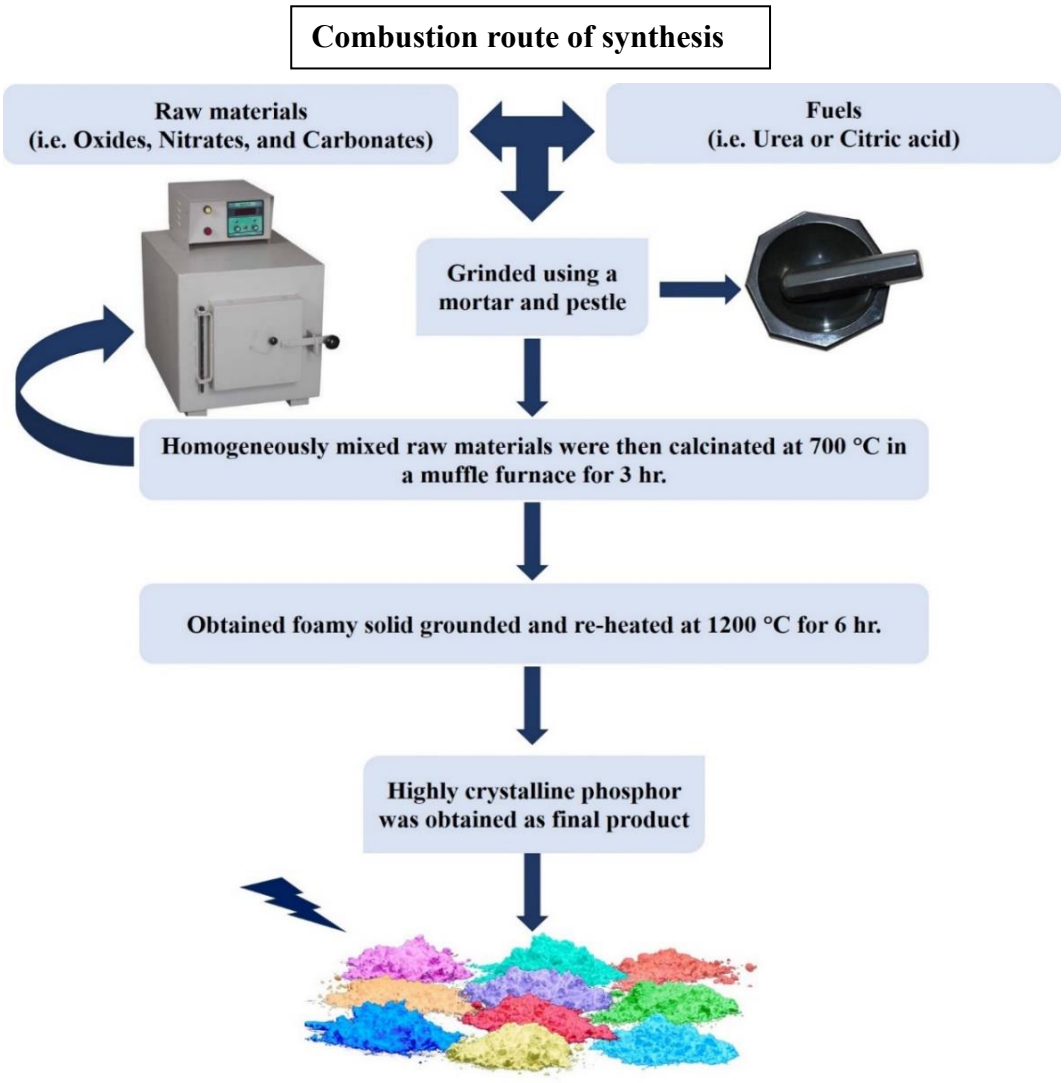
Chapter-2

Synthesis Method and Characterizations

Highlights

This chapter presents the information regarding the synthesis of materials and the synthesis method taken into account. A detailed knowledge of the combustion route of synthesis was discussed, including the principle, associated parameters, and precautions that must be taken. Secondly, the instrumentation techniques used for the structural and luminescence characterization were discussed, including XRD, SEM, FTIR, PL, and TL. These characterization techniques were discussed based on their working principles and their experimental results.



