Chapter 2

Materials and methods
## Chapter 2. Materials and Methods

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2.1 Synthesis of nanoparticles

Various methods have been reported for the synthesis of nanoparticles depending on the material of interest, size regime and their applications. The experimental technique gains importance based on its capability for the reproduction of size and shape and the control over the average size. Nanoparticles can be prepared either by allowing the atom to fuse together until the desired size is attained (bottom-up) or by breaking a bulk material (top-down) to the predetermined size. The bottom-up approach allows better control in the preparation of particles of desired size. In the nucleation process, a phase change either from vapor or liquid to solid phase is involved and the growth of the nanograin can be suitably controlled.

There are basically two broad areas of synthesis for nanocrystalline materials, namely physical and chemical methods [49-51]. The widely used physical method is ‘solid state reaction’ through mechanical deformations [52-53]. In this method, nanocrystalline materials are produced by structural degradation of coarser-grained structures induced by the application of high mechanical energy. ‘Laser ablation’ technique uses high power pulsed laser to vaporize cluster ions from surfaces [54]. The wavelength of the laser should be adjusted with the material. This is a general and versatile method virtually applicable to any material. In the ‘arc discharge method’, the metal atom to be evaporated serves as electrodes in the vacuum chamber and generates a discharge
between the electrodes [55]. When arc current is increased metal droplets in the form of smoke is produced. The small metal particles are formed from the smoke particles. In addition, various other physical methods such as inert-gas evaporation technique, spray pyrolysis, microwave decomposition etc., are also used for the preparation of nanocrystalline materials [56-59].

Solution based chemical methods are generally used to improve homogeneity and purity and also to reduce particle size called as wet chemical methods. The ‘sol-gel’ technique can be used for the production of nanomaterials by starting with soluble, highly dispersed metal alkoxides or soluble salts on the molecule level and fixing the dispersion state in a gel by the hydrolysis and condensation reaction [60]. In ‘co-precipitation’ method, soluble metallic salts are dissolved in aqueous solvent and precipitation is achieved by adding cation species as carbonates or hydroxides. The low processing temperatures and homogeneity of mixed precursors leads to the small size particles of the order of nanoscale are the added advantages of this method.

Nano-sized calcium titanate particles have been synthesized by various physical and chemical methods including thermal decomposition, chemical vapor deposition, sol–gel, thermal vapor transport, condensation and hydrothermal [61-68]. Searching new methodology to synthesize uniform nano-sized calcium titanate particles is of great importance for both fundamental study and
practical applications. Indeed, there is a great demand for economically viable and low temperature synthesizing methods to achieve better quality nanostructured materials. Solution combustion synthesis (SCS) is a promising technique for the preparation of nanopowders which can be scalable easily to industry level. This process is simple, quick and economic, does not involve complicated set-ups [69]. It is mainly based on the basics of propellant chemistry.

### 2.2 Chemicals used for synthesis of phosphors

This chapter mainly describes the starting materials used for the synthesis of phosphors and elaborates procedure of preparation method we adopted. Further, it describes the details of experimental procedure of characterization we used for the analysis of prepared phosphors for solid state lighting applications (SSL). The chemicals of analar or equivalent grade chemicals were used for the synthesis of nanophosphors as tabulated in Table 2.1.

