heat flow from the sample, which is governed by thermal diffusion equations. This theory gives an exact equation for the magnitude and phase of the PA signal as a function of the optical, thermal and geometrical properties of the sample, the cell and the gas within the cell. Although the thermal part of the theory has been treated exactly, the acoustic part is treated in an approximate heuristic manner, which is, however, valid for most experimental conditions.

The Rosencwaig-Gersho (R-G) theory is a one-dimensional analysis of the production of photoacoustic signal in a simple cylindrical cell as shown in Fig. 2.1. The cell has a diameter D and length L. It is assumed that the length L is small compared to the wavelength of the generated acoustic signal.
Fig. 2.1 Cross-sectional view of a simple cylindrical photoacoustic cell

B, S, L and G represent backing material, sample, boundary layer of gas and gas medium respectively.

A microphone (not shown in figure) detects the average pressure produced in the cell. The solid sample is considered to be in the form of a disc of diameter $D$ and length $l_s$. The back surface is against a poor thermal conductor of thickness $l_b$. The length of the gas column in the cell is $l_g$. It is also assumed that, the gas and the backing material do not absorb light. The parameters, which are important in the theoretical formulation, are defined below.

\[ K = \text{thermal conductivity (cal cm}^{-1}\text{s}^{-1}\text{K}^{-1}) \]

\[ \rho = \text{density (g cm}^{-3}) \]

\[ c = \text{specific heat capacity (cal g}^{-1}\text{K}^{-1}) \]

\[ \alpha = \frac{K}{\rho c} = \text{thermal diffusivity (cm}^2\text{s}^{-1}) \]

\[ a = \left( \frac{\omega}{2\alpha} \right)^{1/2} = \text{thermal diffusion coefficient (cm}^{-1}) \]
\[ \omega = 2\pi \nu, \text{ where } \nu \text{ is the modulation frequency of the light beam} \]

\[ \mu = \sqrt{\frac{a}{\rho}} = \text{thermal diffusion length (cm)} \]

According to R-G theory, it is seen that, when a sinusoidally modulated beam of light with wavelength \( \lambda \) and intensity \( I_o \) is incident on the sample, the complex envelope of the sinusoidal pressure variation \( Q \) is given by [6],

\[
Q = \frac{\beta I_o \gamma P_o}{2\sqrt{2}T_0 K_s L_x a_r (\beta_r^2 - \sigma_r^2) (g+1) \left( (r+1)(b-1)e^{\sigma_r I} + 2(b-r)e^{-\beta_r I} \right)} \left[ (r-1)(b+1)e^{\sigma_r I} - (r+1)(b-1)e^{-\sigma_r I} \right]
\]

(2.1)

Here,

\[ \gamma = \text{ratio of specific heats of the gas medium in front of the sample} \]

\[ P_o = \text{ambient pressure} \]

\[ T_0 = \text{sum of ambient and d.c. temperature at the surface} \]

\[ \beta = \text{optical absorption coefficient} \]

\[
b = \frac{K_s a_h}{K_s a_x}
\]

(2.2)

\[
g = \frac{K_s a_x}{K_s a_i}
\]

(2.3)

\[ \sigma = (1+i)a \]

(2.4)

\[ r = \frac{1-i}{2a} \]

(2.5)

The subscripts \( s, b \) and \( g \) denote the sample, backing and gas medium respectively.
Special cases

The difficulty in interpreting Eq. (2.1) can be reduced by examining various special cases. The special cases are determined by the relative magnitudes of the optical absorption length \( l_\beta = 1/\beta \), the thermal diffusion length \( \mu \) and thickness \( l \) of the sample respectively. Also, it is convenient to define

\[
Y = \frac{\gamma P_0 I_0}{2\sqrt{2} T_0 l_R}
\]  

(2.6)

which always appears as a constant factor in the expression for \( Q \).

We consider the case of optically opaque solids, which is relevant in our case. In this case, most of the light is absorbed within a distance that is small compared to \( l_\beta \) and essentially no light is transmitted.