2.1 Synthesis Method

There have been several methods of phosphor synthesis were developed to synthesize the phosphors for the device applications. Nowadays, the solid-state reaction (SSR), the combustion route of synthesis, the sol-gel technique of material synthesis, and hydrothermal synthesis are the commonly employed material synthesis routes followed by researchers. Herein, we selected a two-step combustion route of synthesis for the phosphors preparation because it is simple, fast, reliable, and emits no emissions during the synthesis.

2.1.1 Combustion Rute of Synthesis

Combustion synthesis is a process characterized by the rapid oxidation of oxidants by fuel, which leads to the generation of a substantial amount of heat [1,2]. This process involves a series of exothermal chemical reaction between the fuel and the oxidants, resulting in both heat production and a transformation of chemical composition. This method is highly versatile and has found applications in the preparation of various kind of materials, including oxides, perovskites, ceramics, and semiconductors [3,4]. In recent years, the combustion route of synthesis has become vital in diverse scientific disciplines, including materials science, physics, and chemistry owing to its capability to produce micro- and nanocrystalline particles with scientific and technological implications [5,6].

The combustion process works in two fundamental ways:

(i) Propagation mode: In this mode of combustion, the reaction is begun by initiating ignition in a localized area, after which it spreads throughout the entire sample via a self-sustained combustion wave.

(ii) Volume reaction mode: By the volume reaction mode of combustion, the entire sample undergoes uniform heating to the ignition temperature, resulting in a simultaneous combustion reaction throughout the sample. This mode is also known as thermal explosion.

The volume reaction mode is particularly well-suited for the weak exothermic process of combustion, which requires material pre-heating before explosion. However, the propagation mode is widely applied as it forms the essential basis of the combustion process. In the propagation mode of combustion, the combustion wave moves through the whole medium, comprising both the fuel and the oxidants. As a result, the structure and properties of the reaction media play a substantial role during the combustion of the raw materials [7-9].

Based on the different media's, wherein the combustion taking place, this process of combustion is classified in two classes: (i) homogeneous and (ii) heterogeneous combustion. In the case of homogeneous reaction, the heat production and chemical reaction occur

uniformly, along with even heat transfer [10-12]. On the other hand, in heterogeneous reaction, heat production is discrete, and heat transfer remain uneven. Various control parameters are employed to manage the combustion reaction in synthesizing the materials for its diverse applications. Precise calculation of input materials and organization of control parameters such as flame characteristics, temperature variations, precursor chemical compositions, fuel-oxidant ratio, atmospheric conditions, and the composition of produced gases are crucial. Furthermore, this method finds utility in the synthesis of various complex compounds, including binary compounds, perovskites, and other complicated oxides.

2.1.1.1 Merits and Demerits

Compared to conventional solid-state reactions, combustion synthesis offers several advantages:

(i) Utilization of heat energy produced from exothermic reactions reduces energy consumption from the external source of energy during the reaction (heating).

(ii) The simplicity and low cost of equipment required for combustion synthesis contribute to more economical industrial production.

(iii) The exceptionally high temperatures facilitate the production of pure materials by eliminating additional impurities through evaporation.

(iv) This reaction is too rapid, leading to swift conversion of raw materials into the final products in very short timeframe.

However, there are some drawbacks of this method:

(i) The combustion process involves the sudden ignition of fuel and oxidants, leading to explosive conditions.

(ii) Material synthesis using this method may result in multiphase formation due to uneven temperatures during the combustion process, which may result in material agglomeration.

This study entitle “Luminescence Studies of Rare Earth Doped Perovskite Phosphors” describes the luminescence studies of total 25 samples which are synthesized using the combustion route of synthesis.

Figure 2.1 provides an illustration of the steps involved in combustion synthesis.