<table>
<thead>
<tr>
<th>Sl. no.</th>
<th>Chemical name</th>
<th>Chemical formula</th>
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</tr>
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<tbody>
<tr>
<td>1</td>
<td>Calcium nitrate</td>
<td>Ca(NO₃)₂</td>
<td>Merk / Sigma Aldrich</td>
</tr>
<tr>
<td>2</td>
<td>Calcium carbonate</td>
<td>Ca(CO₃)₂</td>
<td>Merk / Sigma Aldrich</td>
</tr>
<tr>
<td>3</td>
<td>Urea</td>
<td>CO(NH₂)₂</td>
<td>Merk / Sigma Aldrich</td>
</tr>
<tr>
<td>4</td>
<td>Titanium oxide</td>
<td>TiO₂</td>
<td>Degusa</td>
</tr>
<tr>
<td>5</td>
<td>n-butyl titanate</td>
<td>Ti(OC₄H₉)₄</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>6</td>
<td>Nitric acid</td>
<td>HNO₃</td>
<td>SLN Chemtech</td>
</tr>
<tr>
<td>7</td>
<td>Samarium nitrate</td>
<td>Sm(NO₃)₃</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>8</td>
<td>Europium nitrate</td>
<td>Eu(NO₃)₃</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>9</td>
<td>Terbium nitrate</td>
<td>Tb(NO₃)₂</td>
<td>Sigma Aldrich</td>
</tr>
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</table>
2.2.1 Combustion chamber

The combustion process was performed in an electric muffle furnace supplied by Tempo Instruments and Equipment, Bombay. The furnace used for synthesizing the nanophosphors is shown in the Fig.2.1. It operates on 240 V AC, 13.75 A current. It has power rating of 3.3 kW and an operating volume of (35 x 15 x 15) cm³. The heating element is Kanthal wire (Fe-67%, Cr-25%, Al-5% and Co-3%) of 18SWG. The average heating rate was maintained at 10 °C per minute. Chromel–Alumel thermocouple (Cr-Al:1200 °C, HIMA) was used to measure the furnace temperature. A suitable exhaust fan for ventilating the fumes emanating from the combustion process was positioned approximately at 10 feet above the furnace so that the convection current does not affect the combustion process.

Fig.2.1. Muffel furnace used for phosphor synthesis.
2.2.2 Stochiometric calculations

The stoichiometry of reaction mixture was calculated based on the total oxidizing (O) and reducing (F) valencies of the oxidizer and the fuel, keeping O/F ratio unity, using the concepts of propellant chemistry [26]. Carbon, hydrogen and calcium/strontium/barium were considered as reducing elements with the corresponding values +4, +1 and +2 respectively, and oxygen was considered as oxidizing element with the value of −2. The valence of nitrogen was considered to be zero because of its conversion to molecular nitrogen during combustion. Oxidizing elements have positive valencies and reducing elements have negative valencies.

The total oxidizing valency of metal nitrates can be calculated by arithmetic summation of oxidizing and reducing valencies of elements present in oxidizer. Similarly, the total reducing valency of a reducer (fuel) can also be obtained by arithmetic summation of oxidizing and reducing valencies of elements present in it.

\[
(\phi_e)_{\text{Oxidizer/fuel}} = \frac{\sum \text{all oxidizing and reducing valencies of elements in oxidizer}}{(-1) \sum \text{oxidizing and reducing valencies of elements in fuel}} \]

2.3 Procedure for synthesis

Nanophosphors were synthesized by using the chemicals mentioned above. The starting materials used for the synthesis of analar grade host nitrate and dopent nitrate, and the fuel were dissolved in a minimum quantity of double distilled water in a
cylindrical Pyrex dish (100 mm diameter x 50 mm height) of approximately 300 ml capacity and stirred well using magnetic stirrer for uniform distribution of the particles. Then the dish containing the heterogeneous mixture was introduced in to a muffle furnace maintained at 500±10 °C. The solution mixture boils and then froths and swells, forming foam. Finally, a voluminous fluffy powder is obtained. Further the as formed product was calcined to a very high temperature around 800-1000 °C in order to get highly crystalline nanophosphors. The flow chart for the preparation of nanophosphors is given in Fig. 2.2. The detailed steps involved during combustion synthesis for the titanate is shown in Fig. 2.3. The detail description of the sample preparation is given in their respective chapters.

