Chapter 2

Crystal growth and characterization

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2.1 Crystal growth

A material can be transformed into the form of a single crystal by slow and gradual transformation from melt, solution or vapor phase [50]. While a number of techniques adopting one of these three basic methods can be employed for growing small crystal samples, development of device quality crystal is quite a challenging task. Ultra small value of absorption coefficient and refractive index variation for laser applications, high radiation hardness and absence of non-radiative decay mechanism for scintillators, high resistivity and long carrier lifetime for semiconductor devices etc. are some of the criteria that needs to be complied, before a crystal can be used for the practical applications. The suitability of a particular technique for a given crystal is guided by material properties like thermal expansion, melt viscosity, thermal conductivities and chemical stabilities of melt/solid, requirement of size and quality etc. The flow chart of Fig. 2.1 gives an overview of various techniques commonly used for crystal growth. The pie chart of Fig. 2.2 shows relative share of (a) type and numbers of applications and (b) usage of basic growth methods among all types of crystals grown globally. Though 60% of the total numbers of crystals are semiconductor, majority being “Si”, demand for other applications is also substantial. Though melt techniques are applicable to only those materials which melt congruently without undergoing any structural transformations, it is globally most extensively used method [53, 54]. This pre-condition is met by Scheelites and feasibility of achieving high growth rates makes it most preferred choice. Among other melt techniques, Czochralski (CZ) technique is considered to be the most appropriate technique for the growth of tetragonal Scheelites having melting temperatures in the range of 900-1600°C [6].
2.2 Czochralski (CZ) Technique:

This technique was first developed by Jan Czochralski, a polish chemist, in 1918 [55]. Over the time many variations of this techniques like LECP method, High pressure CZ method, Verneuil,
TSSG etc. were evolved [54, 136]. Particular advantage of this technique lies in the convenience with which growth conditions viz temperature gradients, growth orientation and the ambient can be modified to suit requirements dictated by the material properties. As it is possible to observe the process of seeding and growth, corrective measures can also be taken in real time. These points make CZ as the most versatile and preferred technique for crystal growth.

In this technique, the starting charge, which could be pre-synthesized phase in powder form, or a stoichiometric mixture of constituents or polycrystalline chunks, is taken in a crucible and melted through inductive or resistive heating. The schematic of CZ growth is shown in Fig. 2.3. A seed crystal is slowly lowered and brought in contact with the melt at the center of the crucible. The melt temperature is so adjusted as to establish thermal equilibrium between the rotating seed and the melt. The seed is thereafter withdrawn (pulled) in a controlled way ensuring that pull rate is smaller or equal to the rate of melt crystallization establishing again a dynamic equilibrium between the two phases. As the seed is withdrawn its diameter is slowly increased to a desired value which is typically half of the crucible diameter. Thereafter efforts are made to maintain a constant diameter which renders cylindrical bottle like characteristic shape to the CZ grown crystals. These changes are generally effected by changing the melt temperature, though pull rates are also modulated in some cases. When the desired length of the crystal is achieved, the growth is terminated by snapping off the crystal /melt interface either through rapid lifting or by raising the melt temperature. After the detachment, it is retained close to the melt surface and cooled down to the room temperature in the same growth chamber in most cases.
2.2.1 Fundamental consideration for growth

The selection of parameters for CZ growth depends upon the (a) thermal conductivity of both solid and liquid phases, (b) anisotropy in thermal expansion (c) melt viscosity and its chemical properties (d) difference in solubilities of dopant in liquid and solid phases (e) melt microstructure, (f) dimensional and quality requirement etc.

As the growth proceeds, the shape of solid/melt interface which could be flat, convex or concave as shown in Fig. 2.4 also changes. This shape determines the stability of growth process and it also has deterministic effect on strain and dislocation in growing crystals. Ideally solid melt interface should be flat for crystal homogeneity and minimal thermal stress but in practice it rarely occurs. For stable growth the interface shape should be slightly convex towards the melt as shown in Fig. 2.4 a [137]. The growing crystal can get detached from the melt unpredictably if the interface shape is either flat or concave.
Fig. 2.4: Schematics of crystal/melt interface shape during CZ growth (a) convex, (b) concave and (c) flat.