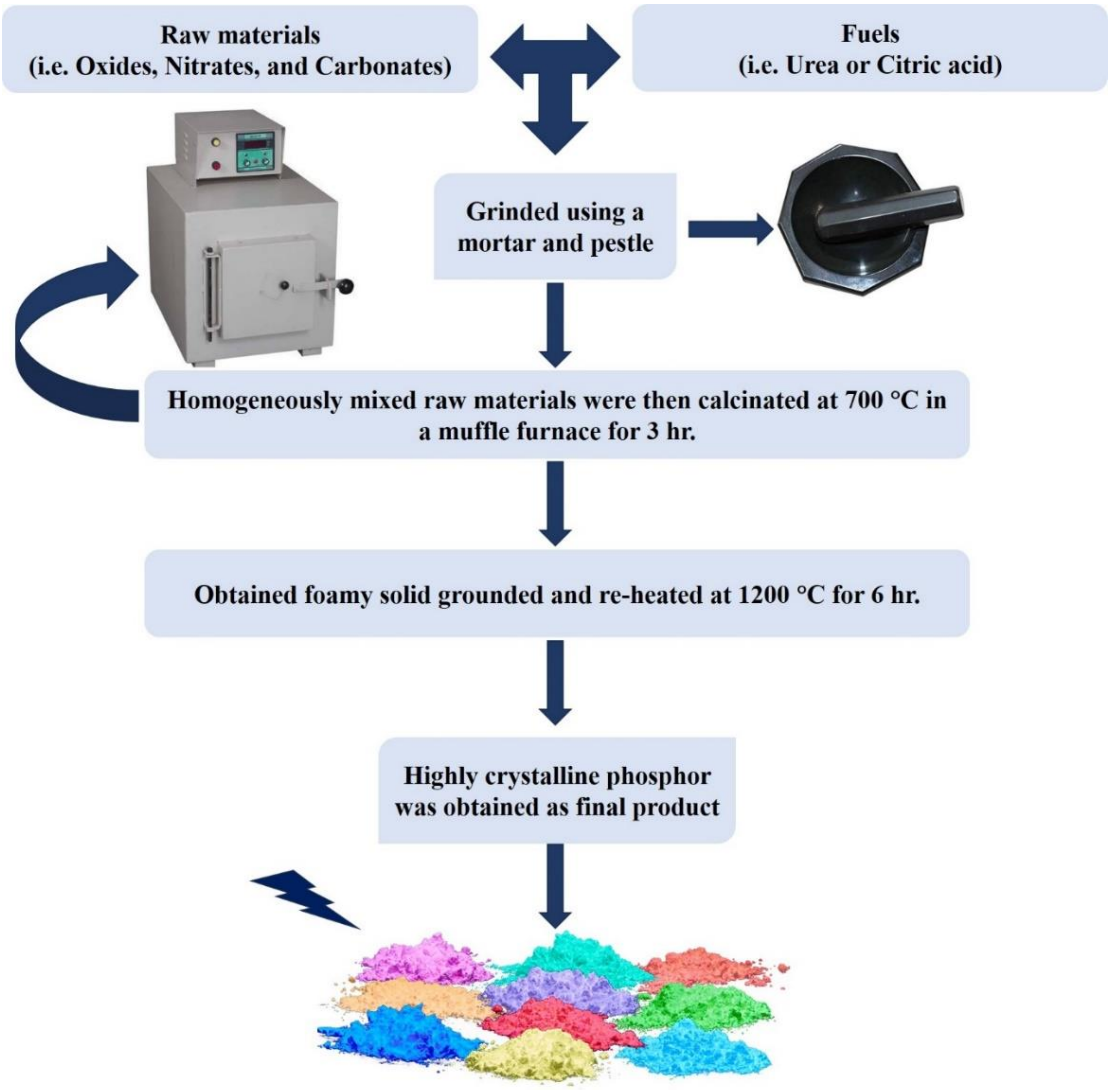


Figure 2.1. Flow chart of combustion route of material synthesis.

