CHAPTER 2

METHODS FOR SAMPLE PREPARATION,
CHARACTERIZATION TOOLS AND
INSTRUMENTATION

2.1 INTRODUCTION

This chapter gives a description of the methods employed for the synthesis of the phosphors, the characterization techniques and the instruments used to investigate the properties of the materials used in this study in detail. Although, there is a broad range of phosphors, but the current work is restricted to the study of phosphate based phosphors doped with rare earth ions (K$_3$Gd(PO$_4$)$_2$:Sm$^{3+}$, K$_3$Y(PO$_4$)$_2$:Eu$^{3+}$, K$_3$Gd(PO$_4$)$_2$:Tb$^{3+}$, K$_3$Gd(PO$_4$)$_2$:Eu$^{3+}$, K$_3$La(PO$_4$)$_2$:Eu$^{3+}$). The phosphor materials were synthesized by solid state, combustion and citrate gel combustion methods. The crystal structure and phases of the samples were identified by using PXRD. The morphological information of the samples was obtained from SEM and TEM. The luminescence properties were studied by using spectroscopic techniques PL and TL and the optical and surface properties was studied by using DRS and XPS.

2.2 PREPARATION OF SAMPLES

Due to their great potential in various applications such as in devices and luminous paints on highways, airports, in textiles materials, etc., phosphors have been commonly studied [1, 2]. The efficiency of phosphors, not only depends upon activator ions and host material used but strongly depends on the synthesis method used. The different methods used to synthesize phosphors are categorized in figure 2.1. For preparing the samples in the present study, Solid State Method, Combustion Method and Citrate Gel Combustion Method are used. A brief account of the methods used is given below:
2.2.1 SOLID STATE METHOD

A solid-state reaction is commonly employed to synthesize the phosphors in bulk form, from the mixture of solids as starting materials. This method involves heating metal oxides or carbonates at eminent temperature for a prolonged time in order to bring the reactions as solids do not react together at room temperature. In order to complete the reaction on time without melting the constituents the temperature is maintained. The aspects in which the probability and the rate of a solid state reaction consists of being the reaction condition, structural properties of reactants, surface area of the solids, their reactivity and thermodynamic free energy change associated with the reaction. In the absence of the solvents, solid state reaction allows the reactants to chemically react. In solid state method, reaction time and the temperature bear a reciprocal relation. Figure 2.2 shows the flow chart for the solid state synthesis used in the present study.
Figure 2.2: Flow chart for solid state synthesis.

In the solid state method, the stoichiometric proportions of the raw materials (carbonates/oxides) that constitute the host material and the dopant activators are grounded thoroughly and fired at high temperatures (800–1500°C) in air or in a controlled atmosphere (N₂, C, CO, or N₂ with 2-5% of H₂). In this method, repeated grinding and heating is required. In general, the purity of starting materials is high in order to minimize the formation of secondary phases. By solid solution, the formation of doped phosphor is critical and is highly dependent on the reaction temperature and calcination conditions such as firing temperature, duration of firing, firing atmosphere. The rate of heating and cooling for a particular phosphor are optimized empirically. The morphology (particle size and shape) of the final product is related to the morphology of starting chemicals and flux of reaction.

Solid state method has the only advantage that the precursors are readily accessible, however the method suffers from many disadvantages, i.e., formation of the final product as inhomogeneous, formation of large particles (in micrometer range) with low surface area, and hence mechanical particle size reduction is required, which
introduces impurity and defects and the presence of defects, which are harmful to the luminescence.

2.2.2 COMBUSTION METHOD

To overcome the drawbacks of the solid state synthesis, a common alternative synthetic route (combustion synthesis) is used (Zhang et al., 2008; Sharma et al., 2008; Peng et al., 2004; Luitel et al., 2009). This method does not require further calcinations and repeated heating. Combustion synthesis is a novel technique used for the synthesis of nanophosphors and received great attention in the past few years. In 1988, this method was accidentally discovered in Prof. Patil’s Laboratory in India (Ekambaram et al., 2005). Using this method Prof. Patil synthesized fine particles of α-alumina and related oxide materials in his laboratory (Patil, 2008). Combustion synthesis is also known as self-propagating high temperature synthesis. This is an effective, low-cost method for the production of homogeneous, very fine agglomerated powders without intermediate decomposition and calcination steps (Fumo et al., 1996; Shea et al., 1996). Owing to its ability to generate fine size of particles without high temperature annealing and extra steps such as grinding or milling, combustion synthesis is a promising technique for phosphor particle preparation.

Figure 2.3: Flowchart for combustion synthesis
When the mixture of fuel and oxidizer are ignited a highly exothermic reaction occurs between the metal nitrate (oxidizer) and fuel with the evolution of heat and light. In combustion synthesis, the common fuels used are urea (CH$_4$N$_2$O), carbohydrazide (CH$_4$N$_4$O), oxalyl dihydrazide (C$_2$H$_6$N$_4$O$_2$), glycine (C$_2$H$_5$NO$_2$), diformyl hydrazine (C$_2$H$_4$N$_2$O$_2$) etc. and the nitrate salts are preferred as oxidizer because they serve as water-soluble low temperature nitrogen source.

