Chapter 2

Instrumentation, Synthesis and Fundamentals of Alkaline Earth Aluminates

In theory, there is no difference between theory and practice.
In practice, there is a big difference.

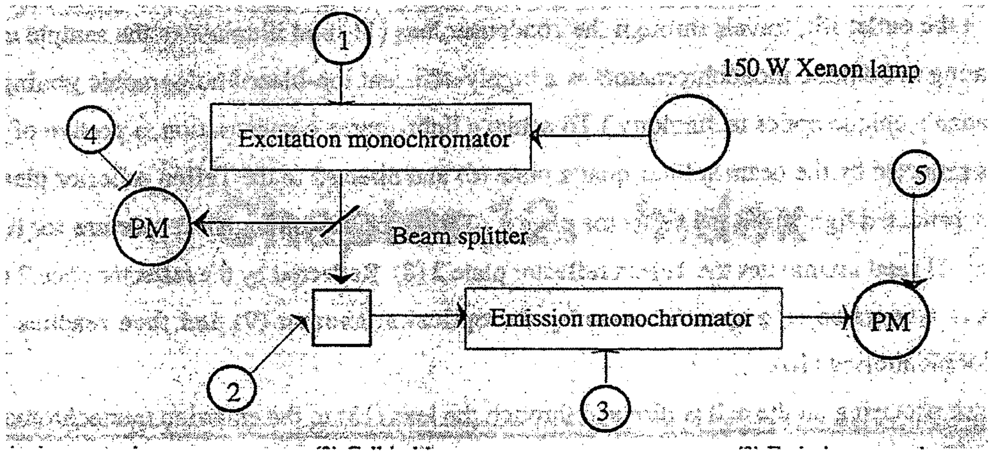
2.1 Introduction

In this chapter a brief description of the instrumentation used in this study and more importantly the reason behind their preference will be given. The techniques have been excessively utilized for determination of phase of the phosphor and their luminescent properties as well. These techniques are: X-Ray Diffraction technique, Spectroflurophotometer for detection of the photoluminescence characteristics and Nucleonix make TL reader for observing the radiation induced defects in the phosphor material.

This will be followed by detailed experimental procedure for the phosphor synthesis and the brief information of the structure of the $3SrO.Al_2O_3$ phosphor.

2.2. Optical System of Spectrofluorophotometer

The spectrofluorophotometer irradiates a sample with excitation light and measures the fluorescence emitted from the irradiated sample to perform a qualitative or quantitative analysis. A typical configuration of the spectrofluorophotometer is schematically described below (Fig. 2.1taking the RF-5301 PC instrument as an example).



1)Excitation monochromator, (2) Cell holder, (3) Emission monochromator,

4) Monitor side photomultiplier tube, (5) Fluorescence side photomultiplier tube

Figure 2.1. Block diagram of RF-5301 PC [1]

The excitation monochromator (1) isolates a band of a particular wavelength from the light from the Xenon lamp to obtain excitation light. Since brighter excitation light will contribute to higher sensitivity of the spectrofluorophotometer, the excitation monochromator incorporates a diffraction grating with a larger aperture to collect the largest possible amount of light.

The cell holder (2) holds a cell filled with sample. The emission monochromator (3) selectively receives fluorescence emitted from the sample and its photomultiplier tube measures the intensity of the fluorescence. This monochromator has a diffraction grating whose size is the same as that of the excitation monochromator to collect the greatest possible amount of light. The photomultiplier tube (4) is for monitoring. Generally, the Xenon lamps used on spectrofluorophotometers are characterized by very high emission intensity and an uninterrupted radiation spectrum. However, their tendency to unstable light emission will result in greater signal noise if no counter measure is incorporated. In addition, the non-uniformity in the radiation spectrum of the Xenon lamp and in the spectral sensitivity characteristics of the photomultiplier tube (these criteria are generally called instrument functions) causes distortion in the spectrum. To overcome these factors, the photomultiplier tube (4) monitors a portion of excitation light and feeds the resultant signal back to the photomultiplier tube (5) for fluorescence scanning. (This scheme is called the light-source compensation system.)

The optical system of the RF-5301PC instrument is illustrated in Fig. 2.2 A 150 W Xenon lamp (1) serves as the light source. The uniquely designed lamp housing contains generated ozone in it and decomposes the ozone by means of the heat produced by the lamp. The bright spot on the Xenon lamp is magnified and converged by the ellipsoidal mirror (2) and then further converged on the inlet slit of the slit Assy. (excitation side) (3) by the concave mirror (4). A portion of the light isolated by the concave grating (5) passes through the outlet slit, travels through the condenser lens (11) and illuminates the sample cell. (The concave grating in both the monochromators is a highly-efficient ion-blazed holographic grating). To achieve light -source compensation, a portion of the excitation light is reflected by the beam splitter quartz plate (6) and directed to the Teflon reflector plate 1 (7). The diffusely reflected light from the reflector plate (7) then passes through the aperture for light quantity balancing (21) and illuminates the Teflon reflector plate 2 (8). Reflected by the reflector plate 2 (8), the diffuse light is attenuated to a specific ratio by the optical attenuator (9) and then reaches the photomultiplier for monitoring (10). The fluorescence occurring on the cell is directed through the lens (13) to the emission monochromator that comprises the slit Assy. (14) and the concave grating

(15). Then, the isolated lights introduced through the concave mirror (16) into the photomultiplier for photometry (17) and the resultant electrical signal is fed to the preamplifier.

The spectra recorded using the above instrument displays the spectra along with the peak data and the same can be copied to any other format, which is user-friendly software.