The shape of the interface is governed by heat flow pattern established due to temperature gradients, crystal rotation and pulling rates besides density, viscosity and conductivity of the melt. Fig. 2.5 shows various possible heat flow paths that can exist during CZ growth [138]. Contribution of each of these paths is a complex function of both radial and axial gradients which can also be modified by changing dimension and material of seed holder, seed and crystal diameters, growth station geometry and ambient gas flow and pressure [139-144]. For stable growth, heat from melt (H_L) and the latent heat of crystallization (H_F) need to be conducted through the growing crystal i.e. H_S = (H_L + H_F). The heat balance equation at the growth interface can be therefore written as

$$\Delta H_s f \rho_s = k_s \left( \frac{dT}{dx} \right)_s - k_i \left( \frac{dT}{dx} \right)_i$$  \hspace{1cm} (2.1)
where $k_s$ and $k_l$ are thermal conductivities of solid and liquid phases respectively. $(dT/dx)_s$ and $(dT/dx)_l$ are gradients inside the solid and in melt, $\rho_s$ is density of solid, $f$ is growth rate and $\Delta H_v$ is latent heat of crystallization per unit volume.

Fig. 2.5: Heat flow and convective currents during a Czochralski growth process.

The growth rate is a function of the crystal ($D_s$) and crucible ($D_c$) diameters and the densities in the molten ($\rho_m$) and solid ($\rho_s$) states. Net growth rate $f$ (gm/h) that can be achieved for a crystal pull rate of $P$ (mm/h) is given by Eq. 2.2.

$$f = \frac{P}{1 - \left( \frac{\rho_s}{\rho_m} \right) \left( \frac{D_s}{D_c} \right)^2}$$  \hspace{1cm} (2.2)

The upper limit for the growth rate is determined by (i) thermoelastic properties of the crystal, (ii) segregation of dopant/impurity ions at the growth interface and their diffusion to the bulk, (iii) ease with which defects can be generated during growth etc. Materials having high thermal
conductivity and Burger vector can be pulled at relatively faster rates, provided segregation effects are not the limiting factor. The upper limit for the pull rate in this case is decided by the temperature gradient that can be maintained above the solid-melt interface.

The maximum acceptable axial temperature gradient can be found out by Eq. 2.3 [140].

$$\frac{dT}{dx}_{\text{max}} = \left[ \frac{4 \varepsilon / \alpha}{a^{3/2}} \right] \left[ h \right]^{1/2} \left[ 1 - 0.5ha \right]$$

(2.3)

where \(a\) is the radius of crystal and \(h\) is the ratio of heat loss per unit time from unit surface area of the crystal when it is one degree above ambient temperature. \(\varepsilon\) is the breaking strain and \(\alpha\) is thermal expansion coefficient. The value of maximum axial temperature gradient depends on radius and breaking strain of the crystal. If the breaking strain is smaller than elastic strain, then under the conditions of large axial temperature gradient the crystal cracks. Crystal cracking during growth or annealing is quite common in optical materials. In several cases this has been traced to small value of thermal conductivity and anisotropic thermal expansion. Hence, for the successful crystal growth it is important to have an idea about thermal expansion along different crystallographic directions. To grow crack-free crystal, the growth should be carried out along the axis that has smaller expansion coefficient and under axial gradient not exceeding the value obtained from Eq. 2.3. In actual crystal growth, seed and crucible rotation can change the temperature distribution which in turn affects the perfection of crystal and facets area [142]. The rate at which the grown crystal must be cooled without developing any cracks is inversely proportional to the crystal diameter and this dependence is given by Eq. 2.4 [141].

$$\frac{dT}{dt}_{\text{max}} = k \varepsilon / \alpha a^2$$

(2.4)
This value depends on the crystal diameter which is controlled by the combination of melt temperature and pull rate of the crystal.