In combustion method, the stoichiometric ratio of precursor materials typically metal nitrates (oxidizers) and a suitable organic fuel (reducer) are calculated based upon propellant chemistry. At a certain temperature, when the reaction is started, the mixture which is induced to boil undergoes dehydration, ignites and burns to yield a voluminous foamy and homogeneous product that requires grinding to obtain a powdered product. The entire reaction takes few minutes to form the final product. The flow chart of the procedure used for phosphor preparation by combustion method is given in Figure 2.3. Thus, combustion synthesis proves to be a flexible, simple, quick and straightforward process for the synthesis of a range of nanosized materials. This method provides high purity, high crystallinity and high homogeneity even at low firing temperature. This method not only produces nanosize oxide materials, but also allows for uniform (homogeneous) doping of the host lattice with the activator ions. The peak reaction temperature depends on the fuel and the oxidizer molar ratio (fuel/oxidizer).

### 2.2.3 CITRATE GEL COMBUSTION METHOD

The citrate gel combustion method was developed by Marcilly & co-workers in 1970 (Marcilly et al., 1970). This method is one of the new methods for the synthesis of nanomaterials (Chu et al., 2000). The gel combustion technique involves a mixture of reagents which transforms to the oxides easily (such as nitrates) and a fuel (citric acid) which acts as a reagent reducer. The method is actually self-sustainable after the reaction has initiated and, owing to the exothermic characteristic of the reaction, high temperatures guarantee the crystallization and formation nanomaterials in a short period of time. This prevents the agglomeration of particles being formed instantaneously (Peng et al., 2004).
The citrate gel method is a versatile method for synthesis of multicomponent oxides. In this method, the analytical grade metal nitrates and citric acid are dissolved in a minimum quantity of deionized water. The mixed solution is heated to 80°C on a hot plate with continuous stirring. During evaporation, the solution became viscous and finally formed a very viscous gel. With further heating the viscous gel began frothing. The gel is placed in the preheated furnace at 600°C–700°C. After a few minutes, the gel automatically ignited and burnt with glowing flints. The auto ignition is completed within a minute, yielding the black-colored ash termed as a precursor. The as-prepared powders of the samples were heated separately at 800°C to get the final product. Figure 2.4 shows the flow chart for citrate gel combustion synthesis. The advantages of these methods are the ability to produce complex compositions, good homogeneity through mixing at the molecular level in the solution and control of the stoichiometry. Low firing temperatures are required for the decomposition of the resin to the oxide.

2.3 CHARACTERIZATION TOOLS
To assure that the appropriate materials with suitable properties are synthesized a variety of characterization techniques are used. Brief discussions of the instruments utilized for the characterization of synthesized materials in the present study are given below:
2.3.1 POWDER X-RAY DIFFRACTION

German physicist W.C. Roentgen in 1895, discovered invisible rays which are known as X-rays. These rays affect photographic film similar to that of light, but more penetrating than light. It was in 1912, when German physicist Van Laue established the wave like nature of X-rays. In the same year, two English physicists W.H. Bragg and his son W.L. Bragg successfully analyzed the same experiment and derived the conditions for diffraction from a 3d-periodic arrangement of atoms. The X-rays are electromagnetic radiation and lay in between gamma and ultraviolet rays and thus having wavelengths in the range of 0.5-2.5 Å.

Powder X-ray diffraction (PXD) is a popular and versatile non-destructive technique employed for the identification of structural properties of the crystalline materials. This technique is also used for the identification of the phases, determination of crystallite size, lattice constants of a material. The term 'powder' really means that the crystalline grains are randomly oriented in the material and the material is in powder form. The X-ray diffractometer consists of three basic elements: an X-ray source, a sample holder, and an X-ray detector (Figure 2.5). The X-rays are produced in a cathode ray tube by heating a filament to produce electrons, which are then accelerated towards a target by applying a voltage.

![Figure 2.5: The Powder X-ray diffraction system.](image)

The X-ray diffraction can be explained in simple terms by the reflection of an X-ray beam from a stack of parallel equidistant atomic planes. When a crystal containing
regular repeating arrays of atoms is irradiated by a monochromatic X–ray beam, it generates unique diffraction pattern by scattering the incident radiation at specific angles following Bragg’s condition. The Bragg’s law is given by

\[ n\lambda = 2d_{hkl}\sin\theta \]

where \( n \) is an integer, \( \lambda \) is the wavelength of the incident light rays, \( d_{hkl} \) is the interplaner spacing, \( \theta \) is the angle of incidence also known as the Bragg angle. This law relates the wavelength of electromagnetic radiation to the diffraction angle and lattice spacing in a crystalline sample as shown in Figure 2.6. The figure 2.6 shows the X-rays incident on the parallel planes of atoms in the crystal, with each plane reflecting at a very small fraction in the radiation. The diffracted beams are formed when the reflections from the parallel planes of atoms interfere constructively.