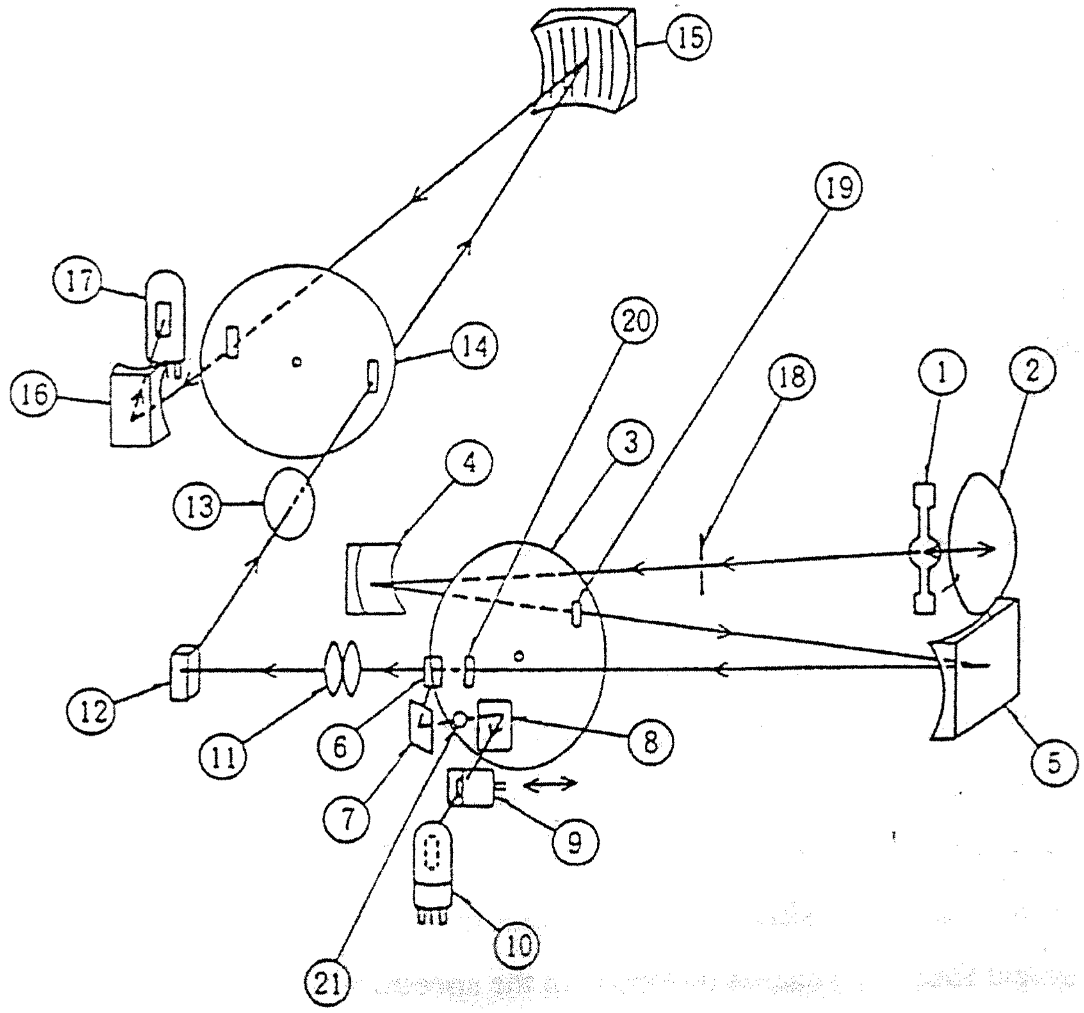


Figure 2.2. Optical System of RF-5301PC

[1] Xenon lamp, 150 W
[2] Ellipsoidal mirror, SiO_2-coated
[3] Slit Assy., excitation side
[4] Concave mirror
[5] Concave grating (for excitation)
[6] Beam splitter quartz plate
[7] Teflon reflector plate I
[8] Teflon reflector plate 2
[9] Optical attenuator
[10] Photomultiplier for monitoring, R212-14
[11] Condenser lens (dual-lens)
[12] Cell
[13] Condenser lens
[14] Slit Assy., emission side
[15] Concave grating (for emission)
[16] Concave mirror
[17] Photomultiplier for photometry, R3788-02
[18] Focal point
[19] Inlet Slit
[20] Outlet slit
[21] Aperture for light quantity balancing

From routine analysis to research, employing highest level of sensitivity in the world! Compared to absorbance methods, fluorescence sensitivity is tens to thousands times better – this means that one can analyze nano grams to pico gram samples with great results. Fluorescence can be used also to identify a specific molecule in a complex background. When the compound of interest does not exhibit natural fluorescence, functional group-specific probes may be used to label the compound & assist our research, the synchronous scanning mode allows mixtures of fluorochromes to be analyzes. The personal computer directly controls the instrument for data acquition & processing. The windows friendly operating environment allows us to perform measurement, data processing, editing & recording in one continuous operation with a click of the mouse. Using the copy graph function, measurement data or spectra may be easily transferred to word processing or spreads heat software for preparation of documents or additional calculations. The essence of fluorescence analysis is sensitivity. The high throughput optical system in the RF-5301PC employs a blazed holographic grating, photomultiplier & digital circuit to provide the highest level S/N ratio attainable. High speed scanning. High speed scanning up to 5500 nm/min allows us to measure a spectrum in seconds. And since monochromator slewing is conducted at an ultra-high speed of about 20000nm/min, setting of two or more wavelengths can be performed quickly & easily. High resolution and extended range The band pass on the RF-5301PC may be set as narrow as 1.5nm, which makes is possible to distinguish fluorescent peaks from the background emission. The wave length range of 220 to 750 nm can be extended to 900nm with an optional R-928 photomultiplier. Built in performance checks. When the instrument is switched on, operating conditions of the spectrophotometer are automatically verified. Separately, a noise level (S/N ratio) & the light source (xenon lamp) usage are built in features to help maintain the instrument in its optimum condition, providing absolute confidence in either quality of the data. Versatile sample compartment size. The sample compartment measuring 140mm, 170mm deep & 140mm high, enables use of micro cells, high sensitivity cells, or low cells, etc., for a wide range of applications. Unique high performance features in the RF-5301PC. Wavelength search functions allow the optimum excitation & emission wavelengths to be found in about two minutes. Vertical optics with dynode feedback, Vertical optics in the RF-5301 PC minimize light loss in measurement with an LC flow cell a micro cell or small test tube. This design assures exceptionally high signal to noise ratio and provides the ability to attain excellent analysis results using very small volumes of precious samples. The dynode feedback enhances RF-5301PC performance by raising or lowering negative high voltage to the detector in response to differences in the excitation energy at wavelengths. Dynode feedback which expands the dynamic range of the signal detecting system is significantly superior to ratio methods.

Automatic shutter protects sample an automatic shutter in the RF-5301PC excitation path closes immediately when measurement ceases, thereby protecting the sample from photodecomposition. See the difference with windows performance working in the windows 2.1 environments makes operation intuitive. The software is driven by pull-down menus displayed at the top of your screen that can be selected with just a click of the mouse. Many convenient and time saving features The RF-5301PC software is the ideal software to meet all our research needs, from teaching to method development and quality assurance. Follow changes in intensity over time for kinetic assays or perform quantitative analysis on several samples. One can save time & effort with features that allow for onscreen data manipulation.

Spectrum measurement mode performs emission & excitation scans with ease, or overlay the two for interpretation. Obtain & differentiate excitation & emission spectra using color & line Pattern assignments. Zoom in using the mouse or zoom out with the radar function to auto scale all data on-screen. The software picks & tabulates peaks & valleys automatically and if one needs a fast spectral scan in any measurement mode, the pop up scan function displays it on- screen in seconds. Simple but powerful for extensive data processing operations such as first through fourth order derivative, mathematical smoothing functions, log conversions & offsets are easily performed with the RF-5301PC software [2]. Display up to ten spectral curves simultaneously or use mathematical transformations to maximize our results. Select the source & destination channels along with the desired calculation & the results are redisplayed on the screen. The following is the photograph of the RF 5301PC along with solid sample holder.