2.2.2 Crystal growth system

The schematics of CZ growth as mentioned in Fig. 2.3 is in practice realized through the use of a system called “CZ crystal puller” which consists of the following components.

1. A power supply to melt the material and maintain high temperature through either induction heating of the crucible or joule heating.

2. A crucible to contain the molten material. Thick walled crucibles of platinum (Pt)/iridium (Ir)/graphite also act as heat susceptor in case of induction heating.

3. The growth chamber with an opening at the top allowing entry of the pull rod along with seed crystal connected through a seed holder also has a viewing port for monitoring crystal melt interface. The chamber also provides (a) housing the crucible, (b) thermal shields required for adjusting temperature gradients and (c) controlled ambient

4. Mechanism for pulling, rotation and crystal weighing, which is used as input for diameter control.

5. Electronic/Computer controlled system for maintaining the crystal diameter through adjustment of heater power/furnace temperature in case of resistance heater[144].

Schematic of a typical CZ puller system is shown in Fig. 2.6 and the photograph of an automatic diameter controlled crystal puller system Model: Oxypuller, Cyberstar, France used for the present work is given in Fig. 2.7. This system employed 50 kW and 8-20 kHz induction supply, a weighing head of 20 kg capacity with an accuracy of 1 mg to monitor total crystal translation of 600 mm with positioning accuracy of 0.01 mm.
Fig. 2.6: Schematic of a typical CZ puller system

Fig. 2.7: Photograph of the Crystal puller system [Oxypuller: Cyberstar]
The feedback for heater power control, called the error signal was generated based on the difference between the mass growth rates calculated as per the input parameters and value measured in real time. A flat bottom Pt crucible of 50 mm diameter and 50 mm length and 2 mm wall thickness was used as susceptor of heat for melting of the starting charge. The crucible was surrounded by thermal shield made up of ceramic cylinders and fibrous zirconia wool. In different growth experiments the temperature gradient in the growth zone could be adjusted in the range of 20°C/cm to 80°C/cm by changing the arrangements of thermal shields and also by suitable adjustment of the crucible position with respect to the induction coil [145]. Starting charge for growth was taken in the form of either (a) pre-synthesized powder of desired phase, (b) stoichiometric mixture of constituents oxides for in situ formation of desired phase or (c) crystalline chunks from transparent portions of the material once crystallized. The input parameters for PC control are diameters and heights of the seed, shoulder, cylindrical and tail portions, densities of crystal and the melt, pull rate, rotation rate and translation height for crystal detachment. Accurate system control also required inputs on proportion and integration term as governed by thermal inertia of the hot zone and temperature oscillation occurring in the melt which in turn depend on the material properties.

The starting charge is first melted by ramping up the heater power, allowed to stabilize close to its melting point and a seed crystal connected to an alumina pull rod through a platinum (Pt) seed holder is brought in contact with the melt. The heater power is adjusted to attain no growth or melting state by monitoring weight signal. This process called seeding is one of the most critical factors in CZ growth. Crystal pulling is first initiated in manual control mode and dynamic equilibrium is again established to match the mass growth rate with preset value of growth rate calculated from dimensional data fed to the controls. The system is put into automatic control
mode only when the difference between the measured and the pre-set values of growth rates, called the error signal is close to zero. Fig. 2.8 shows the changes in power, weight, length and growth rate during a typical growth experiment.

Fig. 2.8: The changes in power, weight, growth rate and length with time during growth of NBW crystal shown in the inset. Different regions marked in the time scale correspond to the regions where (a) seed, (b) shoulder, (c) parallel and (d) tail regions of the crystal.
Table 2.1: Typical parameters used in growth of 20 mm diameter crystals