Titanyl nitrate \((\text{TiO(NO}_3)_2)\) was prepared by taking N-butyl titanate \(\text{Ti(OC}_4\text{H}_9)_4;\text{ Degusa})\) in a cylindrical petri dish and minimum quantity of doubled distilled water was added to N-hydrolyze butyl titanate to titanyl hydroxide. Further addition of nitric acid to the reaction mixture, titanyl nitrate was formed. The corresponding chemical reactions can be written as

\[
\text{Ti(OC}_4\text{H}_9)_4 + 3 \text{H}_2\text{O} \rightarrow \text{TiO(OH)}_2 + 4 \text{C}_4\text{H}_9\text{OH} \quad \cdots \cdots \quad (2.2)
\]

\[
\text{TiO(OH)}_2 + 2 \text{HNO}_3 \rightarrow \text{TiO(NO}_3)_2 + 2 \text{H}_2\text{O} \quad \cdots \cdots \quad (2.3)
\]

The stiochiometric quantities of calcium nitrate \((\text{Ca(NO}_3)_2;\text{ Sigma Aldrich}),\) titanyl nitrate \((\text{TiO(NO}_3)_2;\text{Sigma Aldrich}),\) samarium nitrate \((\text{Sm(NO}_3)_3; \text{Sigma Aldrich})\)and urea \((\text{NH}_2\text{CONH}_2;\text{ AR})\) were
dissolved in a double distilled water and stirred well using a magnetic stirrer for 5-10 min. The cylindrical petri dish containing the solution was introduced into preheated muffle furnace maintained at 500 ±10 °C. The auto ignited solution mixture with flames on the surface rapidly proceeded throughout the entire volume forming a white voluminous foamy product. The complete reaction can be written as

\[
3\text{Ca(NO}_3\text{)}_2 + 3\text{TiO(NO}_3\text{)}_2 + 10\text{ CO (NH}_2\text{)}_2 \rightarrow \\
3\text{CaTiO}_3 + 10\text{ CO}_2 + 16\text{ N}_2 + 20\text{ H}_2\text{O} \quad \text{...(2.4)}
\]

Theoretical equations assuming complete combustion of the redox mixture used for the synthesis with RE\(^{3+}\) dopant ions are given in their respective chapters.

---

2.2 Flow chart for the preparation of nanophosphors
Fig. 2.3. Pictures (a - e) of various stages of the preparation of nanostructured materials from combustion process

2.3.1 Solid State Method

Stoichiometric amounts of Ca(CO$_3$)$_2$ and TiO$_2$ were sufficiently ground for 30 min in agate mortar. The resulted powder mixture was packed in an alumina crucible and heated in muffle furnace at 900 °C for 2 h. The flow chart of this method of preparation is as shown below.
2.3.2 Modified Solid State Method

Stoichiometric amounts of tetra-n-butyl titanate (Ti(OC\textsubscript{4}H\textsubscript{9})\textsubscript{4}) and calcium nitrate (Ca(NO\textsubscript{3})\textsubscript{2}.4H\textsubscript{2}O) were grounded in an agate and mortor for ~2 h. The hydrolysis of Ti(OC\textsubscript{4}H\textsubscript{9})\textsubscript{4} started readily during grinding process accompanied by the evaporation of butanol. The C\textsubscript{4}H\textsubscript{9}OH mixture turns soft semi solid and underwent gradual color changes from colorless to white. Finally white precursor was calcined at 700 °C for 2 h in air atmosphere to get whitish powder product. The flow chart of this method of preparation is as shown below.
2.4 Instruments used

The purity of the nanophosphors is examined by powder X-ray diffractometer (PXRD) (PANalytical X’Pert Pro) using Cu Kα radiation. The surface morphology of the phosphor has been examined using scanning electron microscope (SEM) (JOEL JSM 840 A). Transmission electron microscope (TEM) analysis was performed on a Hitachi H-8100 equipped with EDS. UV-VIS absorption of the samples was recorded on SL 159 ELICO UV – VIS Spectrophotometer. The FT-IR studies have been performed on a Perkin Elmer Spectrometer (Spectrum 1000). TL measurements were carried out at room temperature and IR filter was used in Nucleonix T reader. UV-irradiation (3-30 min) was done using standard UV lamp peak at 254 nm with a power of 15 W was used. The photoluminescence (PL) measurements was performed on a Horiba Spectrofluorimeter (Fluorolog-3) equipped with 150 W Xenon lamp as an excitation source.