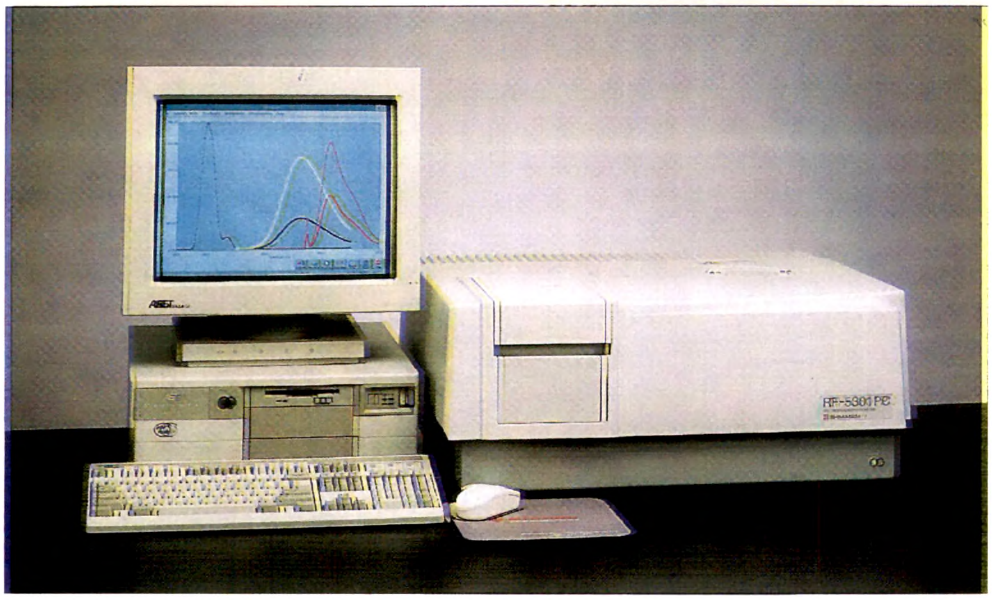


Figure 2.3. Spectrofluorophotometer, RF-5301PC

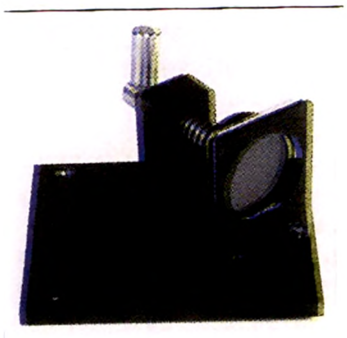


Figure 2.4. Spectrofluorophotometer Powder Sample Holder

Table 2.1 Hardware specifications

Light source	150W xenon lamp. Ozone resolving type lamp housing
Excitation & emission mono chromators	Concave, blazed holographic grating,f/2.5, 1300 grooves/mm.
Wavelength scale	220-900nm
Measuring wavelength range	220-750nm & 0 order as standard. 220-900nm with the optional R928 photomultiplier.
Spectral bandwidth	6-step selection of 1.5,3,5,10,15 & 20nm.(6nm bandwidth is available for half sample height on the excitation only)
Wavelength accuracy	±1.5nm
Light source compensation	Dynode feedback system with monochromatic light monitoring.
Sensitivity	The S/N ratio is 150 or higher for the Raman line of distilled water (350nm excitation wavelength ,5nm spectral band width ,& 2 second response for 98% of the full scale).
Wavelength scanning	7-step selection of survey(about 5500nm/min), super (about 3000nm/min), very fast ,fast, medium , slow & very slow.
Wavelength slewing speed	About 20000nm/min.
Response	8-step selection of 0.02,0.03,0.1,0.25,0.5,2,4& 8 seconds or 98% of the full scale.
Sensitivity selection	2-steps of high & low. (the sensitivity at high is about 50 times that of low).
Interface	RS-232C interface, interface for the auto sampler , and interface for sipper unit.
Dimensions & weight	667W*530D*270Hmm ;43 kg.
Power requirements	220V, 15 amps, 50Hz
Operational temperature range	
Operational humidity range	40-80 %(below 70% with temperature higher than 30 °C)

Table 2.2 Software Specifications

Measurement	Excitation, emission & synchronous spectrum measurement ,time-course measurement, quantization, automatic search of optimal excitation & emission wavelengths ,Popup Scan.
Data processing	Arithmetic calculation between spectra & between a spectrum & a constant, smoothing,1st through 4th derivatives,1/Y,logarithmic conversion, data printout(with or without activity value computation),peak pick, point pick, area calculation, averaging(in quantitation), generation of calibration curves of 1st through 3rd order.
Filing	Save, recall,& delete ,of data. Conversion into ASCII & DIF formats.
Data output	Automatic scale adjustment, readout of data at user –specified point, data printout(preview function provided),selection of colors & types of curves
Maintenance	automatic monitoring of signal-to-noise ratio, monitoring of the run time of light source lamp.
User interface	Speed –box (assigns icons for commonly used menu commands).
Other functions	Data exchange via clipboard, auto response control, and automatic shutter.
PC requirements	IBM-PC/AT or 100% compatible;! 486 or higher CPU ; 8 Mbytes or larger main memory. Operates on MS –windows version 3.1 or higher.

2.2.1. Measurement Procedure

A solid sample holder is provided with the fluorometer. It enables collection of front face fluorescence at an angle of 22.5°. The powder sample was spread on it. The sample holder was fixed into sample compartment. When analyzing the sample, optical axis runs along the centerline of powder surface. First the excitation spectra were recorded by setting the emission wavelength at the zero order and keeping other parameters as specified in the manual. The excitation bands were identified from these spectra and the emission spectra were scanned for identified excitation wavelength. This was necessary to know the approximate nature of EX spectrum, so it is necessary to select a particular band in the emission for scanning the excitation. Therefore for proper excitation spectra the emission wavelength was set at the position as identified from the earlier emission spectrum. The excitation and emission spectra were recorded with spectrometer slit fixed at 1.5 mm.

2.3. Thermoluminescence (TL) Glow Curve Recorder

The thermoluminescence glow curve reader consists of a specimen holder along with heater, a temperature programmer, a photomultiplier tube as detector, a high voltage unit, a .D.C. amplifier and a suitable displaying or recording device, as shown in Fig. 2.5 [3]. Also Fig.2.6 presents the TL detection head and Sr-90 beta source.

Figure 2.5. Thermoluminescence Setup

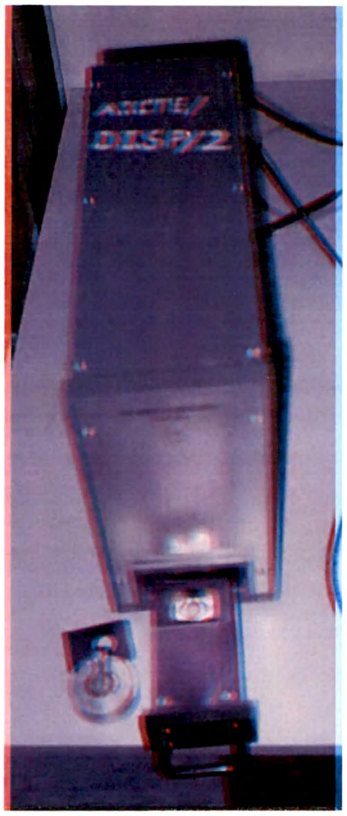


Figure 2.6. Kanthal Strip and TL detection head. Right side is the Sr-90 beta source used in the present investigation.

Radioactive Sources for Irradiation:

For β- irradiation Sr-90 source is used and a test dose of 10Gy is given to study the TL of the phosphors.