<table>
<thead>
<tr>
<th>Crystal</th>
<th>PbMoO₄</th>
<th>BaWO₄</th>
<th>NaBi(WO₄)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point</td>
<td>1064 °C</td>
<td>1475 °C</td>
<td>950 °C</td>
</tr>
<tr>
<td>Rotation</td>
<td>20 rpm</td>
<td>15 rpm</td>
<td>15 rpm</td>
</tr>
<tr>
<td>Pull rate</td>
<td>2 mm/h</td>
<td>3 mm/h</td>
<td>2 mm/h</td>
</tr>
<tr>
<td>Gradient</td>
<td>30°/cm</td>
<td>75°/cm</td>
<td>60°/cm</td>
</tr>
<tr>
<td>Ambient</td>
<td>Atm &amp; Argon flow</td>
<td>Normal Atmosphere</td>
<td>Normal Atmosphere</td>
</tr>
</tbody>
</table>

2.3 Characterization

2.3.1 Melting Behavior

Preliminary examinations of phase formation, its melting/solidification behavior were studied by Differential thermal analysis (DTA) experiments. DTA is a thermoanalytic technique where temperature dependence of material properties are studied [146]. In a DTA system two identical crucibles with sample in one and a reference (empty crucible) in the second are placed in a furnace in close proximity with a thermocouple located beneath each of them as shown in the schematics of Fig. 2.9. The furnace is heated with a uniform rate and differences between the temperatures of the two crucibles are measured as a function of time. This temperature difference indicates endothermic/exothermic reaction or phase change and its magnitude occurring in sample. The system is first calibrated for enthalpy by measuring peak areas on standard samples over specified temperature ranges.
Fig. 2.9: A schematic of differential thermal analysis technique (DTA)

The information that can be inferred by analyzing the shape of DTA pattern for a material from binary system are shown in Fig. 2.10.

Fig. 2.10: Representation of a DTA curve obtained for various compositions in a binary systems. [Reproduced from book “Differential thermal analysis” by R.C. Mackenzie, Academic press (1972)].

The DTA pattern of a sample provides information about (i) melting/freezing temperatures, (ii) heat of crystallization and (iii) crystalline/glassy nature of a given material. In case of multicomponent system large numbers of peaks are observed and its careful analysis can provide valuable information about its phase diagram. DTA pattern that is expected for different composition in a binary system is shown in Fig. 2.10. The DTA of a congruently melting compound D would be a single sharp peak as shown at location ‘2’ of Fig. 2.10. Presence of
multiple peaks indicates presence of more number of phases. The DTA measurements for the present work were carried out on SETARAM model TGA-92.

2.3.2 Structure

Identification of the phase formed during material synthesis and calculation of structural parameters of the crystal were done through the analysis of X-ray powder diffraction pattern (XRD). For such measurements the wavelength of X-rays should be of the same order of magnitude as the distances between atoms or ions in a molecule or crystal (Å, $10^{-10}$ m). The fundamental of these measurements lie in constructive interference of X-ray beam diffracted from different layers of crystalline solid as shown schematically in Fig. 2.11. The atoms in a crystal are arranged in a regular pattern such that constructive interference between two reflected rays occurs only for certain incident angles of the X-ray beam for which Bragg’s condition is satisfied [147].

$2d \sin \theta = n \lambda$

Fig. 2.11: Bragg law  Fig. 2.12: Schematic of X-ray powder diffractometer.
The XRD is used for the determination of crystal structure, grain size, texture and residual stress of materials and compounds. The scattered X-ray intensity is proportional to the square of the Fourier transform of the charge density:

\[
I(q) \propto \left| \int d^3r \ e^{i\mathbf{q}\cdot\mathbf{r}} \rho(\mathbf{r}) \right|^2
\]

(2.5)

where \( \rho \) is the charge density. As X-rays are predominantly diffracted by electron density clouds, analysis of the diffraction angles can be used to produce an electron density map of a given crystal or crystalline structure.

Fig. 2.13: XRD patterns of a single crystal, imperfect crystal and for glasses

For perfect crystals, \( I(q) \) consist of delta functions while for imperfect crystals, the peaks are broadened. Strains, defects, finite size effects and instrumental resolution cause broadening in diffraction peaks. For liquids and glasses \( I(q) \) is a continuous and slowly varying function. XRD patterns of a single crystal, imperfect crystal and for glasses are shown in Fig.2.13. Various informations that can be derived from the powder pattern is shown in the flow chart of Fig. 2.14 [149].
Fig. 2.14: Schematics of the information which one can be obtained from XRD pattern [149].