2.4.1 Powder X-Ray Diffraction (PXRD)

X-ray diffractometer is non-destructive method which can analyze the crystalline states under normal atmospheric conditions. X-rays focused on a sample fixed on the axis of the spectrometer (goniometer) are diffracted by the sample. Computer analysis of the peak positions and intensities associated with this pattern enables qualitative analysis, lattice constant determination and/or stress determination of the sample. The peak angles and profiles may be
used to determine particle diameters and degree of crystallization, and are useful in conducting precise X-ray structural analysis.

In 1913, English physicists Sir W.H. Bragg and his son Sir W.L. Bragg developed a relationship to explain the cleavage faces of crystals appear to reflect X-ray beams at certain angles of incidence theta, \( \theta \). They came up with Bragg’s law which is

\[
\begin{align*}
  n \lambda = 2d \sin \theta \\
\end{align*}
\]

where \( d \) is the interplanar spacing, \( \lambda \) is the wavelength of the incident X-ray beam and \( n \) is an integer. Fig. 2.4 shows the schematic diagram related to the Bragg’s law.

![Bragg’s law](image)

Fig. 2.4. Bragg’s law for the periodic arrangement of atoms

Almost 95% of all solid materials can be described as crystalline. When x-rays interact with crystalline substance, there will be a diffraction pattern. The x-ray diffraction of a pure substance is like the fingerprint of the substance. The sample that will be prepared to perform the x-ray diffraction is in the form of powder. Normally the size of the powder will be between 0.1 - 40 \( \mu \text{m} \).
Fig. 2.5 shows PXRD instrument used for the present studies. X-rays are produced due to the high electron bombardment to the target material. The X-rays will then be directed to the sample and it will show a diffraction pattern. This pattern will then be detected by the detector and it will interpret the data needed for the sample.

![X-ray chamber used for diffraction measurements](image)

Fig. 2.5. X-ray chamber used for diffraction measurements

The main use of the powder diffraction is to identify different phases in the sample by a match procedure. It is important to have a smooth plane surface. The smaller the size of the sample, the matching will be better and a better result can be obtained. The ideal sample is a homogenous sample and the crystallites are randomly distributed. The sample will be pressed into the sample holder so that it will posses a smooth flat surface. If the atoms are organized in a periodic manner the constructive and destructive interference will occur.
2.4.1.1 Rietveld refinement

Until 1970, powder diffraction was viewed primarily as a tool for phase identification and quantitative analysis. Its use for structure refinement was limited to simple systems because of severe peak overlap. Rietveld (1967) came up with a new approach to extract maximum crystal structure information from powder diffraction data using the method of least squares [70, 71]. The introduction of Rietveld method has greatly enhanced the use of powder diffraction data for structure refinement and has provided a major boost to structure solution from powder data in a systematic way [72,73].

In Rietveld refinement of a crystal structure from powder diffraction data, every observation in the powder diffraction profile is considered as intensity measurement. The powder diffraction profile is calculated using the following information: (i) background intensity, (ii) lattice parameters and space group (peak positions), (iii) atomic positions and atomic displacement parameters (peak intensities), (iv) 2θ dependent analytical function (peak shapes and peak width) and occupation factors.

For Rietveld refinement, the powder data must be collected accurately in digitized form using a properly aligned and calibrated diffractometer. Factors such as suitable radiation (e.g. conventional X-rays, synchrotron X-ray or neutron), the wavelength, diffractometer
geometry (e.g. Debye-Scherrer, transmission, Bragg-Brentano), sample preparation, step-scan increments, counting time etc, must be evaluated carefully based on the characteristics of the sample under study before collecting the data.