The specimen is spread uniformly (5mg weighed) over a metallic strip of Kanthal (Fe-72 %, Ce- 23 %, Al – 3 %, and Co – 2 %). The strip is narrow and has a circular depression of 15 mm at its center. A chromel-alumel thermocouple is spot welded to record the temperature of the specimen. The uniform heating rate that is controlled by the temperature programmer maintains a linear relationship between the rise in temperature versus time. The photomultiplier tube is housed in a light-tight cylinder and a high voltage is applied to it. When the kanthal strip is loaded with the irradiated specimen which is placed in front of the photomultiplier window, the light emitted by the specimen during heating is recorded through the photomultiplier window. The light emitted by the specimen during heating is detected by a photomultiplier tube and is recorded through auto ranging D.C. amplifier by the output device.

In the present study, the thermoluminescence glow curves of the samples were taken on a Nucleonix make Windows Based thermoluminescence reader. The system consists of a PMT housing with drawer assembly, high voltage module, AM576 TL data acquisition module with auto ranging facility, Temperature programmer controller unit, power supply unit, AD-DA card and a personal computer system along with required hardware and software. Block diagram is given in Fig 2.7.

The power supply provides four different outputs with a ripple and noise better than 3 mV at full load for all the supplies. The TL data acquisition module AM 576 is a two bit module which converts the PMT current into a proportional voltage signal which is in built auto ranging facility. Due to this facility one can record TL intensity as a digitized signal and can be transferred to the computer.

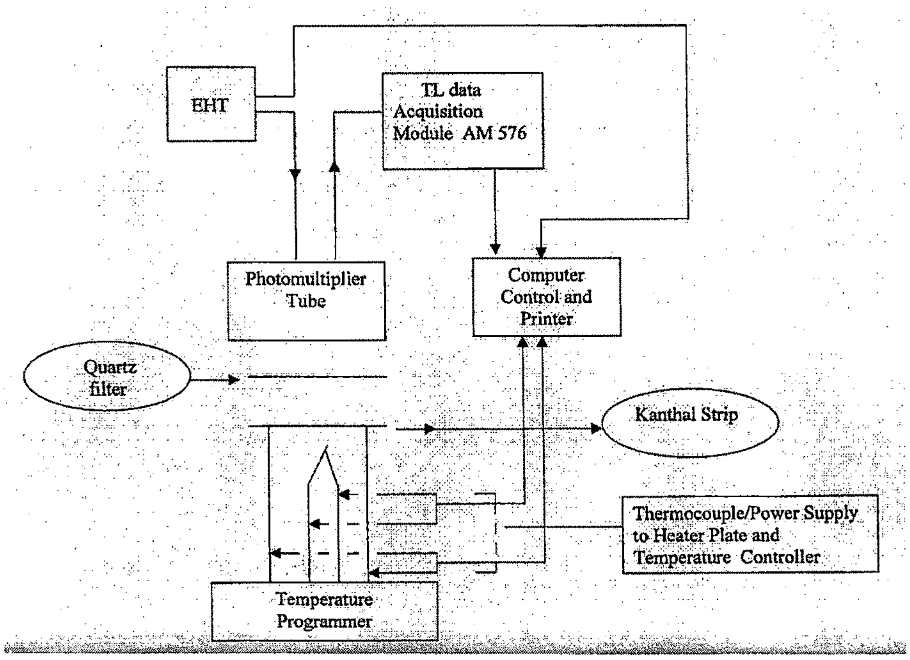


Figure 2.7. Block Diagram of TL Set-up

The temperature controller T C 575 works in PC programmable mode as well as ISO mode. The temperature range is from room temperature to 500 ^{0}C, with an accuracy of $\pm 2\ ^0$C. Temperature is increased by resistive heating and is measured by a thermocouple sensor. Various type of heating profiles, temperature in different regions, time heating rates, etc. can be set through the windows program specially developed for TL acquisition. The controller accepts DAC output signal from the AD – DA card to make up for the various functions. The high voltage unit, HV 501 generates EHT in the range of 0 – 1500 V, 1 mA, which is used for biasing the PMT. The ripple and noise is better than 15 mV. The PMT (type EMI 9924 B) and heater drawer assembly is a compact, light leakage free housing with PMT mounted inside. There is a IR cut-off, i.e. heat absorbing filter provided just below the PMT window. The housing has a kanthal strip with a circular depression of 15 mm diameter for loading of TL materials.

Among the computer components are, an IBM compatible Pentium-III 750 MHz or above with 64 MB RAM, 1.44 MB mini FDD, 40 GB Hard disc drive, SVGA color monitor and mouse and A4 size Inkjet printer, with color cartridge. The window-based software is developed in Visual C^{++} 4.0. The following is the procedure for making the TL measurements.

2.3.1. Procedure to Measure TL more accurately using NUCLEONIX PC based TL Reader System:

Precautions to be observed for measurements with TL materials in powder form :

a. It is very important to measure the powder accurately and place it into the kanthal strip.
b. Accuracy depends mainly on the accurate weight measurement.
c. Powder should not be placed on the kanthal strip as a heap but should be spread uniformly. This ensures that while heating takes place all the particles in the powder get heated up to the same temperature.
d. While disposing from the kanthal strip, it should be gently brushed aside, so that powder particles fall on to the collection tray.
e. Any particle left out may contribute to the next measurement as a residual TL adding to the next sample, measurement being inaccurate to that extent.

III Choosing appropriate heating profile :

a. Depending on the type of TL material (CaSO4, LiF or other material) and the form in which it is used (disc, rod, chip, powder crystals, pellets etc.) the heating profile is to be chosen.
b. The purpose of choosing most appropriate heating profile is primarily to maximize TL output and leave minimum residual TL in it. Also to minimize the contributions due to thermal and IR emissions.
c. Most commonly used heating profiles are

   1 Linear, 2 Linear with cooling region included into total run time, 3 Linear clamped (Single plateau), 4 Linear clamped with cooling region included in run time.

d. For Teflon coated disc, it is desirable to choose either linear clamped or linear clamped with cooling region. Longer clamped duration may be required to ensure that TL emission is complete and residual TL is completely removed.
e. Clamping temperature around 300°C is more than is enough in majority of cases for normal TL materials (other than pottery, sand and geological samples)
f. Thermal emission starts above 300 ° onwards hence it is important that we restrict heating to set temperatures up to maximum of 300 °C Up to 350 °C in some cases provided there is good IR cut-off filtering done.
g. For low-level TL measurements if it is provided it helps in any spurious signal due to oxidation and other effects.
h. For low-level TL measurements it is better to choose a heating profile of " Linear clamped with cooling region included ". Because some TL curve may extend in to this region. Also restrict clamping to 300 °C to restrict thermal contribution.

Some time it may be better to clamp at 300 °C for certain time say 5 to 10 sec or even more to ensure that no residual TL is left. In which choose profile "C(4)" . For powder clamping for 5 to 10 sec may be enough.

After first time TL acquisition, if you rerun the sample, you will get background profile, which will also indicate if there is some residual TL. For Teflon embedded / coated discs, recommended profile is "C (4)" and it is essential to clamp it for longer duration of the order of 40 to 60 sec. {Profile region {1-2}}. Linear heating region (0-1) may be about 60 sec and total run time can be about 150 sec to include some cooling region.

i. The best way to require for background is after the TL glow curve acquisition, once again acquire for back ground and save this file as bdg.gtl (by default). This way if it is done it will indicate whether TL has been fully extracted and what extent of residual TL is remaining in the background.

For better accuracy, at least three measurements are to be taken and averaged.