Typical divergence of X-ray beam in powder XRD instrument is of the order of 500 arc seconds, whereas the actual spread of the diffraction peak of a good crystal is just a few arc seconds. The measurements of true diffraction peak width of a single crystal, therefore requires high resolution XRD (HR-XRD) where the divergence and wavelength spread of incident and diffracted X-ray beam is limited through Beam conditioners (comprising of crystal monochromators and slits) to get collimated and monochromatic beam. Movement in different directions, tilt and rotation of sample stage help in precise placement of sample. Fig. 2.15 shows a schematic diagram of a triple-axis HRXRD instrument. Structural perfection of a single crystal can be determined by recording the rocking curve where a well collimated X-ray beam incident on the crystallographic plane of the sample being rocked by just few degree. Spread of the peak recorded for the diffracted beam is a measure of the degree of strain in the lattice.
While large number of peaks are observed for powder samples, for single crystal single peak corresponding to the particular crystallographic plane and higher harmonics of the diffracted beam are observed. A typical X-ray powder diffraction system mainly consists of X-ray generator, goniometer, sample holder, and X-ray detector as shown in Fig. 2.12 [148]. The schematics of the Rigaku powder X-Ray diffractometer Model-RINT 2000 is shown in Fig. 2.12. The XRD pattern was recorded by employing Cu K\(\alpha\) line (\(\lambda = 1.54056 \text{ Å}\)) and scanning with a step size of 0.02°. Samples for measurements were prepared by crushing the transparent crystal chunks into ~10μm particles.

2.3.3 Orientation

**Back-Reflection Laue Technique** was used for orienting the crystals where the symmetry of a projection was determined from Laue grams.
Fig. 2.16 shows the diagram for back-reflection laue experiments. One side of the cone of Laue reflections is defined by the transmitted beam. The film intersects the cone, with the diffraction spots generally lying on a hyperbola which are seen to lie on curves in the film. The Bragg angle is fixed for every set of planes in the crystal. Each set of planes picks out and diffracts the particular wavelength from the white radiation that satisfies the Bragg law for the values of d and q involved. Each curve therefore corresponds to a different wavelength. The spots lying on any one curve are reflections from planes belonging to one zone. Laue reflections from planes of the same zone all lie on the surface of an imaginary cone whose axis is the zone axis. Beam which are diffracted in a backward direction are recorded on a film placed between the x-ray source and the crystal in the back-reflection method [150].

Quick orientation of optical crystals is however carried out by Conoscopic interference technique [151] which is based on optical birefringence exhibited due to anisotropic refractive indices. When linearly polarized light is incident on such a crystal at an angle to the optic axis, it effectively decomposes into two mutually orthogonal components.

![Conoscopic interference patterns for a uniaxial crystal](image)
These components then travel through crystal at different phase velocities and the emerging light is elliptically polarized, which gives information about the optic axis when analyzed through another polarizer. Using a cone of incident light, the resulting interference fringes, which are characteristic of the crystal type, its crystal orientation, and sample thickness, can be examined. Fig. 2.17 shows the schematics of a conoscopic interference technique.

2.3.4 Optical transmission

Optical transmission/absorption measurements were carried out on a spectrophotometer which measures the fraction of incident light transmitted/ absorbed through a sample [152]. The ratio of the intensity of light passing through a sample (I), to the intensity of light before it passes through the sample (I₀) is called the transmittance, and is usually expressed as a percentage (%T). The absorbance, A, is based on the transmittance as

\[ A = - \log(\%T / 100) \]  

(2.6)