The model-parameters that may be refined include not only positional, thermal and site occupancy of the atoms in the starting structural model but also parameters for the background, lattice, instrumental geometrical-optical features, specimen aberrations (e.g. specimen displacement and transparency), an amorphous component and specimen reflection-profile-broadening factors (e.g. crystallite size and micro strain). Multiple phases may be refined simultaneously for quantitative phase analysis.

The criteria for the best fit are based on the several $R$ factors, developed from the well established single crystal diffraction methodology. The various $R$ factors include, $R_p$ - $R$ profile, $R_{wp}$ - $R$ weighted profile, $R_b$ - $R$ Bragg factor, etc. the Rietveld refinement can be terminated as soon as the model is well refined. This can be seen when best fit is obtained between observed and calculated powder diffraction patterns and the changes in the individual parameters are no longer significant. In the present study, the Rietveld refinement was performed through the FULLPROF program [74]. The packing diagrams of corresponding samples after Rietveld refinement are reported. The refined parameters such as occupancy, atomic functional positions volume and $R_f$ factors are obtained.
2.5 Scanning Electron Microscopy (SEM)

SEM utilizes electrons rather than light to form an image. It has many advantages over optical microscope. It is based on the wavenature of the electrons accelerated with high voltage leads to high resolution. SEM can be used to delve into the surface morphology of thin film samples [75]. A schematic diagram of SEM is shown in Fig. 2.6.

A beam of electrons is produced at the top of the microscope by heating of a metallic filament. The electron beam follows a vertical path through the column of the microscope, which focus and direct the beam down towards the sample. Once it hits the sample, the backscattered or secondary electrons are ejected from the sample. Detectors collect the secondary or backscattered electrons and convert them to a signal that is sent to a viewing screen similar to the one in an ordinary television producing an image. All these are carried out under high vacuum. In the present study Hitachi table top TM-3000 scanning electron microscope was used to study the morphology of the samples and is shown in the Fig.2.7.
Fig. 2.6. Schematic diagram of SEM.

Fig. 2.7. (a) Overview of table top TM3000 SEM and (b) Sample chamber.
2.6 Transmission Electron Microscopy (TEM)

TEM is used to obtain information from samples that are thin enough to transmit electrons. In TEM the whole area of interest is illuminated simultaneously. The schematic diagram of TEM is given in the Fig.2.8. An electron source is required which can produce large total current, so that whole region of interest is illuminated at a useful intensity, even when examining at magnifications of 100x or less. The transmitted electrons are generally used to form either an image or a diffraction pattern of the specimen. The diffraction lens (The lens immediately after the objective lens) is focused on the plane where image is formed by the objective lens. Subsequent lenses are used to magnify this further and hence a highly magnified image can be formed on the final screen. The diffraction lens is focused on the plane where the objective lens forms a diffraction pattern. Again the lenses below the diffraction lens are used to magnify further the diffraction pattern. There are two different ways of obtaining images of sample in TEM: a) conventional imaging and b) high resolution imaging. First method involves the use of an aperture in the back focal plane, which allows only one electron beam to contribute to the image.

This method of obtaining image information therefore excludes the possibility of observing the periodicity of crystalline samples, since interference of at least two beams are required in the image plane to obtain such periodic information and contrast arises either from diffraction contrast or phase contrast. The second method
of obtaining an image also involves the use of an aperture, but in this case the direct beam and a number of diffracted beams are allowed to contribute to the image. When using the microscope in the conventional image mode, the objective aperture is used to select only one electron beam to form the image.

A bright field image is formed if directly transmitted beam is selected and a dark field image is formed if a diffracted beam is selected. If the crystal has been set up in such a way that only one strong diffraction beam is excited, and then this beam is selected for imaging. This technique is usually used when crystal defects are imaged. A diffraction pattern is formed in the back focal plane of the objective lens. Hence if the diffraction lens is focused onto the back
plane of the objective lens, rather than on to the first image plane and objective aperture is removed, the diffraction pattern will be visible on final screen. There are two methods which are commonly available a) selected area electron diffraction (SAED) using an aperture to select the area b) selected area diffraction using a focused electron probe to analyze the selected area gives the chemical composition of the compound [76].