Case (a) Thermally thin solids \((\mu >> l, \mu >> l_\beta)\)

Using the approximations \( e^{-\beta l} \approx 0 \), \( e^{+\sigma l} \approx 1 \) and \(|r| >> 1\), we get

\[
Q \approx \left(1 - i\right) \left(\frac{\mu_b}{K_h}\right) Y
\]  

(2.7)

In this case, the signal is independent of \( \beta \). This would be the case for a very black absorber such as carbon black. The signal is quite strong, depends on the thermal properties of the backing material and varies as \( \omega^{-1} \).

Case (b): Thermally thick solids \((\mu < l, \mu > l_\beta)\)

Setting \( e^{-\beta l} \approx 0 \), \( e^{-\sigma l} \approx 0 \) and \(|r| > 1\),
\[ Q = \frac{(1-i)}{2a_t} \left( \frac{\mu_r}{K_r} \right) Y \]  
(2.8)

Eq. (2.8) is similar to Eq. (2.7), except that the thermal parameters of the backing material are now replaced by those of the sample. Here also, the signal is independent of \( \beta \) and varies as \( \omega^{-1} \).

**Case (c): Thermally thick solids (\( \mu << l_s, \mu < l_\beta \))**

Setting \( e^{-\beta l_s} \approx 0, e^{-\alpha l_s} \approx 0 \) and \( |r| < 1 \)

\[ Q \approx \frac{i\beta \mu_r}{2a_t} \left( \frac{\mu_r}{K_r} \right) Y \]  
(2.9)

This is a very interesting and important case because even though the sample is optically opaque, it is not photoacoustically opaque, as long as \( \mu < l_\beta \) i.e., acoustic signal is proportional to \( \beta \). The signal is also dependent on the thermal properties of the sample and varies as \( \omega^{-3\beta} \).

### 2.2.2 Thermal diffusivity measurement using photoacoustic technique

Thermal diffusivity is of direct importance in thermal transport properties as it determines the rate of periodic or transient heat propagation through a medium. It is defined as \( \alpha = \frac{K}{\rho c} \) where, \( K \), \( \rho \) and \( c \) are thermal conductivity, density and heat capacity of the medium. Two kinds of techniques have been commonly used to determine thermal diffusivity: Transient heat flow methods [13] and periodic heat flow methods [14]. In the transient heat flow method, an addition or removal of thermal energy from the sample induces a transitory temperature change and \( \alpha \) is
determined from a measurement of the temperature as a function of time at one or more points along the sample. In periodic heat flow methods, the thermal energy supplied to the sample is modulated at a fixed period. Consequently, the temperature at all points in the sample vary with the same period and \( \alpha \) is then determined from the amplitude and phase of the thermal wave in the sample.

The photoacoustic technique [7], which belongs to the periodic heat flow method, is an effective method for determining thermal parameters of various materials, when the PA signal is measured as a function of modulation frequency. The method enables one to measure indirectly, and with high sensitivity, the surface temperature of the sample by non-contact means. The PA technique has been used to measure the thermal diffusivities of a wide variety of samples [15-21].

One of the parameters which determines the amplitude of the PA signal is the thermal diffusion length \( \mu \) given by, \( \mu = \left( \frac{\alpha}{\pi f} \right)^{1/2} \), where \( \alpha \) is the thermal diffusivity of the sample and \( f \) is the modulation frequency. In the thermally thick regime (\( \mu_s < l_s \), where \( l_s \) is the sample thickness), the PA signal is independent of the thermal properties of the backing material on which the sample is mounted, where as in the thermally thin regime (\( \mu_s > l_s \)), the PA signal gets modified by the thermal properties of the backing material as well. For an appropriate sample thickness, one can obtain a cross over from a thermally thin regime to a thermally thick regime by increasing the modulation frequency. The amplitude versus modulation frequency plot then shows a change in slope at the characteristic frequency \( f_c \) at which the cross over takes place. According to R-G theory, the characteristic frequency \( f_c \) is related to the thermal diffusivity of the sample as,
\[ f_c = \frac{\alpha}{I_c^2} \]  \hspace{1cm} (2.10)

Once \( f_c \) is determined, thermal diffusivity can be obtained from Eq. (2.10) as,

\[ \alpha = f_c I_c^2 \]  \hspace{1cm} (2.11)

Thermal diffusivity \( \alpha \), although a derived characteristic of a substance, is of direct importance in heat flow studies as it determines the rate of periodic or transient heat propagation through the medium. It has got dimensions \((\text{length})^2 \text{(time)}^{-1}\).