2.2 Material Characterization Techniques

2.2.1 X-ray Diffraction (XRD)

XRD is a powerful analytical technique utilized in order to study the crystal structure of the synthesized materials [13]. It provides vision of the arrangement of atoms within a solid and gives the valuable information about its crystallographic properties, such as lattice parameters and crystal symmetry. XRD working on Bragg's law, according to which the X-rays strike a crystalline material at a specific angle, they are diffracted by the crystal lattice [14]. The resulting diffraction pattern consists of characteristic peaks that correspond to the different planes of the crystal lattice. By analyzing the position of diffraction angles and intensities of these diffraction peaks, the crystal structure, unit cell dimensions, and type of crystal present in a sample can be determine. It is used to identify unknown materials, study phase changes,

and investigate the effects of different parameters, such as temperature, pressure, and mechanical stress on crystalline structure. By means of fitting the data with the standard reported data, the study of XRD pattern can be accomplished. In this study, we used Fullprof suite software of XRD data analysis [15].

2.2.1.1 Instrument Used to Monitor Diffraction Patterns:

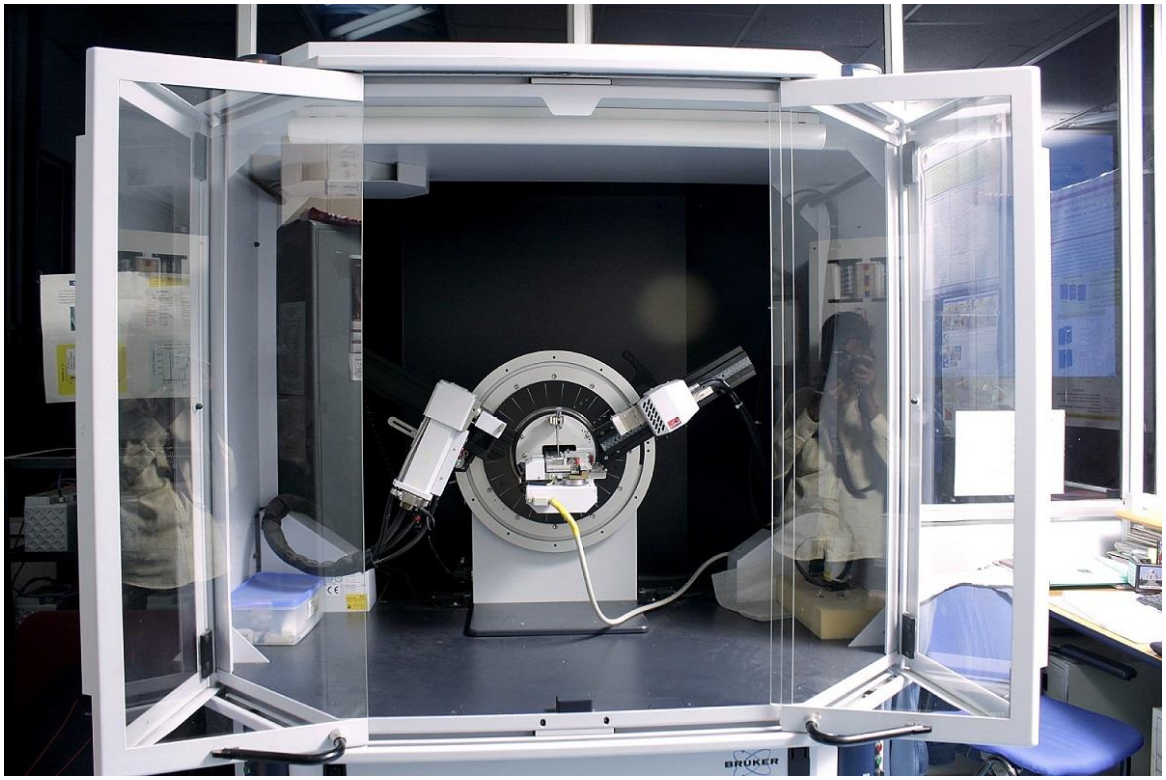


Figure 2.2. Bruker D8 Advance diffractometer.