The first method is used in conjunction with a de-focused electron beam so that a large area of the sample is illuminated with electron and hence this large area is contributing to the generation of diffraction of beams. The technique involves inserting an aperture in the first image plane so that only those electrons generated from the area defined by the aperture will be able to contribute to the diffraction pattern. The other technique simply involves condensing the electron probe to the area of interest, so that the probe position uniquely defines the region from where the diffraction beam originates. The electron probe mode is the most common method of obtaining the diffraction pattern. In the present study the Hitachi H-8100 (accelerating voltage up to 200 kV La B6 filament) and equipped with an ultra high resolution objective pole piece in the top entry configuration was used. The cleaved samples are examined under the transmission electron microscope in order to study the nature of the defect (dislocation) structure and the inter planar spacing. The
selected area electron diffraction (SAED) patterns are also obtained in certain cases.

2.7 Fourier Transform Infrared Spectroscopy (FTIR)

The spectroscopy of the coupled rotational and vibrational excitations is an exquisite probe for structural studies and also for the determination of the internal atomic motions of gas-phase molecules. This is carried out with the aid of vibrational spectroscopy and is conducted with the Fourier transform infrared spectrometer based on a scanning interferometer that modulates a broadband infrared source based on its optical frequency components.

![Schematic diagram of FTIR instrument](image)

**Fig.2.9. Schematic diagram of FTIR instrument**

The ratio of the sample to reference intensity spectra gives the transmission spectrum of the sample. The absorption or transmission peaks of an infrared spectrum correspond to the frequencies of vibration between bonds of the atoms. Also different materials produce different types of spectra because no two materials have
unique combination of atoms. Hence every IR spectrum results in a positive identification of every different kind of materials. This feature makes IR spectroscopy quite useful in material characterization. Schematic of a FTIR spectrometer is as shown in Fig. 2.9. The instrument used for FTIR measurements is Perkin Elmer FTIR spectrometer, (spectrum 1000) with KBr pellets was used to study the FTIR of as-formed and calcined samples. The photographic view of the FTIR instrument is shown in Fig.2.10.

![FTIR Instrument](image)

**Fig.2.10. Photographic view of FTIR instrument**

### 2.8 UV-Visible absorption spectroscopy

In the present study, the UV-Visible absorption of the samples was recorded on SL 159 ELICO UV-Vis Spectrophotometer. The schematic view for UV-Vis measurements was shown in Fig.2.11.
SL 159 Scanning UV-Visible Spectrophotometer consists of the followings

- Microprocessor based with Printer Interface.
- Optional PC compatibility with RS 232C Interface.
- Automatic 6 position holder.
- 21 CFR PART 11 Compliant Software.

2.9 Photoluminescence (PL)

The schematic representation of spectrofluorimeter can be seen in Fig.2.12. The light from an excitation source passes through a monochromator, and strikes the sample. A proportion of the incident light is absorbed by the sample, and some of the molecules in the sample fluoresce. The fluorescent light emitted passes through a second monochromator and reaches a detector. Various light sources may be used as excitation sources, including lasers, photodiodes and lamps.
Xenon arc lamp has a continuous emission spectrum with nearly constant intensity in the range from 300-800 nm.

**2.9.1 Excitation and Emission spectra**

The spectrofluorimeter with dual monochromators and a continuous excitation light source can record both excitation spectrum and emission spectrum. When measuring emission spectra, the wavelength of the excitation light is kept constant, preferably at a wavelength of high absorption, and the emission monochromator scans the spectrum. For measuring excitation spectra, the wavelength
passing through the emission monochromator is kept constant and the excitation monochromator is subjected to scanning. The excitation spectrum generally is identical to the absorption spectrum as the emission intensity is proportional to the absorption. Lifetime and quantum yields are two important properties of a phosphor and they can tell us about the quality of a phosphor. The instrument used for the measurement of PL is Horiba Jobin spectrofluorimeter (Fig.2.13).