We have used a modified PA phase lag technique [22] for the determination of thermal diffusivity in our experiments. In this technique, a single beam PA cell that can be rotated through 180° about a vertical axis is used. PA signal is measured with front and rear surface illuminations of the sample, one after the other. If \( \psi_F \) and \( \psi_R \) denote the PA signal phases during front surface and rear surface illuminations respectively, it can be shown that [22],

\[ \tan \Delta \psi = \tan(\psi_F - \psi_R) = \tanh(a/I_c)\tan(a/I_c) \]  \hspace{1cm} (2.12)

Thermal diffusivity can be calculated from the above expression using the relation,

\[ a = \left(\frac{\pi f}{\alpha}\right)^{1/3} \]  \hspace{1cm} . A schematic diagram of the experimental setup is shown in Fig. 2.2.

A He-Cd laser of wavelength 442 nm and intensity \( \approx 120 \text{ mW} \) is used as the source of light. A mechanical chopper (Model SR540) is used to modulate the light beam. An electret microphone is used to detect the acoustic signal, the output of which is fed to a dual phase lock-in amplifier (Model SR830). The advantage of this technique is that measurement at only a single modulation frequency is enough to determine thermal diffusivity.
2.3 Photopyroelectric Spectroscopy

Photothermal techniques have proved to be very useful in various fields such as spectroscopy, thermal characterization and non-destructive evaluation. Like the photoacoustic technique, the single beam photopyroelectric (PPE) technique is a well established photothermal method used for spectroscopic and thermal characterization of various materials as well as for studies of thermophysical properties of gases [23-31]. The basic principle of the single beam PPE technique is
that, when a periodically modulated energy from a source impinges on the surface of a sample, the sample absorbs some of the incident energy, and in turn, produces a localized temperature increase following a non-radiative deexcitation process. This periodic temperature variation in the sample can be directly detected with a pyroelectric transducer, which is in contact with the sample. The transducer is made of a thin film pyroelectric material [e.g. polyvinylidene difluoride (PVDF)]. The PPE signal from the pyroelectric transducer is due to a temperature dependent change in polarization of the pyroelectric material [23-25].

The PPE technique is the only photothermal technique based on the direct detection of photothermal heating, i.e., on the temperature changes. Therefore, it has a number of advantages over other detection schemes involving secondary mechanisms [32, 33], since each conversion step in the signal generation degrades the overall signal to noise ratio, sensitivity and band width performance and complicates the theoretical interpretation of results. A PPE experiment is rather simple to design and the specimen needs no special preparation. The materials that can be investigated range from weakly absorbing solids like thin films [24, 34-36] or liquids [37], semiconductors [38], surfaces and absorbates [32, 35, 39, 40] to strongly absorbing solids [41] and liquids [42, 43] or diffusing materials [23].

Mandelis and Zver in 1985 [30] put forward a one-dimensional analysis of the photopyroelectric model of a solid sample in intimate contact with a pyroelectric thin film, supported on a backing material. They were successful in deriving a general expression for the pyroelectric voltage developed in the detector due to light absorption in the sample. The calculations showed that the photopyroelectric voltage is governed by the interplay between the optical absorption in the sample and in the
pyroelectric transducer itself. These theoretical calculations helped to establish photopyroelectric spectroscopy as a valid spectroscopic technique with high promise in the realm of non-destructive probing of samples with minimal preparation. These features set this technique ahead of photoacoustic and photothermal deflection spectroscopies in certain respects.

In 1989, Chirtoc and Mihailiscu [27], generalized the theory by Mandelis and Zver, to understand the role played by finite reflectance at the sample pyroelectric interface and the mechanism responsible for the peak inversions observed in the reflection mode PPE spectroscopy [42, 44], since these questions have found no satisfactory answers in the framework of the former theory. It is seen that, the assumption of an arbitrary value for reflectance, completely changes the physical nature of the PPE effect, featuring simultaneous optical absorption and transmission characteristics. Also, it creates very diverse experimental opportunities for optical and thermal investigations of solid, liquid and gaseous substances.