XRD measurements for all prepared phosphors under study were conducted at UGC-CSR centre of Indore. The diffraction patterns were recorded using Bruker D8 X-ray diffractometer. This machine employs Cu-Kα as the X-ray source, generating X-rays with a wavelength of 0.15406 nm under an effective energy of 40 kV and an effective current of 40 mA. The measurements were executed for diffraction angle ranging from 10° to 80°, in increments of 0.02° per second.

2.2.1.2 Applications of XRD

XRD is a widely recognized technique utilized for discerning synthesized materials, including minerals, ceramics, and artificially prepared substances. Moreover, it facilitates the availability of multiple crystal phases within mixtures if it is available. Additionally, XRD is employed in determining the crystalline structure and assessing the proportion of amorphous materials in partially crystalline mixtures. This technique is instrumental in conducting structural analyses and unit-cell identification for highly crystalline substances. Furthermore,

XRD is utilized for quantitatively assessing the quantities of various phases through peak-ratio calculations and whole-pattern refinement. It also enables the crystallite size calculation by analyzing peak broadening, as well as the characterization of crystallite shape through the examination of peak symmetry in XRD patterns [16].

2.2.2 Scanning Electron Microscopy (SEM)

SEM is a tool to read the surface and particle sizes of the materials by employing a high-powered electron beam to image the objects at extremely fine magnification, ranging from micro to nanoscale [17]. SEM attached with EDAX facility provides compositional analysis of the phosphors and materials. SEM is primarily employed for the examination of material surfaces. As per the principle, a highly energized electron beam is focused onto the material, generating secondary electrons based on the material's structure and morphology [18]. These secondary electrons were then collected via the detector operating at high potential. These electrons, once spotted, it produces a scintillation effect within photomultiplier tube, converting them in the electronic signals [19]. These signals undergo additional amplification via the video amplifier and are subsequently processed by the system to construct a three-dimensional photograph of material. The resulting image is form by the interface among incident electrons and the material. This interaction yields a variety of signals which provide info regarding surface geography and composition.

2.2.2.1 Instrument Used to SEM Micrograph Recording

Figure 2.3. Carl Zeiss Model Supra 55 FESEM.

The SEM-EDAX analysis were carried out at A-to-Z laboratory Bombay, shown in Figure 2.3. More details are found in the following link.

Link: https://www.labatoz.com/instrument-company/26/FESEM

2.2.2.2 Applications of SEM

SEM finds extensive applications in diverse fields of science and technology, providing valuable insights into microscopic processes underlying their studies and enabling macroscopic inferences. It is a prevalent tool used for investigating various aspects of objects or materials, including surface topography, morphology, as well as crystallographic details like particle structure and material porosity.

2.2.3 Fourier Transform Infrared (FTIR)

FTIR is technique plays a pivotal role in various research domains, including chemical science, physical science, and material research. It is utilized to acquire infra-red band of both liquid and solid materials, employing either transmittance or absorption mode of the IR instrument [20,21]. This technique utilized to distinguish the existence of organic and inorganic functional groups within fresh prepared materials. Through the mathematical tool application, specifically Fourier transform, the data collected from the interferogram is translated into a definitive spectrum. This spectrum represents distinct modes of absorption or transmittance corresponding to the specific bond formations within prepared material. The FTIR spectrometer is primarily recorded within the range of 400-4000 cm^{-1}, allowing for the determination of prevailing functional groups within material through the IR transmittance. This technique is very useful for identifying functional groups forms within the materials, detecting contaminants, identifying impurities [22].

2.2.3.1 Instrument Used to FTIR Study

Figure 2.4. JASCO-4600 IR spectrometer.

The FTIR spectra measurements of the as-prepared phosphors were conducted at the Physics Department, Faculty of Science, The M. S. U. of Baroda. For the spectra measurements, we employed KBr (potassium bromide) pellet technique, wherein, the KBr and phosphor were taken in 99:1 ratio and grounded using mortar and pestle. Later, the pellet of the mixture was made using a pelletizer by applying 3 Toor of pressure. The FTIR spectra was acquired using JASCO-4600 IR spectrometer, shown in Figure 2.4. The IR spectra of all the phosphors under study were recorded in transmittance mode, covering a wavenumber region between 400 and 4000 cm^{-1}.