The TL reproducibility of phosphor is found to be ± 2 %

2.4. X-ray diffractometer (XRD)

This is an easy technique for the characterization of known as well as unknown samples. The simplicity of this technique is due to the specific value of 'd' spacing for a compound. These 'd' values are automatically generated from the computer program. An important feature of diffractometer is its ability to focus into a sharp line, the radiation that is Bragg reflected from an extended specimen area. In this instrument, essentially monochromatic radiation is used and the X-ray detector is placed on the circumference of a circle centered on the powder specimen. The essential feature of diffractometer is shown in fig.2.9. Powder specimen C, in the form of a flat plate, is supported on a table H, Which can be rotated about an axis O, perpendicular to the plane of the paper. The X-ray source is S the line focal point on the target T of the X-ray tube, S is also normal to the plane of the drawing and therefore parallel to the diffractometer axis θ. X-rays diverge from this source and are diffracted by the specimen to form a convergent diffracted beam which comes to a focus at the slit F and then enters the counter G .A and B are special slits which define and collimate the incident and diffracted beams.

The receiving slits and counter are supported on the carriage E, which may be rotated about the axis θ and whose angular position 2θ may be read on the graduated scale K or directly on a X-ray recorder as is the situation with the 'PHILIPS' diffractometer, which was used for the characterization of samples in this study. The supports E and H are mechanically coupled so that a rotation counter through 2θ degrees is automatically accompanied by rotation of the specimen through θ degrees. This coupling ensures that the angles of incident on and reflection from, the flat specimen will always be equal to one another and will be equal to half angle of diffraction, an arrangement necessary to preserve focusing conditions.

For recording the diffractogram of a powdered specimen, the counter is set near $2\theta = 10^{\circ}$ run up to 100° and collected to a counting rate meter. The output is connected to a PC the d values are calculated automatically. The counter is then driven at a constant angular velocity through increasing values of 2θ until the whole angular range is scanned. At the same time, the paper chart on the recorder moves at a constant speed' so that the distances along the length of the chart are proportional to 2 θ. This gives a record of counts per second versus diffraction angle 2 θ [4].

For taking the XRD patterns of samples in the work, a X- ray diffractometer of 'PHILIPS' make was used.

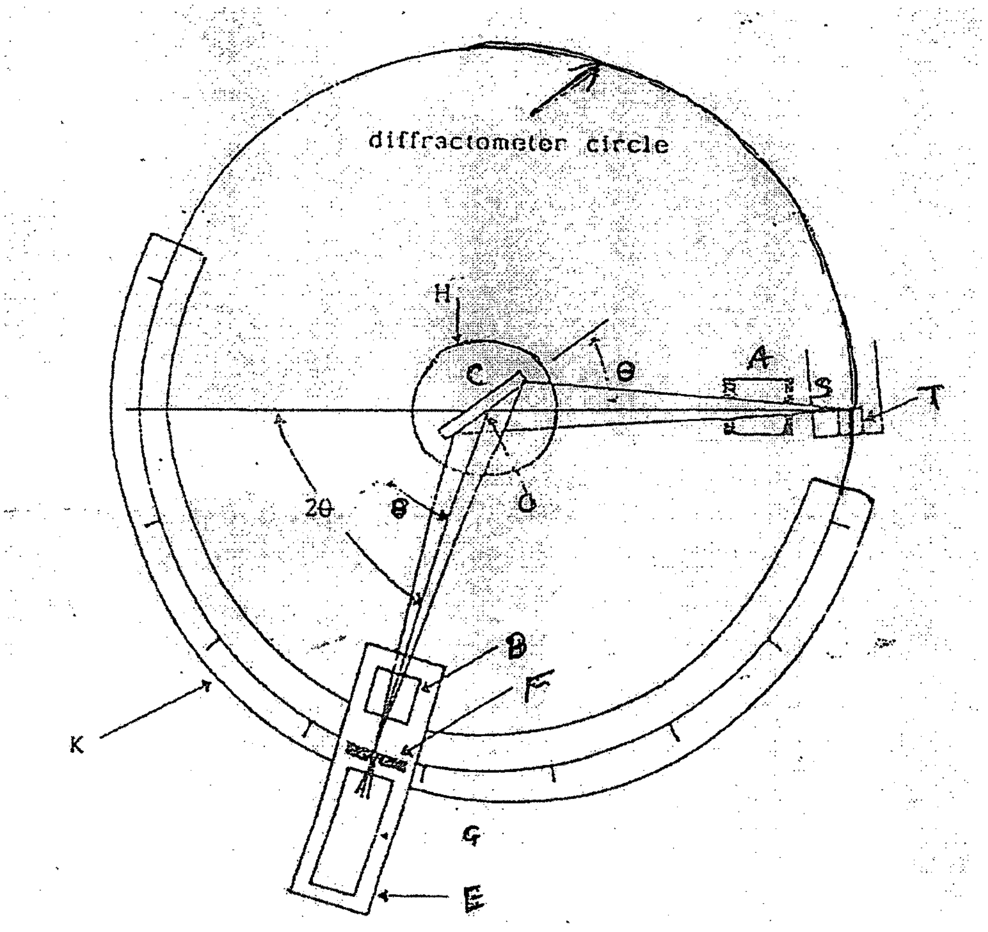


Figure 2.8. X-ray diffractometer line diagram.

2.5. Brief introduction to alkaline earth aluminates

Alkaline earth aluminates for the past few decades have opened a new challenge in the field of phosphor technology by showing their long light persistence property. Researchers around the globe have studied this material as this has potentially replaced the use of ZnS:Cu (in which radioactive element was used as an activator) for long persistence green phosphor with longer decay time compared to that of ZnS:Cu. Moreover the radioactive element used in this compound makes it very harmful [5]. Recent advances in the field have led to an improvement in rare earth based phosphor technology. Alkaline earth aluminates as a host material are being pursued with a great interest. The list of applications of materials having alkaline earth aluminates as host matrix is endless. Almost all phases of alkaline earth aluminates doped with rare earths find applications as refractory oxides in the steel and cement industries [6]. Of these strontium aluminates doped with rare earths are of great interest in material science because of their phosphorescence. The $SrO-Al_2O_3$ system exists in many phases at different calcining temperature and with proper doping of rare earths has found various applications. The different phases show different optical and luminescence properties [6]. Their bright luminescence has attracted attention in the lamps, cathode ray tubes and plasma display panels (PDP) [7]. A number of important applications such as radiation detectors, sensors for structure damage and temperature, in addition to traditional luminous paints have been investigated and reported [8]. Luminophores of alkaline earth aluminates doped with rare earths are used in projection screens, field emission and plasma displays, scanning systems, etc. Luminophores also find wide applications in other fields such as light sources, passive indicators in road safety devices, fillers for films, in polygraphy (luminescent ink) in diverse systems and electronic control panel [9].