Complete characterization of a material requires the determination of thermal transport properties such as thermal conductivity and heat capacity. Conventional techniques used to measure thermal conductivity include the well known steady state and transient methods. Comparatively large size samples, typically of size $5\text{mm}^3$ or higher are needed while using these techniques to avoid boundary effects. Moreover, large temperature rise often becomes necessary to obtain a reasonable signal-to-noise ratio, leading to considerable temperature gradient being setup in the sample. However, techniques for high resolution measurements of specific heat capacity are well established [45, 46].
It has been shown that the photothermal techniques allow the simultaneous measurement of specific heat capacity $c_p$ and thermal conductivity $K$. The photoacoustic technique has been used for the simultaneous determination of thermal diffusivity, thermal conductivity and heat capacity of liquid crystalline compounds [48], but some restrictions are imposed on this technique, because considerable complications arise in the design of the cell due to the presence of a coupling fluid. Marinelli et al. [47] were quite successful in developing a technique for determining thermal diffusivity, thermal conductivity and heat capacity simultaneously at low temperatures with the pyroelectric detector kept in vacuum. The boundary conditions involved in the theory of this method are not easy to satisfy at temperatures above room temperature. We have used a photopyroelectric technique for the simultaneous determination of thermal conductivity and heat capacity of samples in which the pyroelectric transducer is in contact with a thermally thick backing medium [49]. The advantage of a thermally thick backing medium is that there will be sufficient heat exchange between the heated pyroelectric detector and the backing so that, signal fluctuations can be reduced to a minimum.

2.3.1 Principle of the technique.

The PPE technique is based on the use of a pyroelectric transducer to detect the temperature rise due to periodic heating of a sample by induced light. A one-dimensional geometry as shown in Fig. 2.3 is assumed where $g$, $s$, $d$ and $b$ refer to the gas medium in front of the sample, the sample, the pyroelectric detector and the backing medium respectively. Since the observed signal output is affected by the
impedance of the detector and subsequent detection electronics, an equivalent circuit as shown in Fig. 2.4 is considered.

Fig. 2.3 One-dimensional geometry of PPE set up

$g$, $s$, $d$ and $b$ refer to the gas medium in front of the sample, the sample, the pyroelectric detector and the backing medium respectively.

Fig. 2.4 Equivalent circuit for (i) the pyroelectric transducer (ii) the copper backing and (iii) the detection electronics

Here, the pyroelectric detector is described as an ideal current source with a parallel leakage resistance $R_d$, with a capacitance $C_d$ supported on a backing having an equivalent parallel load resistance $R_b$ and capacitance $C_b$, while the detection electronics is represented by an input capacitance $C_e$ and a parallel load resistance.
For an optically opaque and thermally thick sample and pyroelectric detector, the expression for temperature dependent PPE amplitude and phase are given by [49]

\[
V(f,T) = \frac{I_0 \eta_s A R_s}{L_d \left[ 1 + \left( \frac{f}{f_c} \right)^2 \right]^{1/2}} \exp \left[ \frac{\pi f}{\alpha_s(T)} \right] \frac{P(T)}{\rho_d(T)e_{rs}(T)} \frac{e_s(T)}{e_d(T) + 1} \left( \frac{\pi f}{\alpha_s(T)} \right)^{1/2} L_s
\]

(2.13)

and

\[
\phi(f,T) = -\tan^{-1} \left( \frac{f}{f_c} \right) - \left( \frac{\pi f}{\alpha_s(T)} \right)^{1/2} L_s
\]

(2.14)

where

- \( I_0 \) = intensity of incident radiation
- \( \eta_s \) = non-radiative quantum efficiency
- \( A \) = area of the pyroelectric transducer
- \( R_d \) = resistance of the detector
- \( P(T) \) = pyroelectric coefficient of the detector
- \( \rho_d(T) \) = density of the detector
- \( C_{pd}(T) \) = heat capacity of the detector
- \( f_c \) = critical frequency = \( \frac{1}{2\pi RC} \), with

\[
\frac{1}{R} = \frac{1}{R_d} + \frac{1}{R_b} + \frac{1}{R_c} \quad \text{and} \quad C = C_d + C_c + C_b
\]