More details of the instrument are found from the following link.

Link: http://www.jascoint.co.jp/asia/products/spectroscopy/ftir/ftir4600.html

2.2.3.2 Applications of FTIR

FTIR spectroscopy offers insights into a diverse array of materials, including isolated substances and biomaterials, such as connection tissues, individual cells, and various biological liquids. This technique is applicable for the analysis of nearly entirely carbon-based compounds and certain inorganic materials. It finds extensive use in both qualitative and quantitative analyses. Moreover, IR spectroscopy imposes no phase restrictions on samples; they can be in the form of gas, liquid, or solid, thereby broadening the scope of potential applications [23].

2.2.4 Photoluminescence (PL)

A brief discussion on the photoluminescence phenomenon is already discussed in section 1.2.4.1.

2.2.4.1 Instrument Used Photoluminescence Study

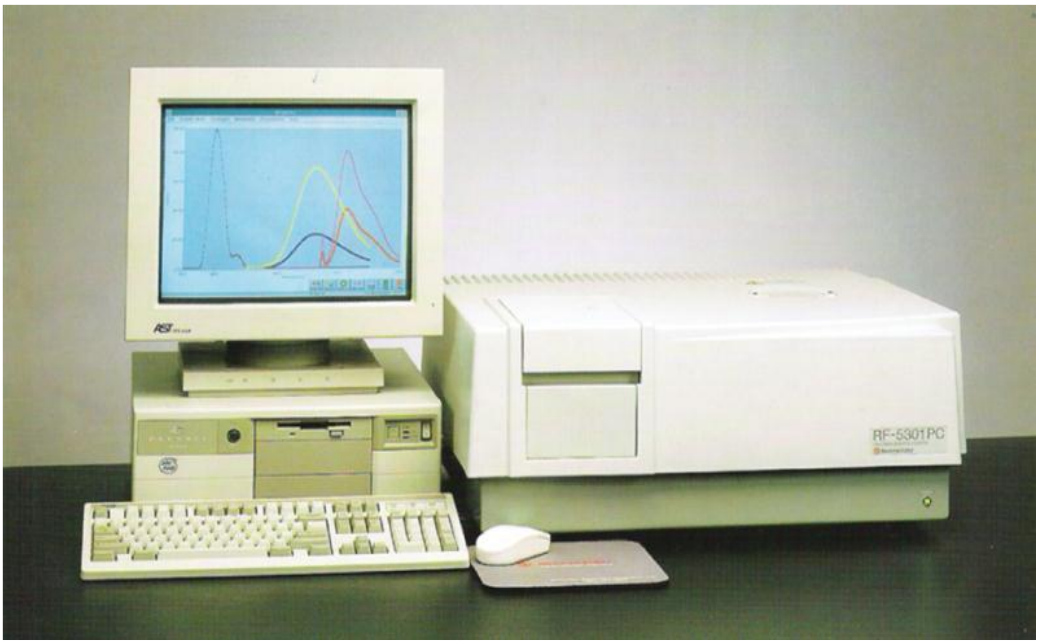


Figure 2.5. Shimadzu Spectro-fluorophotometer (Model: RF5301 PC; Shimadzu Japan).

The PL spectra of all the phosphor materials was recorded at ambient temperature condition using a Shimadzu Spectro-fluorophotometer (model: RF5301 PC; Shimadzu Japan), wherein a xenon lamp is utilized as the excitation medium, shown in Figure 2.5. The spectra measurements were conducted at the Department of Applied Physics of The M.S. University of Baroda. More details of the equipment were found from the link given below. https://speciation.net/Database/Instruments/Shimadzu-Europe/RF5301-Spectrofluorophotometer-;i2704

2.2.4.2 Applications of Photoluminescence

Photoluminescence is extensively used in numerous arenas, together with materials science, chemistry, and electronics, to study the properties and characteristics of semiconductors, nanoparticles, and other optically active materials. Moreover, in recent research, the WLEDs found the centre of attraction [24-26].