![Figure 2.6: Reflection of X-rays by crystal planes (constructive interference).](image)

When the detector is rotated at a double angular velocity by scanning the sample through a range of 2\( \theta \) angles, all possible diffraction directions of the lattice should be achieved due to the random orientation of the powdered material. The recorded pattern consists of several components, the most common being \( K_\alpha \) and \( K_\beta \). Copper is the most common target material for powder diffraction with wavelength CuK\( \alpha \) radiation = 1.5418 Å. The X-rays are collimated and directed onto the sample. As the sample and the detector are rotated, the intensity of the reflected X-rays is recorded.
The recorded diffraction pattern consists of peak positions and their corresponding intensities, which provides information about crystalline phases, the size of the unit cell and also on the arrangement of atoms in the unit cell. The main feature of crystalline materials is the sharp diffraction peaks with long range translational order. In several cases, small sized crystallites or nano-materials lead to peak broadening. The peak broadening can be used to determine the average crystalline size from the decay-Scherrer formula (Cullity, 1956):

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]

where \( \beta \) is the full width at half maximum of a diffraction line located at an angle of in radians, \( D \) is the diameter of crystal particle, \( \lambda \) is the wavelength of the X-ray and \( \theta \) is the diffraction angle.

Figure 2.7: XRD instrument (Model D8-Advance of Bruker, Germany).
To confirm the formation of various compounds, and powder X–ray diffraction (PXD) patterns were obtained using Cu K–alpha radiation from a Bruker model D8–Advance diffractometer. The energy and wavelength of which was 8.04 keV and 1.54 Å respectively. The applied voltage was 40 kV and current was 40 mA. Figure 2.7 shows a picture of the diffractometer used. The recorded PXD patterns were compared with the standard data available in JCPDS cards (files). Usually, broadening of the peaks is observed for nanocrystalline materials and the broadenings can be used to calculate the average grain size of particles.

2.3.2 TRANSMISSION ELECTRON MICROSCOPE
Transmission electron microscope (TEM) is a microscopy technique in which a beam of focused high-energy electrons is transmitted through a very thin sample and interacting with the sample as it passes through. From the interaction of the electrons transmitted through the sample images are formed that reveals information about its particle size, morphology, crystallinity and interparticle interactions. Due to small de Broglie wavelength of electrons, TEMs are capable of imaging at a significantly higher resolution than light microscopes which enables the instrument proficient to examine fine detail— even as small as a single column of atoms, which is tens of thousands times smaller than the smallest resolvable object in a light microscope. In this imaging technique, a beam of electrons is allowed to shine through the specimen. Whatever portion is transmitted is projected onto a phosphor screen. It is an exceptional technique as it can focus on a single nanoparticle and can determine its crystallite size. This technique is applicable to a variety of materials such as metals, ceramics, semiconductors, minerals, polymers, etc. (Graef, 2000; Fultz and Howe, 2008). The schematic diagram of TEM is shown in Figure 2.8 that consists of an electron gun, voltage generator, vacuum system, electromagnetic lenses and recording devices.

To enlight the sample generally thermionic gun (tungsten filament, LaB$_6$ crystal, etc.) or field emission gun is employed as an electron source and the electrons generated are accelerated at chosen voltages by a voltage generator. After passing through the condenser lens system, the electron beam is intended towards a thin sample. Typically, the thickness of TEM specimen lies in the range of 50 to 100 nm and ought to be transparent to the electron beam. In order to prevent the scattering of electrons by the
atmosphere inside the microscope, microscope column is maintained at high vacuum levels. Both transmitted electrons (i.e. image mode) and diffracted electrons (i.e. diffraction mode) reveals the required information.

![Ray diagram of Transmission Electron Microscope.](image)

In the present study, TEM images are captured by using a, Hitachi (H-7500) TEM (Figure 2.9). It has operating voltage between 40–120 kV, high-resolution scanning (1.5 nm) and channeling, X-ray mapping and line-scanning as well as the usual TEM facilities like a resolution of 0.36 nm (point–to–point), an electron probe of size down to 10 nm, capability of resolving 0.14 nm lattice fringes and maximum specimen tilts of ±20 degree along both the axes. This technique is used to investigate the nanostructure of the synthesized samples. The particle size and morphology are studied by capturing TEM images.
For TEM analysis, the nanophosphors are dispersed well in an appropriate insoluble solvent and are suspended on carbon coated 400 mesh size copper grids. Moreover, microscope can be used to analyze elements down to Sodium atom with 11 electrons (Na (Z = 11)). It can be used in typical applications such as routine analysis at moderate spatial resolution, but with high contrast, mostly on polymers, organic specimen in general and inorganic powders, spatial distribution of defects, Bright Field and Dark Field techniques and lattice imaging. Figure 2.9 shows a picture of transmission electron microscope. The TEM photographs are taken with a special film camera attached to the microscope and are subsequently developed and printed for analysis. A calibrated scale gives the actual size of the particle/clusters.