- \( f \) = modulation frequency
- \( \alpha_s(T) \) = thermal diffusivity of the sample
- \( e_s(T) \) = thermal effusivity of the sample
For a thermally thick sample ($\mu_s < L_s$) and a thermally thick pyroelectric detector ($\mu_d < L_d$) the expressions for the PPE phase and amplitude give formulae for the values of thermal diffusivity and thermal effusivity of the sample. This allows the determination of thermal conductivity and heat capacity of the sample, if the sample density is known. It is clear from Eqs. (2.13) and (2.14) that, thermal diffusivity $\alpha_s(T)$ of the sample can be calculated from the phase of the PPE signal, which when substituted into the expression for the PPE amplitude gives the thermal effusivity of the sample. Thermal conductivity and heat capacity of the sample can be calculated using the following relations.

$$K_s(T) = e_s(T)\left[\alpha_s(T)\right]^T_2$$  (2.15)

$$C_p(T) = \frac{e_s(T)}{\rho_s(T)\left[\alpha_s(T)\right]^T_2}$$  (2.16)

2.3.2 Measurement of thermal parameters

A schematic diagram of the PPE sample cell used for the measurements is shown in Fig. 2.5. A 120 mW He-Cd laser of $\lambda = 442$ nm is used as the optical heating source. A mechanical chopper (Model SR540) is used to modulate the light beam. A PVDF film of thickness 28 $\mu$m with pyroelectric coefficient $= 0.25 \times 10^{-8}$ V cm$^{-1}$ K$^{-1}$ at room temperature has been used as the pyroelectric detector. The room temperature values of the resistance and capacitance of the pyroelectric detector are 50 $\Omega$ and 750 pF respectively [50]. The sample is attached to the pyroelectric detector by means of a thermally very thin layer of a compound, whose contribution to the signal is negligible. The pyroelectric detector attached to the sample is placed on a thermally thick backing medium made up of copper, which satisfies the boundary
Fig. 2.5 Schematic diagram of the PPE cell

1. PVDF detector 2. sample 3. glass window 4. copper ring 5. teflon outer cover
condition \( b_{bd} > 1 \). The sample configuration for the PPE set up to measure thermal parameters is shown in Fig. 2.6. The frequency of modulation of light is kept above 30 Hz to ensure the thermal thickness of the sample, detector and backing medium. The signal output is measured using a dual phase lock-in amplifier (Model SR 830). A block diagram of the experimental set up is shown in Fig. 2.7.

Fig. 2.6 The sample configuration for the PPE setup

Fig. 2.7 Block diagram of the PPE set up
2.4. Photoc conductivity experiments

The basic requirements for a photoc conductivity set up include a radiation source of sufficient intensity in the required spectral range, a conductivity cell in which sample is mounted and irradiated with the light beam and necessary instruments to measure the signal produced.

A schematic diagram of the photoc conductivity cell used in our experiments is shown in Fig. 2.8. The cell consists of the following parts, (i) an outer chamber, (ii) a cylindrical tube which acts as liquid nitrogen reservoir for the purpose of making low temperature measurements and (iii) a sample holder. External electrical connections to the cell are provided through a port provided on the top plate of the chamber. This port is provided with four BNC connectors for connections from the sample, a D-type connector for taking the signal from the temperature sensor and another connector for heater supply.

2.4.1 Measurement of Photoc conductivity

Photoconductivity measurements can be carried out either by d.c. (steady state) method or by a.c. (pulsed excitation) method. For the present investigations, we have used the d.c. method. In this method, the dark current \( I_d \) and the current under steady state illumination \( I_{ill} \) are measured. The photocurrent is given by [51]

\[
I_{ph} = I_{ill} - I_d
\]  

(2.17)

Photoconductivity can be measured by either the two-probe method or the four-probe method, depending on the resistivity and geometry of the sample. If the samples have high resistivity, contact resistance can be neglected and two-probe technique can be used, provided the sample has a regular shape. We have used the
Fig. 2.8 A schematic diagram of the photoconductivity cell
(1) sample holder (2) heater (3) glass window (4) heater supply (5) connector for temperature sensor (6) liquid nitrogen reservoir (7) BNC connectors (8) connector to vacuum pump

two-probe method for our measurements and the block diagram of the experimental set up is shown in Fig. 2.9.