The trivalent rare earth doped alkaline earth aluminates are of great importance due to their potential technological applications as functional photonic materials such as optical fiber amplifiers, lasers and wavelength converting devices. In addition it can also be applied in textile, the dial plates of glow watch, warning signs, etc [10]. The $Sr_3Al_2O_6$ doped with divalent europium and trivalent dysprosium is having an application as mechano-luminescent material which can be utilized in the visualization of stress distribution and other mechano - optical properties [11]. The thrust on research and development studies to find out applications of alkaline earth aluminate system doped with different rare earths are still in progress. In the present work, the material has to serve as an efficient lamp phosphor and also as a suitable dosimeter and thus it has to satisfy some of the basic criteria such as optical absorption in short ultra-violet region, retentivity of luminescent characteristics over long periods of operation at operating temperature of the lamp, etc. The application of this system in the field of dosimetry has not been explored much; so emphasis is given, in the present studies, to find out its suitability as an efficient dosimeter.

In recent years, the different phases of strontium aluminate doped with rare earths have been developed like $Sr_2Al_6O_{11}:Eu^{2+}$, $Sr_4Al_{14}O_{25}:Eu^{2+}$ [12,13], $SrAl_2O_4:Eu^{2+}$ [14], $SrAl_{12}O_{19}:Pr^{3+}$ [15], etc. Different studies on this aspect have already been carried out and reported. Akiyama et al. [11] have reported the new phase $Sr_3Al_2O_6$ at 1300 °C.

Before proceeding for the synthesis and development of any phosphor for a specific application, it is essential to know the crystal structure of host lattices. Therefore, in case of alkaline-earth aluminate (AEA) phosphor it is highly important to explore various crystalline phases that may result due to change in Sr^{2+} ion or the amount of Al_2O_3. The crystal structure of alkaline earth aluminate (AEA) system varies with the different molar ratio of oxides of group IIA and Al^{3+} cations present in a compound. Out of all the phases of the $SrO.Al_2O_3$ system the less studied $3SrO.Al_2O_3$ has been described in this thesis. This phase has always considered as an intermediate phase during the formation of the $SrAl_2O_4$ at 900 °C but very less attention has been paid to its luminescence characteristics. This work throws light on the application of the $Sr_3Al_2O_6$ phase in the filed of light emitting phosphor as well as in the field of radiation monitoring.

The $SrO-Al_2O_3$ system is of interest because of the use of the intermediate compounds for hydraulic cements, laser matrices, and long-duration photoluminescence or thermoluminescence pigments [16]. But comparing with the magnesium and calcium counterparts, the knowledge of phase diagram of strontium aluminates is quite limited.
By comparison with the closely related and better-known system $CaO-Al_2O_3$, the $SrO-Al_2O_3$ phase diagram has many uncertainties, even the melting points and, more importantly, the existence of some compounds. In the system, four intermediate compounds, i.e., $SrO-6Al_2O_3$, $SrO-2Al_2O_3$, $SrO-Al_2O_3$, and $3SrO-Al_2O_3$ have been

proven to exist for a long time [17-21]. Then, Dear [22] reported the presence of a new compound with formula 5SrO-Al_2O_3.

In the SrO–Al_2O_3 system, five different crystalline compounds ($Sr_3Al_2O_6$, $SrAl_2O_4$, $Sr_4Al_{14}O_{25}$, $SrAl_4O_7$ and $SrAl_{12}O_{19}$) existed. Conventionally, they were produced by a conventional solid-state reaction of mechanically mixed powders. The inevitable inhomogeneity that is inherent to this technique inhibits the required compositional and microstructural homogeneity of sintered products.

The europium-doped strontium aluminates have attracted much attention since they show excellent properties such as high quantum efficiency [23], long persistence phosphorescence and good stability [24,25] when compared with sulfide phosphorescent phosphors. These properties result in a wide application of the material in many fields [26,27].

A partial phase diagram including five intermediate compounds was proposed by Massazza [28,29] and is still the most frequently cited diagram. Song et al.[30] studied the sequence of phase transformation of SrO-Al_2O_3 and 3SrO-Al_2O_3 and observed two compounds at 1000 °C, but only SrO-Al_2O_3 existing at 1250 °C, the latter is discrepant with other reports. The metastable compound 4SrO-7Al_2O_3 was synthesized by several authors,[31-34] but was not shown in any of the earlier phase diagrams [28,29,34]. Andre′ et al. [35] investigated the phase transformation concerning the 4SrO-7Al_2O_3 and SrO-2Al_2O_3, and proposed modification of a small part of the SrO-Al_2O_3 phase diagram after Massazza [28,29].

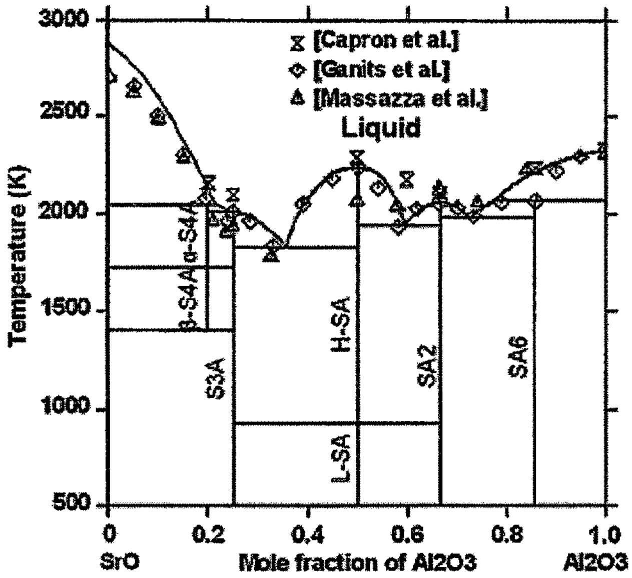


Figure 2.9. Calculated phase diagram compared with experimental data ($S = SrO$, $A = Al_2O_3$)

The $Sr_3Al_2O_6$ structure has been described as being related to the more familiar ABO_3 perovskite structure [36,37]. The noteworthy feature of the strontium aluminate structure is a puckered six-membered AlO_4 tetrahedral ring, with the average bridging Al- O bond length, 1.768 (8)Å, slightly greater than the average nonbridging Al-O bond length, 1.746 (5) Å. In the unit cell (Fig. 2), eight such separate $Al_{16}O_8$ rings surround each of eight vacant sites, and account for all 48 Al and 144 O atoms. The Sr atoms cross-link the aluminate rings and occupy 56 body-centering positions of 64 pseudocells (a'= a/4). The eight vacant pseudo-cells are situated at $\frac{1}{8}\frac{1}{8}\frac{1}{8}$ and its symmetry-related positions. The remaining 16 Sr atoms and the 48 Al atoms occupy the corners of the pseudo-cells. There is no systematic variation in either the Al–O distances or the various O–Al–O angles across the series and these are unexceptional.