2.3.3 SCANNING ELECTRON MICROSCOPE

The scanning electron microscope is a type of electron microscope also known as SEM based on scanning a finely focused electron beam across the surfaces of a specimen. This is a surface technique which is fundamentally designed to capture images of three dimensional objects on specimen surfaces. The SEM provides a highly magnified image
of the surface of a material that is very similar to what one would expect if one could actually see the surface. The magnification tends to simplify image interpretations considerably, but reliance on intuitive reactions to SEM images can, on occasion, lead to erroneous results. The resolution of the SEM can approach a few nm and it can operate at magnifications that are easily adjusted from about 10–300,000X.

The first SEM image of silicon steel presenting electron channeling contrast obtained in 1935 by Max Knoll [Max et al., 1935]. Subsequent to this, Manfred von Ardenne in 1937 worked on the physical principles of the SEM and beam specimen interactions [Ardenne et al., 1938; Ardenne et al., 1986]. In 1965, Professor Sir Charles Oatley and his student Gary Stewart further developed the SEM and it was subsequently marketed by the Cambridge Instrument Company as the "Stereoscan". The first instrument was delivered to DuPont [Ardenne et al., 1986].

Figure 2.10: Schematic ray diagram of Scanning electron microscope.
The basic construction of SEM is shown in figure 2.10. The electrons are generated by means of a thermal emission source, such as a heated tungsten filament, or by a field emission cathode. The electrons are focused into a small beam by a series of electromagnetic lenses in the SEM column. Scanning coils direct and position the focused beam onto the sample surface. The electron beam is scanned in a raster pattern over the surface for imaging. The secondary and backscattered electrons emerge from the specimen surface when it is probed by a primary electron beam with an energy between 5–30 keV from the electron gun. The primary electrons are focused into a fine spot using the condenser and objective lenses (Figure 2.10). The spot is then scanned across a certain area from where the secondary electrons are collected. When secondary electrons arrive at the secondary electron detector an image is formed. The secondary electrons are used to extract the topographic contrast and backscattered electron images are used to extract compositional differences on the surface. The specimen is observed at high magnification.

The surface and morphological feature of the phosphors in the present study is examined by using a Shimadzu SSX–550 Super Scan scanning electron microscopy. To prevent the charging, all samples are sputter/coated with an ultrathin layer of gold.

2.3.4 UV-VIS SPECTROSCOPY

The UV-visible spectroscopy involves the absorption and/or reflectance of light (radiation) in the ultraviolet-visible spectral region. It is used for studying optical and electronic properties of the material. This technique is based on the measurement of the absorption of ultraviolet and visible light after it transmitted through a sample or after reflection from a sample surface. It investigates the interactions between ultraviolet or visible electromagnetic radiation and matter which provides the accurate information about the atomic and molecular structure of the material. The UV-visible spectroscopy provides direct evidence about electron energy jumps between distinct energy levels. The block diagram of the UV-VIS spectrophotometer is shown in figure 2.11. A deuterium and tungsten lamp are usually used as a light source and the light beam passes through the diffraction grating and the slits. The radiation is separated according to its frequency wavelength by a diffraction grating followed by a narrow slit. The slit ensures that the
radiation is of a very narrow waveband that is monochromatic. Detection of the radiation passing through the sample or reference cell can be achieved by either a photomultiplier or a photodiode. Single photodiode detectors and photomultiplier tubes are used with scanning monochromator, which filter the light so that only the light of a single wavelength reaches the detector at one time. The scanning monochromator moves the diffraction grating to step-through each wavelength so that its intensity is measured as a function of wavelength.

A Shimadzu UV-VIS-2600 spectrophotometer equipped with an integrating sphere assembly is used for UV-VIS absorption study in the present work. It is a double beam spectrophotometer which covers the range from 190 nm to 1400 nm i.e. UV-VIS-NIR. Since, this range of wavelength could not be obtained from a single lamp, a combination of two is used. There is a deuterium lamp for the UV part of the spectrum (from 190 nm – 330 nm), and a tungsten/halogen lamp for the visible and near infrared part (300 nm–1400 nm). The combined output of these two bulbs was focused onto a diffraction grating. Figure 2.12 shows the picture of the spectrophotometer used to record the data.
Optical absorption spectra are used to determine band gap of phosphors. Most of the nanocrystals studied here have band gaps that correspond to the UV-visible region of the electromagnetic spectrum.

2.3.4.1 CALCULATION OF BAND GAP

For diffuse reflectance measurements the UV-visible instrument must be equipped with an integrating sphere (Figure 2.13) coated with a white standard, projected to collect the light reflected by the standard and the sample. Modern double-beam spectrophotometers are equipped with sample holders in which the powdered sample and the white standard are tightly packed. The standard is usually BaSO$_4$, MgO, or polytetrafluoroethylene. They exhibit near 100% reflectance in the wavelength range from the near UV to the near IR. In the present study, the diffuse reflectance spectra are recorded using BaSO$_4$ as standard.