The samples are polished and shaped to exact square or rectangular shapes. The electrodes are connected either in coplanar or sandwich mode. In our measurements for bulk samples, the sandwich configuration has been used. The sample is sandwiched between two SnO₂ coated glass plates, which are conducting
Fig. 2.9 Block diagram of the experimental set up for photoconductivity measurements

and transparent. In this arrangement, the sample can be illuminated through one of the electrodes. The contacts are found to be ohmic from a study of the V-I characteristics of the contacts. A Keithly auto arranging pico ammeter (Model 485) is used for measuring current.

2.5 Electrical switching measurements

Basically, electrical switching measurement setup is more or less the same as that of electrical conductivity. The block diagram of the experimental set up is shown in Fig. 2.10.
In the case of switching studies, to get the $V$-$I$ characteristics, a known current is sent through the sample from a constant current source. The voltage developed across the sample is measured by a digital voltmeter. The $V$-$I$ characteristics are determined by varying the current values in steps. Though the current and voltage show a linear variation (ohmic behaviour) initially, for a particular value of current, the voltage across the sample attains a threshold value ($V_{th}$) and further increase in current results in a decrease of voltage and the sample deviates from the ohmic behaviour to a negative resistance region, which leads to a high conducting state.
2.5.1 Measurement of thermal parameters during electrical switching by PPE technique

A cross sectional view of the sample holder used to study thermal parameters during electrical switching is given in Fig. 2.11. The sample holder is made up of a copper rod having a diameter 5 cm.

Fig. 2.11 Cross sectional view of photopyroelectric cell for measurement of thermal parameters during electrical switching
A PVDF film of diameter 10 mm and thickness 28 μm, both side coated with Ni-Cr, supported on a copper backing acts as the PPE detector. The backing is mounted on an adjustable holder made of perspex. Samples of thickness ≈ 0.2 mm are mounted on the PVDF film using a thin layer of heat sink compound whose contribution to the signal is negligible. Electrical connections are taken between points 10 and 11 in Fig. 2.11. The sample can be illuminated through the top electrode, which is made of conducting glass. The pyroelectric voltage is measured between points 8 and 9 in Fig 2.11. Other measurement procedures are as already discussed in the previous sections.

2.6 Radiation Source

Incandescent or arc lamps and lasers are two popular types of light sources currently used for photothermal as well as photoconductivity experiments. The lamp monochromator combination can provide continuous tunability over a wide wavelength range from the infrared to the vacuum ultra violet. High pressure Xenon arc lamps, high pressure Hg lamps, tungsten lamps etc. are the commonly used incandescent sources. A major drawback of these sources is the relatively low bandwidth throughput product. A monochromator output power of 0.1mW is typical for 1nm resolution using a high pressure Xe arc lamp. Consequently, the lamp-monochromator combination is used with strongly absorbing samples or where low resolution suffices.

Lasers are widely accepted light sources in photothermal experiments, especially for measuring weak absorption. This is mainly because of their high
spectral radiance resulting from the extremely narrow line widths and high collimation. Because of spectral purity, lasers can be effectively used for high resolution PA spectroscopy experiments. One main drawback of lasers is their limited tunability.

2.7 Modulation

Modulation of the incident light beam is essential for the generation of photothermal signals. Either the amplitude or the frequency of the incident beam can be modulated, amplitude modulation being the more commonly used method. Amplitude modulation can be achieved by one of the several methods such as mechanical, electrical, electro-optic etc. One of the inexpensive, efficient and common methods to accomplish amplitude modulation is to use a mechanical chopper. The depth of modulation in this case is $\approx 100\%$. While using a mechanical chopper, care should be taken to minimize the vibration noise as this may interfere with the signal generated and cannot be filtered off even by lock-in detection. In the case of electrical CW lasers, modulation can be achieved by varying the discharge tube current. Electro-optic modulation involves changing the plane of an incoming polarized light beam in a non-linear crystal (e.g. KDP, ADP etc.) by the application of a modulated electric field across the crystal. Frequency modulation can be employed to eliminate the photothermal signals generated due to wavelength independent absorption at the cell windows. In dye lasers, rapid frequency change can be obtained by using an electro-optic tuner in place of a birefringent filter. Frequency modulation is well suited for narrow line width absorbers such as atomic and diatomic species.
2.8 UV-Vis-NIR Spectrophotometer