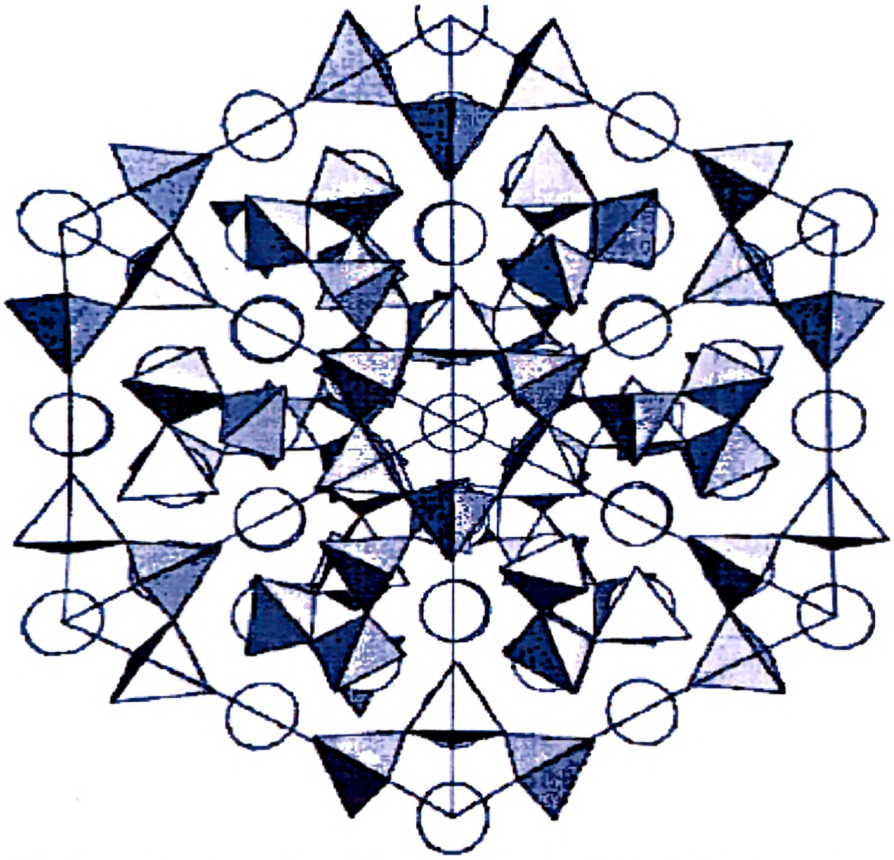


Figure 2.10. Representation of the Al_6O_{18} rings. The shaded tetrahedra represent AlO_4 units and the circles the Sr atoms.

Formation of the new compound or different phases of the SrO-Al_2O_3 system can be achieved by varying the preparative condition, preparation techniques and the type of dopants used. Various synthesis techniques are used to synthesize the alkaline earth aluminates doped with different rare earth ions. Among them the solid state reaction is the most common and easy to use method. But the temperature required for calcining is very high i.e., in the range of 1200°C to 1800°C to get the stable phase of SrO-Al_2O_3 system. When the components are mixed and fired at such high temperatures usually in excess of 1300°C solid state diffusion is induced between the components, and the final product also contains unreacted precursors [6]. In addition, solid state reaction is costly and time consuming due to many hours of required firing at high temperature with an expensive high temperature furnace. To reduce the calcining temperature and time, the use of a flux is necessary. [38,39]. Other techniques like hydrothermal method [40], solid state reaction using spray dried amorphous precursors [6], and laser heated pedestal growth technique [41], combustion process [10], floating zone technique [42], are also used to synthesize alkaline earth aluminates. All these techniques, however, do not solve the problem of multiple phases. To overcome the multiphase issue, researchers have tried the various procedures based on the sol-gel technique. The sol-gel process is an efficient technique for the synthesis of phosphors due to the good mixing of starting materials and relatively low reaction temperature resulting in more homogenous products than those obtained by other synthesis techniques. Some of the reported techniques based on sol-gel synthesis are, base catalyzed sol-gel process [43], sol-gel by using organic precursor [44], Pechini method [45] and sol-gel with reflux [5].

The effect of calcining temperature on the phase stabilization of the strontium aluminate is very interesting from the point of view of its varied applications. The role of rare earths in this regard is very important considering the wide variety of application prospects it shows. In recent years, the different phases of strontium aluminate doped with the rare earths have been developed like $Sr_2Al_6O_{11}:Eu^{2+}$[23],$Sr_4Al_{14}O_{25}:Eu^{2+}$[23,38,14], $SrAl_2O_4:Eu^{2+}$, Dy3+ [5,32,15],$SrAl_{12}O_{19}$[6],$SrAl_4O_7$ [6,9]. These phosphors are known as efficient green and blue emitters and for their long persistent properties. The nanocrystalline phosphor $SrAl_2O_4:Ce^{3+}$, Pr^{3+}, Tb^{3+} [10], has also been reported with rare earth dopant effect on the optical properties of this phosphor. The calcining temperature plays an important role in different phase formations in strontium aluminate ($SrO-Al_2O_3$) system. Different studies on this aspect has already been carried out and reported, in the temperatures range from 750-1100°C [30]. The phases reported are $Sr_3Al_2O_6$ along with $SrAl_2O_4$ and $SrAl_4O_7$. The new phase $Sr_3Al_2O_6$ [30,43,46] is also seen but Morito Akiyama et al [41] have reported this phase at 1300 °C. Lot of discrepancy in the literature exists over the calcining temperature and the corresponding phase formations. As our interest is centered around developing a very strongly emitting phosphor rather than on temperature - dependent phase transformation, we have concentrated on this aspect in the present paper.

Yamaguchi [47] described a sol-gel synthesis of $12SrO-7Al_2O_3$, homologous with $12CaO-7Al_2O_3$, crystallizing at 840-900 °C but decomposing at higher temperature into $3SrO-Al_2O_3$ and $SrO-Al_2O_3$. Recently, Kahlenberg [48] found single crystals of $10SrO-3Al_2O_3$ on the surface of strontium-rich pellets sintered at 1600 °C for 144 h. Xinyu Ye et al [49] describes the thermodynamic comparison of $SrO-Al_2O_3$ system in which he states the $3SrO-Al_2O_3$ as intermediate phase along with $SrO-6Al_2O_3$, $SrO-2Al_2O_3$, $SrO-Al_2O_3$, and $4SrO-Al_2O_3$ are modeled as stoichiometric phases.

Chakoumakos et al. [36] prepared $Sr_3Al_2O_6$ by the solid-state reaction of high-purity Al_2O_3 and $SrCO_3$ at 1300 °C and reported the structure of $Sr_3Al_2O_6$. Akiyama et al. [11,50] prepared Eu^{2+} doped $Sr_3Al_2O_6$ from the mixture of Al_2O_3 and $SrCO_3$ at 1300 °C for 4h with H_3BO_3 as flux. It is found that Eu^{2+} doped $Sr_3Al_2O_6$ emits intense mechanoluminescence at room temperature. Katsumata et al. [42] grew Eu^{2+} and Dy^{3+} doped $Sr_3Al_2O_6$ crystal by a floating-zone technique and investigated the phosphorescence characteristics of $Sr_3Al_2O_6$ crystals. Although $Sr_3Al_2O_6$ was usually prepared at temperature as high as 1300 °C, very few literatures reported the wet chemical synthesis of $Sr_3Al_2O_6$ at lower temperature. The nano-sized fine particles formed at lower temperature may affect the phosphorescence and mechanoluminescence characteristics of $Sr_3Al_2O_6$. It is significantly essential to investigate a low temperature preparation of $Sr_3Al_2O_6$. Li et al. [51] reported the hydrothermal synthesis of $Sr_3Al_2O_6$ and single-phase $Sr_3Al_2O_6$ was obtained from $Sr_3Al_2(OH)_{12}$ as a precursor at 600 °C. Out of all these techniques the sol-gel reflux technique is most appreciable as in this technique the single phase formation is guaranteed.

