CHAPTER - II

MATERIALS & METHODS
MATERIALS AND METHODS

This chapter comprises of two parts.

Part one of this chapter gives the description of materials and methods used for synthesizing phosphors and the part two of this chapter describes various techniques and instrumental methods used for characterization of the prepared phosphors.

1. MATERIALS

A) Chemicals

The synthesis of efficient phosphors required host lattice, activators, fuels and some fluxes. The various chemicals used for the synthesis of the phosphors discussed in this thesis are listed below:

1) Aluminium nitrate nonahydrate [Al(NO$_3$)$_3$.9H$_2$O]
2) Ammonium metavanadate [NH$_4$VO$_3$]
3) Calcium nitrate tetrahydrate [Ca(NO$_3$)$_2$.4H$_2$O]
4) Dysprosium(III) nitrate pentahydrate [Dy(NO$_3$)$_3$.5H$_2$O]
5) Europium(III) nitrate tetrahydrate [Eu(NO$_3$)$_3$.4H$_2$O]
6) Europium(III) nitrate pentahydrate [Eu(NO$_3$)$_3$.5H$_2$O]
7) Gadolinium(III) nitrate hexahydrate [Gd(NO$_3$)$_3$.6H$_2$O]
8) Glycine [NH$_2$CH$_2$COOH]
9) Indium(III) nitrate pentahydrate [In(NO$_3$)$_3$.5H$_2$O]
10) Magnesium nitrate hexahydrate [Mg(NO$_3$)$_2$.6H$_2$O]
11) Strontium nitrate [Sr(NO$_3$)$_2$]
12) Terbium(III) nitrate pentahydrate [Tb(NO$_3$)$_3$.5H$_2$O]
13) Urea [H$_2$NCONH$_2$]
14) Yttrium nitrate tetrahydrate [Y(NO$_3$)$_3$.4H$_2$O]
15) Zinc nitrate hydrate [Zn(NO$_3$)$_2$.xH$_2$O]

Keeping in mind that even a small amount of impurity lowers the luminescent intensity of the phosphors, all these chemicals used for the synthesis of phosphors were of high purity i.e. 99.98% or more purchased from Aldrich. Other chemicals such as acids and solvents used were also of reagent grade/analytical grade.
B) Synthesis of Phosphor

Phosphors consist of a crystalline host materials or a matrix in which a small amount of certain impurities called activators are incorporated. Sometimes a little quantity of flux is also required for the synthesis of these luminescent materials. Phosphor synthesis generally proceeds via two step reactions. In the first step, activator ions are induced into the existing host materials taken for synthesis and in the second step, host materials synthesis and activator introduction takes place simultaneously during the process of firing in the furnace. Activators are primarily responsible for the luminescence in phosphors. The starting materials for the synthesis of phosphors are blended in a ratio which may deviate considerably from the stoichiometric composition of the phosphor. Very thorough mixing of the raw materials before firing is extremely important for the successful synthesis of the phosphor. Some of the best methods used for mixing of raw materials are slurring, wet ball milling, dry ball milling, mortaring etc. The excess components present in the raw materials other than the required amount as per final product of the phosphor, either vaporizes during synthesis or is consumed to create by-products. Sometimes these are removed by washing after the completion of the reaction. The final product thus obtained is very close to the stoichiometric composition of the phosphors [1].

Extensive trials on the preparation and characterization of phosphors of different host materials doped with activators and co-activators become unavoidable before any worthwhile result is obtained. The synthesis of phosphor requires:

i) Starting Materials

The starting materials used in the synthetic processes must be of high purity grade chemical (e.g. analytical reagent grade, luminescent grade) because a small amount of impurity even of ppm level, sometimes changes luminescence characteristics of the phosphor drastically [2]. These impurities which suppress luminescence efficiency of the phosphor are known as killers or quenchers. For example luminescence efficiency of ZnS phosphors reduces drastically by the presence of iron group elements such as Ni^{2+}, Fe^{2+}, Co^{2+}. ZnS:Cu, Al phosphor luminescence efficiency is suppressed more by Ni^{+} presence than Fe^{2+} and Co^{2+} impurities. Cathodoluminescence of this phosphor is completely suppressed by the
presence of 600 ppm Ni^{2+} in 1 mole of ZnS and presence of 300 ppm Ni^{2+} reduces the efficiency of this phosphor up to 30% [3]. Killers effect luminescence efficiency through two possible mechanisms [4], firstly, the killers give rise to deep levels in the forbidden band, which act as non-reductive recombination centers for free electrons in the conduction band and holes in the valence band. Secondly, the excitation energy absorbed by the active center is transferred to killers without emitting radiation.