The DR spectrum is used to calculate the energy band gap of the materials (phosphors) by employing Kubelka–Munk theory (Morales, Mora and Pal, 2007). In the diffuse reflectance (DR) spectra, the ratio of the light scattered from a thick layer of
sample and from a standard reference (exhibiting near 100% reflectance) sample 
\[ R = \frac{R_{\text{Sample}}}{R_{\text{Reference}}} \] 
is measured as a function of the wavelength \( \lambda \).

![A Shimadzu UV-VIS-2600 ISR (Integrating Sphere Assembly).]

Figure 2.13 A Shimadzu UV-VIS-2600 ISR (Integrating Sphere Assembly).

The relation between the diffuse reflectance of the sample \( R \), absorption coefficient \( K \) and scattering coefficient \( S \) is given by the Kubelka–Munk function \( F(R) \)

\[ F(R) = \frac{(1-R)R}{2R} = \frac{K}{S} \] (2.2)

where \( R \) is the diffuse reflectance of the sample, \( K \) is the absorption coefficient and \( S \) is the scattering coefficient. Also, the relation between the band gap \( E_g \) and linear absorption coefficient \( \alpha \) of a material, given by Tauc relation is,

\[ \alpha h\nu = C(h\nu - E_g)^{n/2} \] (2.3)

here \( h\nu \) is energy of a photon and \( C \) is a constant of proportionality. The above relation is modified by using equation [2.2] to

\[ [F(R)h\nu]^{2/n} = C(h\nu - E_g) \] (2.4)

The exponent \( n \) has a value of 1 for direct transitions and 4 for an indirect one. In the case of direct transitions, the top of the valence band and the bottom of the conduction band are at the same momentum value in the Brillouin zone. However, in case of an indirect transition, the top of the valence band and the bottom of the conduction band have
different momenta and thus any electronic transition between the two has to be mediated via the participation of vibrational modes (phonons) (Morales, Mora and Pal, 2007).

### 2.3.5 PHOTOLUMINESCENCE STUDY

Photoluminescence (PL) is a simple, versatile, and non-destructive technique and it requires very little sample manipulation or environmental control. It is used to investigate the luminescence of a material and dynamic processes occurring within a material (Blasse and Grabmair, 1994). Photoluminescence (PL) is the spontaneous emission of photons from a phosphor under the excitation of electromagnetic waves of sufficient energy. When light of adequate energy is directed onto a sample, where several photons are absorbed and imparts excess energy into the material in a process called photo-excitation; and electronic transitions occur. The excess energy can be released by the sample through the emission of light or luminescence (Gilliland, 1997). The PL can be analyzed to provide information about photo-excited states. The PL spectrum reveals transition energies and the PL intensity gives a measure of the relative rates of radiative and nonradiative recombination. A variation of the PL intensity upon change of external parameters, e.g., temperature, excitation energy, power of excitation, can be used to further characterize electronic states and energy bands.

The block diagram of Cary Eclipse spectofluorometer is shown in figure 2.14. The excitation source (Xenon lamp) passes through the excitation monochromator and supplies excitation energy to the sample, emitted luminescence is dispersed in a spectral device, a detector converts the optical signal into an electric signal that is then processed by electronic devices and finally by a control computer. The output of the emission spectrum is the plot of luminescence intensity versus emission wavelength. Different light sources may be used as excitation sources, including lasers, photodiodes and lamps (xenon arcs and mercury-vapor lamps). The technique consists of a light source (xenon lamp) because it has a continuous emission spectrum with nearly constant intensity in the range from 300-800 nm and a sufficient irradiance for measurements down to 200 nm which produces photons. The photons pass through the monochromator that only select the certain wavelength to pass through to the sample cell. Luminescence given off is
detected by and processed by the electric device. Generally photomultiplier tube (PMT) is used as detector.

The apparatus used to record the room temperature photoluminescence excitation and emission spectra of the synthesized phosphors in the present study, is Cary–Eclipse Spectrofluorometer equipped with a 150W Xenon lamp as an excitation source. A photograph of the spectrometer is shown in Figure 2.15. The optical system configuration of the instrument is shown in Figure 2.16. The spectrophotometer consists of two monochromators; one on the excitation side and the other on the emission side, a light source, two detectors; one for measurements and the other for monitoring, a sample holder, a data processor and a graphics plotter. The Cary–Eclipse Spectrofluorometer contains Czerny–Turner monochromators for excitation and emission. The Czerny–Turner design uses all–reflective optics to maintain high resolution over the entire spectral range, and minimize spherical aberrations and re–diffraction.

Figure 2.14: Block diagram of Cary Eclipse spectofluorometer.
Figure 2.15: A Cary-Eclipse Spectrofluorometer.