2.6. Synthesis Technique

Sol-gel reflux technique is generally used to apply energy to chemical reactions.
The reaction takes place as follows. A liquid reaction mixture is placed in a vessel open only at the top. This vessel is connected to a condenser, such that any vapours given off are cooled back to liquid, and fall back into the reaction vessel. The vessel is then heated vigorously for the course of the reaction. The purpose is to thermally accelerate the reaction by conducting it at an elevated temperature (i.e. the solvent's boiling point.).

The advantage of this technique is that it can be left for a long period of time without the need to add more solvent or fear of the reaction vessel boiling dry as any vapour is immediately condensed in the condenser. In addition, as a given solvent will always boil at a certain temperature, one can be sure that the reaction will proceed at a constant temperature. The constant boiling action also serves to continuously mix the solution, although a magnetic stirrer is used to achieve a uniform solution. This technique is useful for performing chemical reactions under controlled conditions that require substantial time for completion.

The diagram shows a typical reflux apparatus for applying energy to chemical reactions. It includes an optional beaker of water between the reactants and the heat.

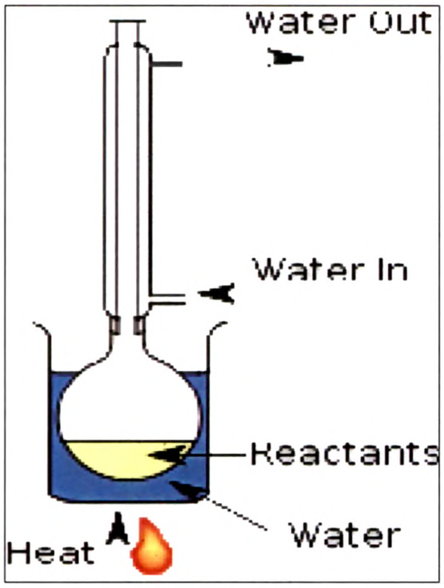


Figure 2.11. Experimental setup of synthesis of $Sr_3Al_2O_6$:R.E. phosphor by reflux sol-gel technique.

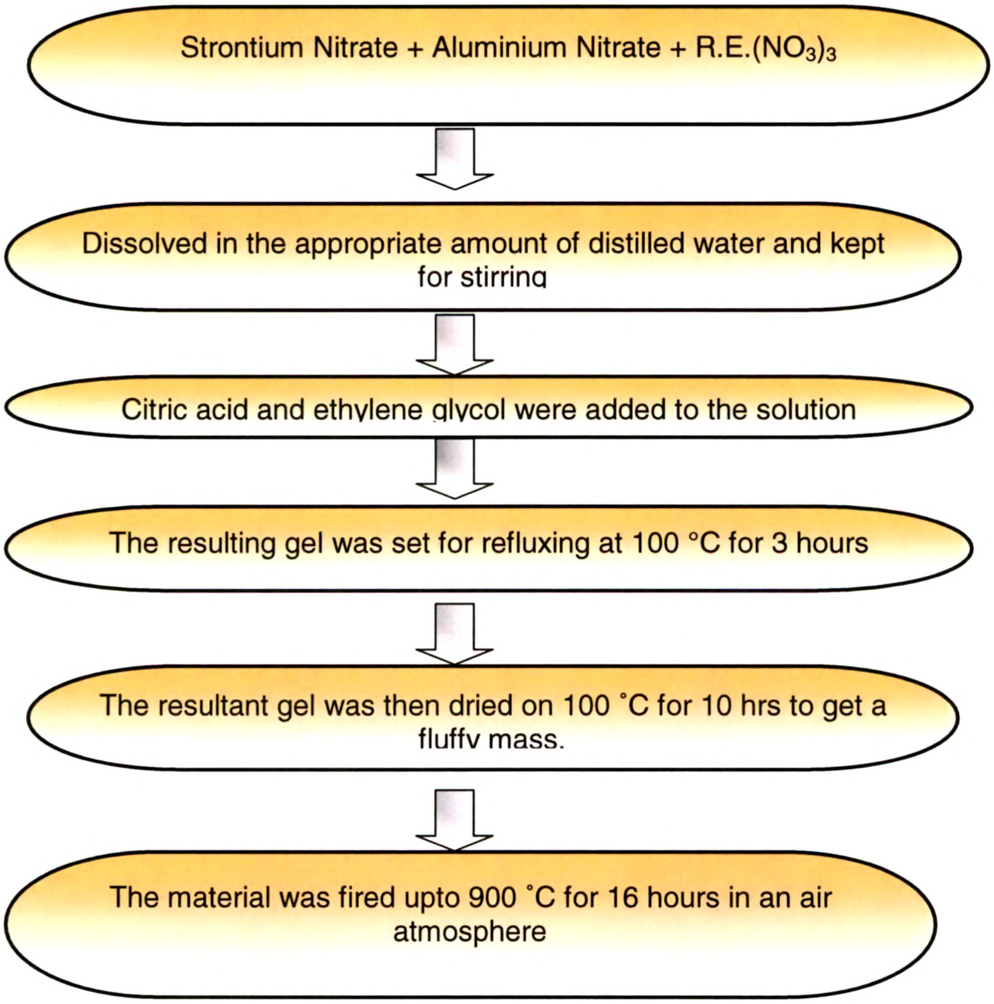
All the phosphor samples studied in this thesis were prepared by the sol-gel reflux technique. The starting materials taken were strontium nitrate, aluminium nitrate and the rare earths in the nitrate form. All of them were acquired from S.D. Fine Chemicals with rare earths of purity 99.9%. The nitrate form of all the rare earths samples were prepared by using aqua regia technique in which the required concentration of rare earth material were dissolved in the mixture of concentrated nitric acid and concentrated hydrochloric acid, usually in a volumetric ratio of 1:3 respectively. Aqua regia can dissolve R.E. because each of its two component acids carries out a different function. The nitric acid is a good oxidizing agent. Chloride ions from the hydrochloric acid from coordination complexes with the R.E. ions, removing them from solution. Reducing the concentration of the R.E.$^{3+}$ ions shifts the equilibrium towards the oxidized form.

The powders were weighed according to the nominal composition of

$$Sr(NO_3)_2+Al(NO_3)_3.9H_2O+RE(NO_3)_3 \text{ (RE = } Eu(NO_3)_3 \text{ or } Tb(NO_3)_3\text{)}.$$

The starting materials strontium and aluminum nitrates were taken in stoichiometric proportions and dissolved in the appropriate amount of distilled water and kept for stirring. Thereafter the rare earths compounds with different concentrations were mixed to the above solution. Citric acid and ethylene glycol were added to the solution after one hour of constant stirring. The resulting gel was set for refluxing at 100°C for 3 hours. The gel thus obtained, was kept for drying in an oven maintained at 100°C for 10 hours. The yellowish gel then transformed into a fluffy material. It was then kept for firing at a temperature maintained at 900°C in a furnace for 16 hours in air. The white powder obtained on firing, was ground using an agate mortar and pestle and was then subjected to various characterizations. The pictorial representation of the synthesis technique is given below in the flow chart form.

2.6.1. Flow-chart of synthesis technique for $Sr_3Al_2O_6$ phosphor



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