![Fig.2.13. Experimental setup used for PL measurements](image)

**2.10 Thermoluminescence**

In the present study, pure and rare earth doped nanotitanates irradiated with swift heavy ion, gamma rays and UV-source at room temperature has been studied. The TSL measurements were carried out using TSL set up (Fig.2.14) assembled with the components supplied by Nucleonix systems private Ltd [77].
PC controlled TLD reader consists of the following as shown in the block diagram Fig.2.15

- LV power supply circuit board.
- HV power supply circuit.
- Temperature controller circuit PCB.
- Micro controller PCB including ACD, DAC and RS22 circuits, I to F connector for auto ranging. PMT, heater transformer, kanthal strip and drawer assembly to load supplies.

Fig.2.14. Experimental setup for TL measurements

Fig.2.15. Block diagram of TL reader
2.10.1 PMT housing and TL sample heating assembly:

This unit has a photomultiplier Tube with appropriate modification in the PMT socket wiring. The cylindrical shell containing the Photomultiplier is fitted on to a rectangular base drawer block containing a heater arrangement and thermocouple, heater rods, connected to a power transformer. The PMT housing unit consists of the following components: Heating Arrangement, Heating Elements, Temperature Sensor, PMT Cooling and High voltage to PMT. It consists of software features like File handling, Configuration and Data acquisition. Functionality of the hardware circuits can be explained as follows.

Power supply circuit generates required low voltages (+5V, +12V) to power up, rest of the electronic circuits to function. A continuously stable voltage in the range of 0-1500 V at 1 mA with good load was applied. This HV circuit board uses a DC to DC converter switched at 30 kHz, RF frequency to generate HV. HV indication is provided on a front panel DPM and a precision, ten turn dial can be used to set the desired HV for biasing the PMT. Current output from the PMT is converted to frequency output by C to F converter circuit. These pulses are counted in a serial counter under programmed control in microcontroller board.

Microcontroller board essentially has an ADC, DAC, EEPROM and a serial counter apart from the serial port and embedded code. Under the command instruction from personal computer through
serial port, the firmware built-in initiates hardware functional cycle which essentially involves heating of the kanthal strip at the programmed heating rate, till it reaches required set temperature and clamping it for the desired duration if defined and follow the natural cooking cycle till the end of run time defined. During this time both temperature output (as read from the amplified thermocouple amplifier built-in into TC board and through ADC built-in into controller board) and TL intensity, (as read and recorded by serial counter through C to F converter), are logged and stored into EEPROM sequentially in to 200 channels (locations). Also DAC is programmed and incremented and output is fed to TC board to achieve programmed heating. As the programmed heating takes place, TL intensity is read.

Personal computer system with front end, TL glow curve data acquisition and analysis software (in VB) provides the required graphics user interface. Easy to use command buttons have been defined on the screen.

2.11 Source of creation of defects

2.11.1 Gamma irradiation

In order to create defects in titanate nanophosphors equal amount of sample powder were measured and covered with a black cardboard to avoid external radiations present in the surroundings. Then these samples were placed in the gamma chamber of energy
1.17 to 1.33 MeV [Irradiated at ISRO / ISAC, Bangalore, as per the standards of Board of Radiation and Isotope Technology, Mumbai]. The source used for measurements is shown in Fig.2.16. The dose rate of the gamma source used is 37 rad s\(^{-1}\). In the present studies the dose range used was 1-6 kGy exposed at room temperature.

Fig.2.16. Gamma source chamber used for irradiation

2.11.2 Calculations

The gamma radiation chamber dose rate = 37 rad/s,

In terms of kGy (1 Gy = 100 rad)

For 1 kGy, \[ \text{time} = \frac{10^4}{37 \times 60} = 45 \text{ min.} \]

Therefore, 45 min. is required for 1 kGy gamma irradiation.