Figure 2.16: Optical system configuration of a fluorescence spectrophotometer.
Specifications:

- Monochromators: Large stigmatic concave grating having 900 lines / mm are used on both excitation and emission sides with eagle mounting (F:3). Blaze wavelengths are 300 nm on excitation side and 400 nm on emission side.
- Measuring wavelength range: 200 nm to 1100 nm and zero order light on both excitation and emission side.
- Light source: 150 W Xenon lamp with ozone self-dissociation function.
- Detector: Photomultiplier R 372 F for measurements and photoelectric tube R 518 for monitoring.

2.3.6 THERMOLUMINESCENCE STUDY
Thermoluminescence (TL) also known as Thermally Stimulated Luminescence (TSL) was came into existence in 1663, when Sir Robert Boyle reported to the Royal Society about "experiments and considerations upon colours with observations on a diamond that shines in the dark" and described how, upon warming a diamond in contact with his body in the dark, he saw a flash. The word thermoluminescence was published in literature for the first time in 1895 (Wiedmann and Schmidt, 1895). In 1897, Hoffman applied this phenomenon for the measurement of cathode rays, X-rays and ultraviolet (UV) radiation intensity by using calcium sulphate doped with manganese (CaSO4: Mn) as a TLD material. The first application of this phenomenon for radiation dosimetry was given in 1953 (Daniels et al., 1953). TL is usually observed in ordered crystals, although the phenomenon also occurs in disordered materials such as glasses (Furtado et al., 1989; Del Nery et al., 1994; Venkateswara Rao et al., 2002; Pandey et al., 2004).

The TL is the phenomenon of emission of light on heating a solid material which has been previously exposed to ionizing radiations. Here, heat is not an exciting agent, but it acts only as a stimulant. Excitation is achieved by any conventional sources like ionizing radiation, α-rays, β-rays, γ-rays and UV rays and X-rays. The process of TL should not be confused with incandescence, which occurs at higher temperatures. To explain the phenomenon of the TL band theory of solid is generally used. When a solid is exposed to
ionizing radiations, electrons and holes are produced. The defects in the solid results in the presence of localized energy level within the forbidden gap. On irradiation, electron and holes can be trapped at these sites. When the solid is heated, these trapped electrons/holes get enough thermal energy to escape from the trap to the conduction band (or valence band). From here they may get retrapped again or may recombine with trapped holes/electrons. The site of recombination is called recombination center. If this recombination is radiative, then center is called luminescence center. Alternatively, a trapped hole can be released by heating which can recombine with a trapped electron resulting in luminescence. Figure 2.17 shows the simplest possible model consisting of two localized levels, an isolated electron trap (T) and a recombination center (RC). This is commonly referred to as the one-trap-one-recombination center model (OTOR).

![Diagram](image)

Figure 2.17: The simple two-level model for the thermoluminescence process.

In Figure 2.17, as the temperature of the sample is increased, the trapped electrons in trap (T) are thermally released into the conduction band, as shown by the arrow (transition 1). These conduction band electrons can either recombine with holes in the recombination center (RC) (transition 2), or they can be retrapped into the electron trap T (transition 3). The intensity of the emitted light is equal to the rate of recombination of holes and electrons in the recombination center (Pagnosis et al., 2006). The standard way of presenting TL data is to plot luminescence intensity as a function of temperature, known
as a ‘glow curve’. The glow curve composed of different peaks occurring at different temperatures. These peaks are related to the electron traps present in the sample. The area under each peak is related to the number of filled traps, which, in turn is related to the amount of radiation initially imparted to the specimen. Defects in the lattice structure are responsible for electron traps.

2.3.6.1 SOURCE FOR IRRADIATION

2.3.6.1.1 GAMMA SOURCE

For gamma irradiation, gamma chamber model GC-1200 (shown in Figure 2.18) having radioactive source “cobalt-60” of Board of Radiation and Isotope Technology (BRIT), Mumbai, installed at the Inter University Accelerator Center, New Delhi is used. Gamma Chamber 1200 unit is designed to house up to 185 TBq (5000Ci) of the Cobalt-60 source and the lead shielding provided is adequate enough to bring down the radiation leakage level on the exterior of the unit well below the accepted standards. It offers an irradiated volume of about 1200cc. The unit mainly consists of the following parts:

a) Source and cylindrical source cage
b) Lead Flask as Biological shield
c) Central drawer with sample chamber
d) Mechanical driver system
e) External cabinet

In this study, the TL properties of the phosphor materials are studied using the Harshaw 3500 TLD (Figure 2.19). The instrument is manually-operated and has a sample drawer for a single element TLD dosimeter, a programmable heating system and a cooled photomultiplier tube (PMT) to measure the TL. The TL glow curve reader runs on WinREMS software, which runs under a Windows operating system. The system is a PC–driven, tabletop instrument for TLD measurement. The time-temperature profile is user-defined in three segments: Preheat Acquire, and Anneal, each with independent
times and temperatures. It also has the facility for flowing nitrogen around the planchet. By eliminating oxygen in the planchet area, unwanted oxygen-induced signals are avoided. The data could also be stored in the form of ASCII files for its utilization in further analysis.