The schematic diagram of a double beam UV/VIS spectrophotometer (model: Techcomp 8500) is shown in Fig. 2.18. Here the light is split into two beams before it reaches the sample. One beam is used as the reference and the other beam passes through the sample. Two separate detectors (photodiodes) are used for the measurement of light passing through the sample and the reference. Usually two lamps, one deuterium lamp for UV and second tungsten lamp for VIS/NIR, are used. Photomultiplier is used for UV/VIS (range 190-850nm) and Cooled PbS detector is used for NIR (range 800-2500nm).
Fig. 2.19 shows typical absorption spectra where region “a” is due to high lying energy levels. Part “b” shows the absorption peaks due to exciton and “c” shows the fundamental absorption with urbach tail. Any impurity causes the absorption in “d” region while “e” shows free carrier absorption. The value and nature of the band gap can be measured by applying power law equation $\alpha = A_k(E-E_g)^n$ to crystal transmission data obtained near the absorption edge.

The measurements were carried out in the wavelength range of 200 to 800 nm and samples were taken in the form of 2 mm thick slices prepared from the transverse section of the ingot. Reflectivity spectra were recorded using integrating sphere and reflectivity attachment.

2.3.5 Luminescence

Luminescence is the phenomenon in which absorption of light of a given wavelength by a molecule is followed by the emission of light at longer wavelengths [153]. Different type of transitions that can occur between ground and excited states are shown in Fig. 2.20. Emission spectrum is the distribution of wavelength-dependent intensity of emitted energy while the
distribution of wavelength-dependent intensity that causes luminescence is known as the luminescence excitation spectrum. The electronic structure and dynamics of an excited state of a molecule may be elucidated from luminescence as it is a property related to the difference between two electronic states, viz. the emitting state and the ground state. The difference in the timing between the absorption of the higher energy photon and emission of secondary photon of lower energy re-emitted is defined by the luminescence decay time or the lifetime of excitation states. Decay time can vary many orders of magnitude for different materials. Based on practical observations of persistence of two types PL was historically called fluorescence for life times shorter than 100µs and much longer lasting up to a few hours and even days is called phosphorescence.

The schematic of Edinburgh fluorescence spectrometer model FLP 920 shown in Fig.2.21 [154] consists of monochromator, sample chamber, emission monochromator and detector. Two types of excitation source viz Xe or H₂ filled flash lamps were used for recording life times in the range of µs and ns respectively. The lamp produces a broad spectrum of high intensity radiation through the UV-Vis-NIR range which is imaged onto the entrance slit of the excitation monochromator. A specific excitation wavelength with a specific bandwidth is selected by the monochromator and passed from an iris (so that the intensity can be controlled) and then focused onto the sample. A portion of any luminescence from the sample is collected by a lens system and focused onto the emission monochromator. The emission monochromator selects a wavelength and spectral bandwidth of this emission and the light is passed into a photomultiplier tube (PMT) for emission in UV-VIS range or into an InGaAs detector for emissions in the near IR region.
The lifetime measurement in this system is based on **Time Correlated Single Photon Counting (TCSPC)** technique [154]. The schematic of this technique is shown in Fig.2.22. TCSPC measures single photons – namely, detection at the quantum limit. The technique requires an excitation source with high repetitive pulse output. The method makes use of the fact that for low level, high repetition rate signals the light intensity is usually so low that the probability to detect one photon in one signal period is much less than one. As the process of capturing a single photon is repeated several thousand or even million times per second, a sufficiently high number of single photons are processed for the resulting fluorescence lifetime measurement. The TCSPC electronics can be compared to a fast stopwatch with two inputs. The clock is started by the START signal pulse and stopped by the STOP signal pulse.
Fig.2.21: The schematic diagram of fluorescence spectrometer FL920.

The time measured for one START – STOP sequence will be represented by an increase of a memory value in a histogram, in which the channels on the x-axis represent the time. With a high repetitive light source millions of START – STOP sequences can be measured in a short time. The resulting histogram counts versus channels will represent the fluorescence intensity versus time.