A UV-Vis-NIR spectrophotometer has been used to determine the optical band gap of samples under investigation. Hitachi model U-3410 double beam recording spectrophotometer has been employed for this purpose. It comprises of a monochromator section (including control section), display section, floppy disk section, graphics plotter and operating section. The system is equipped with various functions, which can be used in combination with a variety of optional accessories for all types of analytical applications and is especially suited for material characterization. This unit has a wavelength range 187 to 2600 nm with 0.07 nm resolution. The wavelength accuracy is 0.2 nm in the UV-Vis range and ±1 nm in the NIR range. The monochromator adopts the model 340 prism/grating double monochromatic system. The lenses used in the conventional monochromator have all been replaced by mirrors to eliminate image deviation due to chromatic aberration. The PbS detector converges the light beam with a toroidal mirror located below the photomultiplier. This permits placing the PbS symmetrically against the sample and reference beams whereby the two beams are completely balanced. A mechanical chopper is placed before the first monochromator to chop the light beam, which minimizes deviation in zero signal. The long life, easily replaceable iodine free tungsten lamp is used as the visible wavelength light source. The photometric output from the detector is fed through the preamplifier to an A/D converter and input into the computer, where it is discriminated into reference signal, sample signal and zero signal for storage by gate signals obtained in synchronization with rotation of the sector mirror for splitting the light beam. The reference signal is compared with a
predetermined standard value and used for controlling the voltage applied to the
dynode of the photomultiplier.

2.9 Sample preparation

As already stated in the previous chapter, there exists a number of techniques to
prepare amorphous materials. Since the amorphous phase is thermodynamically less
stable than the corresponding crystalline form, its preparation can be regarded as the
addition of excess free energy in some manner to the crystalline polymorph, which
can be done by faster rate of cooling.

The most common method for preparing bulk amorphous material is the melt
quenching technique. Amorphous materials produced in this manner are often been
termed as glasses. The distinguishing feature of the melt quenching process of
producing amorphous materials is that the amorphous solid is formed by continuous
hardening (i.e., increase in viscosity) of the melt. On the other hand, crystallization
of the melt occurs as a discontinuous solidification process. An essential prerequisite
for the glass formation from the melt is that the cooling be sufficiently fast to
preclude crystal nucleation and growth. The crystalline phase is thermodynamically
more stable and crystal growth will always dominate over the formation of
amorphous phase if allowed to take place. Cooling rate is often a critical factor in
determining glass formation.

The most usual way of producing samples of easy glass formers is to seal the
charge (1 to 10 g) in a fused silica or quartz ampoule under a good vacuum (∼ 10⁻⁶
Torr) and keep the ampoule in a rocking or rotating furnace at sufficiently elevated
temperatures so that the constituents become molten and can react. The rocking
motion ensures that a thorough mixing of the constituents takes place. The melt can be quenched either slowly by simply switching off the furnace, or more rapidly by plunging the ampoules into air or even more rapidly by bringing the ampoules immediately from the furnace into a liquid, preferably one with a high thermal conductivity and high latent heat of vapourization so that heat is conducted away from the sample as fast as possible without the formation of a thermally insulating vapour layer around the ampoule. In this manner, cooling rates of the order of $10^2$ to $10^3$ K/s are achievable. The parameters that are important in the melt quenching method are, (1) temperature of the furnace, (2) rate of cooling, (3) volume of the charge in the ampoule and (4) thickness of the wall of the ampoule. Materials produced in this manner are often in the form of a plug or a rod.

Chalcogenide glass samples for the present investigations have been prepared by the melt quenching technique. Appropriate quantities of the constituents are weighed and taken in quartz ampoules, which are then evacuated and sealed. The ampoules are then kept in a high temperature furnace and heated slowly to a temperature well above the melting points of the constituents. The ampoules are kept at that temperature for nearly 24 hours and then suddenly quenched to ice water. Then the ampoules are broken open to obtain the shiny glass samples. The amorphous nature of the samples is then confirmed by X-ray diffraction technique.
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