2.2.5 Thermoluminescence (TL)

Thermoluminescence (TL) is a phenomenon that occurs in quartz, minerals, and phosphor materials (ceramics) with wide energy band gaps upon absorption of high-energy radiation [27-30]. A detail on TL phenomenon is already discussed in section 1.2.4.2.

2.2.5.1 Instrument Used Thermoluminescence Glow Curve Measurements

The TL glow curves measurements were accomplished at the "Luminescence Materials Laboratory" at Department of Physics, Faculty of Science, The M. S. U. of Baroda. A PC-controlled TL reader of type TL1009, designed by Nucleonix was utilized for the TL measurements, shown in Figure 2.6. The sample irradiation was done via the Sr-90 beta source available at Applied Physics Department of The M. S. U. of Baroda.

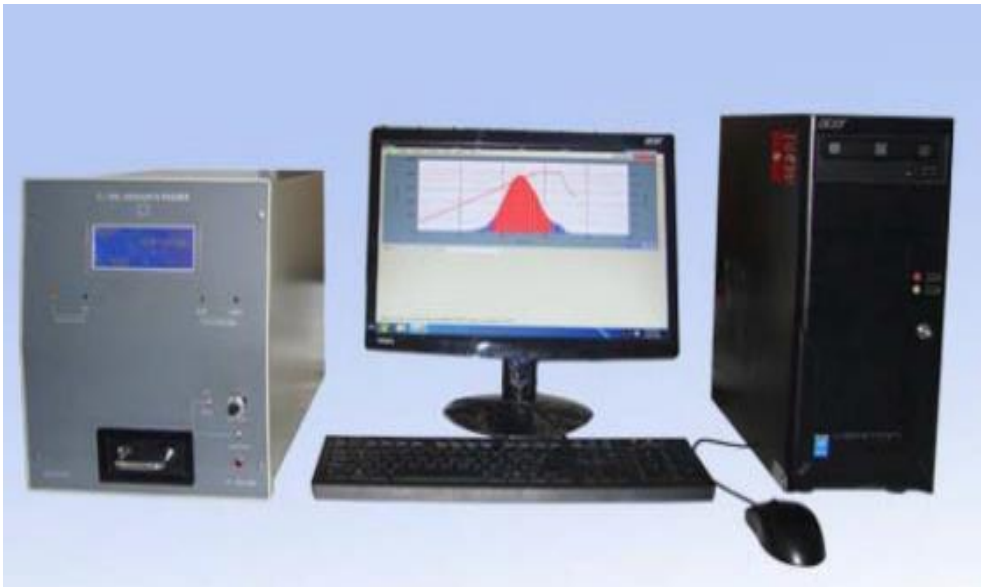


Figure 2.6. PC-controlled TL reader of type TL1009, designed by Nucleonix.

More details are available in following link:
https://www.nucleonix.com/product/tl-research-readers/.

Moreover, some of the TL glow curve measurements were carried out at the Atomic, Molecular and Optical Physics division, Physical Research Laboratory (PRL) at Ahmedabad. The Risø TL/OSL reader DA 15 (Bøtter-Jensen et al., 2003) instrument was used to record the TL glow curves. For the sample irradiation, the Sr-90 beta source was used with dose rate of 0.043 Gy per sec. Figure 2.7 depicts the set-up of Risø TL/OSL reader DA 15 (Bøtter-Jensen et al., 2003) instrument [31].

Figure 2.7 Risø TL/OSL reader DA 15 (Bøtter-Jensen et al., 2003) instrument.

More details are available in following link:
https://www.fysik.dtu.dk/english/research/radphys/research/radiation-instruments/tl_osl_reader/reader-details

2.2.5.2 Applications of Thermoluminescence

The TL is the technique used in archaeology and geology; TL dosimetry, radiation Hardness testing; and environmental geological studies [32].

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