Figure 2.19: The Harshaw 3500 TLD Reader.

2.3.6.2 THERMOLUMINESCENCE MODELS

Theoretical analyses for the TL phenomenon were first given by Randall and Wilkins (Maxia, 1978). They give the basic theory of a single TL peak and suggested a single trap model for that (Figure 2.17). Randall and Wilkins assumed that once an electron is in the conduction band, it would immediately recombine with a hole; (no retrapping) and wrote an equation for TL intensity as follows

\[ I(T) = -\frac{dn}{dt} = s \cdot n \cdot \exp \left( -\frac{E}{kT} \right) \]  

(2.5)

where \( n \) in \((\text{cm}^{-3})\) is the concentration of trapped electrons, \( E \) in (eV), the activation energy, \( s \) \((s^{-1})\) is the frequency factor, \( k \) in (eV/K) Boltzmann’s constant, \( t \) \((s)\) and \( T \) \((K)\) the temperature. Equation 2.5 can be solved for \( I \) and the solution is given by

\[ I(T) = \exp \left( -\frac{E}{kT} \right) \exp \left[ -\left( \frac{s}{\beta} \right) \int_{T_0}^{T} \exp \left( -\frac{E}{kT} \right) dT' \right] \]  

(2.6)
where, \( n_o \) is the initial concentration of trapped electrons at temperature \( T_o \) and \( T = T_o + \beta t \) (where \( T_o \) is the initial temperature K and \( \beta \) (Ks\(^{-1}\)) is the heating rate). Equation 2.6 provides the TL intensity as a function of temperature, when there exists one type of trap and one type of recombination centre.

If the material is maintained at a temperature \( T \) then,

\[
I(t) = I_o \exp(-At)
\]

(2.7)

where \( A \) is a constant equal to \( s \exp(\frac{-E}{kT}) \), and \( I_o \) is the initial intensity at time \( t = 0 \). Equation 2.7 gives the isothermal exponential decay of TL intensity and the TL process is said to follow first order kinetics. Contribution from several types of traps may exist and the delay it may not be exponential as predicted by Equation 2.7 but again, these contributions may be decomposed into several exponentially decaying components.

Garlick and Gibson (May and Partridge, 1964) extended the work done by Randall and Wilkins and made modified the assumption made by them, they assumed that for electrons have same probability of recombination. Therefore, the intensity \( I(T) \)

\[
I(T) = -\frac{dn}{dt} = s' \cdot n^2 \cdot \exp\left(-\frac{E}{kt}\right)
\]

(2.8)

where \( s' = s/N \) is known as the pre–exponential factor and \( N \) is the total number of traps.

\[
I(T) = s' \cdot \exp\left(-\frac{E}{kT}\right) \exp\left[\frac{1}{n_0} + \left(\frac{s}{\beta N}\right) \int_{T_o}^{T} \exp\left(-\frac{E}{kT}\right) dT\right]^{-2}
\]

(2.9)

The solution for the constant temperature \( T \) giving the isothermal decay of luminescence is:

\[
I(t) = \frac{I_o}{(1+A' n_o t)^2}
\]

(2.10)

where \( A' = (s/N)\exp(\frac{-E}{kT}) \), From the equation, the TL process is said to follow first order kinetics.

In many of the materials, the TL glow curves could not be fitted by either the first order kinetics or the second order kinetics. May and Partridge (Lewandowski and
McKeever, 1991) derived an equation, applicable to a TL process following any non-
first-order kinetics, given by

\[
I(T) = c \cdot s' \cdot n_o \exp \left( -\frac{E}{kT} \right) \left[ \frac{(b-1)s}{\beta} \int_{T_o}^{T} \exp \left( -\frac{E}{kT'} \right) dT' + 1 \right]^{\frac{b}{b-1}} 
\]  

(2.11)

where, \(c\) is the concentration of filled traps, \(b\) is the order of kinetics, The above equation
is not valid for \(b = 1\), but when \(b\) approaches to 1, it reduces to first order kinetics and
for \(b = 2\), the equation reduces to second order kinetics.

2.3.6.3 ANALYSIS OF TL GLOW CURVE

A glow curve is a graphical representation of the TL intensity as a function of heating
time or temperature, providing information about parameters corresponding to each peak,
such as activation energy (\(E_\alpha\)), frequency factor (\(s\)) and the order of kinetics (\(b\)). The
values for these parameters may reveal information about the defect with which they are
associated. Therefore, in order to analyze a TL glow curve, several methods have been
adopted, such as:

1. Initial rise method
2. Variable heating rate method
3. Chen’s peak shape method
4. Glow curve deconvolution methods

This section focuses on the theoretical background of the Chen’s peak shape method.
Chen formalism (Chen and Kirsh, 1981) was used to calculate kinetic parameters like the
order of kinetics (\(b\)), activation energy (\(E_\alpha\)) and the frequency factor for each of the
deconvoluted peak of the prepared phosphors. The activation energy (\(E_\alpha\)) can be
estimated from the thermal peak temperature with the following equation:

\[
E_\alpha = C_\alpha \left( \frac{KT_m^2}{\alpha^2} \right) - b_\alpha (2kT_m) 
\]  