Photoluminescence (PL) studies were performed over wavelength range of 300–800 nm and temperature range of 77–300K, employing Edinburg fluorescence spectrometer Model FLP920. The emission was recorded in the reflection geometry by positioning the samples at an angle of 45° to the excitation beam.
For measurements in the spectral domain, a 150 W Xe arc lamp was used as the excitation source and a spectral bandwidth of 1 nm was selected for both excitation and emission monochromators. A hydrogen gas filled flash lamp operating at a repetition rate of 40 kHz was employed for recording the temporal behavior of the luminescence decay. Measurements at low-temperature were carried out by placing the sample in Oxford Cryostat Model Optistat DN. The recorded luminescence spectra were corrected for spectral sensitivity function of the instrument. The correction file was prepared by recording the spectra under identical conditions after replacing the sample by a scatterer. The luminescence measurements were also repeated with cleaved samples to rule out the effects of any surface contamination arising due to polishing. The details of the luminescence mechanism as well as instrument used to measure photoluminescence are given below.

**Thermally stimulated luminescence (TSL)** studies were carried out to probe the defect/ trap structure of the material. In certain materials charge carriers are trapped as a consequence of exposure to very high energy radiation. These trapped centers which arise due to localized defects, or imperfections are stationary states that have no formal time dependence though they are not stable energetically. Heating enables the trapped states to interact with phonons, i.e.
lattice vibrations, to rapidly decay into lower-energy states, causing the emission of photons in the process which is called thermoluminescence [155]. These metastable states or traps occur at different levels in the forbidden band gap that originate from crystal defects. Light is emitted over a range of temperature depending on this activation energy “E” of the trap depth. If E >> several kT (where k is Boltzman’s constant), the trapped charge can remain in the trap for a longer period. The amount of luminescence is proportional to the original dose of radiation received. The TSL glow curve (intensity vs temperature) of small quantities of sample weighing a few mg was recorded in the temperature range of 50 – 200°C employing a linear heating rate of 1K/s. The schematic of TSL setup is shown in Fig. 2.23. A photomultiplier tube with a GaAs photo cathode having almost flat response in the range from 300 nm to 800 nm was used for recording the TSL. The TSL spectra were recorded by quick scanning the monochromator once over the 200 to 700 nm while maintaining the sample temperature just below the rate of glow peak position.

Fig. 2.23: A typical setup for recording thermoluminescence
2.3.6 Composition

The compositional analysis and measurement of trace impurities of grown crystals/materials were carried out by X-ray fluorescence spectrometry (XRF), X-ray photoelectron spectroscopy (XPS), atomic absorption spectrometry (AAS) and Inductively coupled plasma emission spectrometry (ICPAES).

X-ray fluorescence spectrometry (XRF) is one of the most efficient techniques to measure the elemental composition by detecting the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays [156]. Qualitative and quantitative results can be obtained for all elements from beryllium (atomic number 4) to uranium (atomic number 92) and beyond (at trace levels) with a parts per million (ppm) limit by the Panalytical 2400 XRF system. The samples used for this study were taken in the form of a glass bead prepared by diluting the material in a Li₂B₄O₇ matrix.

X-ray photoelectron spectroscopy (XPS) analysis of a few samples was carried out at RRCAT, Indore. XPS spectra obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of photo electrons that escape from the top 1 to 10 nm of the material being analyzed. Elemental composition, the chemical and electronic state elements can be obtained from the XPS spectra [157].

In Atomic absorption spectroscopy (AAS) the electrons of the atoms in the atomizer can be promoted to higher orbitals for a short amount of time by absorbing a set quantity of energy which is specific to a particular electron transition in a particular element, and in general, each
wavelength corresponds to only one element [158]. The technique is useful only for trace analysis.

**Inductively coupled plasma atomic emission spectroscopy (ICPAES)** is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element [159]. The intensity of this emission is indicative of the concentration of the element within the sample.

For AAS and ICPAES measurements the samples were required in the form of dilute solutions. Though both the techniques were used for impurity analysis, the results were only qualitative. This is because of poor solubility of oxide crystals and precipitation of solute on dilution.