(2.12)

with \(\alpha = \tau, \delta, \omega; \tau = T_m - T_1; \delta = T_2 - T_m; \omega = T_2 - T_1; \)

\[
C_\tau = 1.51 + 3.0 (\mu_g - 0.42); \quad C_\delta = 0.976 + 7.3 (\mu_g - 0.42);
\]
\[ C_\omega = 2.52 + 10.2 (\mu_g - 0.42); \]
\[ b_T = 1.58 + 4.2 (\mu_g - 0.42); \]
\[ b_\delta = 0; \quad b_\omega = 1. \]

The nature of the kinetics can be found by the form factor (equation 2.13) where \( T_1 \) and \( T_2 \) are the temperature (corresponds to half of the intensities on the either side of the maximum temperature Tm). Theoretically the value of \( \mu_g \), ranges between 0.42 and 0.52, the value close to 0.42 is for First order kinetics and value close to 0.52 is for second order.

\[ \mu_g = \frac{T_2 - T_m}{T_2 - T_1} \] (2.13)

Once activation energy (E) and order of kinetic have been determined, the frequency factor can be calculated from the following equation (equation 2.14):

\[ \frac{\beta E}{k T_m^2} = s \exp \left\{ \frac{-E}{k T_m} \right\} \left[ 1 + (b - 1) \Delta_m \right] \] (2.14)

where \( \Delta_m = 2k T_m / E \)

### 2.3.7 X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

XPS is a non-destructive and quantitative spectroscopic technique that helps to measure the elemental composition, chemical composition state, binding energy and electronic state of the elements that exist within a material. This technique is also known as Electron Spectroscopy for Chemical Analysis (ESCA). The technique operates on photo-ionization and analyses the kinetic energy distribution of the emitted photoelectrons from a surface. Monochromatic x-ray sources are use as excitation Mg Kα radiation (1253.6 eV) or Al Kα radiation (1486.6 eV) is often used (Moulder et al., 1995). XPS is considered as a surface-analytical technique owed to the very short path of the photoelectrons excited from the solid. An energy analysis of these photoelectrons provides both elemental and chemical bonding information about the material comprising the sample surface. All elements can be detected, except hydrogen and helium. Usually, XPS technique is used to measure organic and inorganic compounds, metal alloys, semiconductors, polymers, elements, catalysts, glasses, ceramics, paints, papers, inks, woods, bio-materials and
many others. It is a surface sensitive in that it analysis at 2nm depth, and its lateral resolution is greater than 150 μm.

This technique involves the process of photoemission and the principle of this is based on the Einstein’s photoelectric effect that explains ejection of electrons from a surface of the material when photons are incident on it. When the X-rays are made to fall on the surface of a sample, the inner level electrons of the surface atoms absorb the X-ray photon energy \( hν \), overcome their binding energy \( (BE) \) and are emitted out of the surface with a certain kinetic energy \( E_{kin} \) (shown in Figure 2.20). This process is described by the Einstein equation (Vickerman, 1997):

\[
E_{kin} = h\nu - BE - \phi
\]  

(2.15)

where, \( h\nu \) is the energy of the X-ray source. MgKα and AlKα are the two generally used sources because of their relatively high energy and narrow width. \( \phi \) is the work function of the instrument. The kinetic energy \( E_{kin} \) of the emitted electron is measured by an analyzer. Therefore, the binding energy \( BE \) of the core level electron can be determined. A characteristic set of XPS peaks at characteristic binding energy values are produced that directly identify each element that exists on the surface of the material being analyzed. These characteristic peaks correspond to the electron configuration of the electron within the atoms, e.g., 1s, 2s, 2p, 3s, 3p, 3d etc. The number of detected electrons in each of the characteristic peak is directly related to the amount of element within the irradiated area.

Figure 2.20: Principle of XPS.
The schematic diagram of XPS technique is shown in figure 2.21. It consists of an x-ray source, an electron energy analyzer and an ultra-high vacuum (UHV) chamber. A monochromatic X-ray beam ejects the photoelectrons from the surface of the sample. The ejected electron is then attracted to the detector of the system using potential difference and accelerated along the hemispherical analyzer from where its kinetic energy will be used to determine the binding energy of the surface of the specimen (Figure 2.21). Such energy is obtained using equation 2.15. The binding energy of each atom is different; hence the energy peaks of different atoms have different heights.

Figure 2.21: Schematic showing the photo electron path from the specimen to the detector.

Figure 2.22: PHI 5000 Versa Probe II Scanning XPS Microprobe.
In this present study, the XPS scans are done with 100 m, 25 W, and 15 kV monochromatic beam. To investigate the surface properties of the phosphors XPS PHI 5000 versa probe was used. The photograph of the apparatus used during the measurements is shown in figure 2.22.

REFERENCES