Sometimes a small amount of added ions increases luminescence efficiency of the phosphor. In case of Y_{2}O_{3}:Eu^{3+} cathodoluminescence efficiency improves up to many folds in presence of small amount of Tb^{3+} [5].

ii) Fluxes

The materials added to the raw materials mixture for the synthesis of phosphors by solid state process, to facilitate crystal growth are called flux [6]. Fluxes are usually compounds of alkali or alkaline earth metals having low melting points. The firing temperature often is little below the melting temperature of the host material. If that is impractical because of excessively high melting temperature of the host material, the crystallization is facilitated at lower temperature by addition of a flux to the raw mix before firing. Hence the liquid phase provided by fluxes play important role in crystal growth. Y_{2}O_{3}:Eu^{3+} phosphor is generally prepared by firing yttrium and europium oxalates co-precipitate. If this phosphor is prepared without addition of any flux then a very high temperature of the order of 1400°C is required. Even Y_{2}SiO_{5}:Ce^{3+}, Tb^{3+} and a series of aluminates phosphors also need fluxes as the, raw mix of these phosphors have high melting point. For these phosphors KF [7] and a mixture of AlF_{3} and MgF_{2} [8] are used as fluxes respectively. In presence of halide flux the phosphor can be prepared at a reduced temperature i.e. 1200°C. Sometime flux also acts as a source of the co-activator in certain phosphors. For example Cl supplied by the flux, also acts as a co-activator in ZnS:Cu, Cl phosphor.

iii) Fuels

Organic fuels react with metal nitrates in combustion method, involving a exothermic reaction between the two leading to the formation and crystallization of the phosphor at low firing temperature. This process is based on the thermochemical concepts used in propellant chemistry [9], in which these organic fuels such as
ethylene glycol, glycine, urea, hydrazine, carbohydrazide and diformyl hydrazine are used. In general, a good fuel should react non-violently, produce non-toxic gases and act as complexant for metal cation [10]. All these fuels contain nitrogen but differ in the reducing power and amounts of gases that generate, which obviously affects the characterization of the reaction products. Hence when complete combustion occurs, between oxidizer and an organic fuel, only the gaseous products are released, making this an environmentally clean processing technique.

iv) Crucibles

The crucibles used for the synthesis and sintering/calcinations of phosphors are made up of clear quartz glass (silica) or alumina. Some materials such as alkali elements react with quartz glass at firing temperatures and hence fired in alumina crucibles. Generally alumina crucibles are employed for the synthesis of phosphors at high firing temperature, as shown in Fig. 2.1.1

![Fig. 2.1.1 Alumina crucibles (a) boat-shaped (b) round crucible with lid](image)

Open boats are preferred for phosphor raw mixes that do not contain volatile constituents at firing temperatures in order to expose the charge fully to the desired atmosphere surrounding the material. Loosely covered crucibles are used for raw mixes containing volatile constituents, permitting some contact with the surrounding atmosphere but still keeping at least some of the volatile part in the crucible.

v) Furnaces

Phosphor firing often requires an electric furnace permitting temperatures between about 500°C and at least 1200°C, better up to 1600°C. Any desired
temperature should be maintained during firing by means of an automatic temperature controller to within ± 20°C or better. A simple on off control is acceptable. For small scale production box-type furnaces (Fig. 2.1.2) are common and for large scale production, tunnel type, continuous furnaces are available. Firing is carried out either in air or in a controlled atmosphere.

vi) Firing Atmospheres

The phosphors are fired in different atmospheres depending on the materials and the desired reactions. Oxygen dominated phosphors such as oxides, silicates, phosphates etc. may be fired in oxidizing (air, O₂), inert (N₂, Ar) or reducing atmospheres (CO, H₂, NH₃). Phosphors doped with Ti⁺, Pb²⁺, Sb³⁺, Mn²⁺, Mn³⁺, or Eu³⁺ ions can be fired in air and phosphors doped with Sn²⁺, Eu²⁺, Ce³⁺ and Tb³⁺ ions are fired in a reducing atmosphere. As the reducing gas, nitrogen containing 2-5 percent hydrogen is the most frequently employed. Tube type furnace (Fig. 2.1.3) can be used for phosphor synthesis in inert atmospheres. For a weak reductive atmosphere active carbon can also be used.
C) PHOSPHOR SYNTHESIS TECHNIQUES

Synthesis of phosphors can be achieved by conventional solid state method [11-16] or by non-conventional methods (wet-chemical) such as sol-gel technique [17-31], co-precipitation technique [32-35], hydrolyzed colloidal reaction [36-38], spray pyrolysis [39-40], hydrothermal technique [41-46], microwave technique [47-49] and combustion method [50-73]. The different techniques are described briefly.

i) Solid-state method

This is conventional method for the synthesis of phosphors. This technique requires temperature higher than 1000°C, because of the refractory nature of the oxide precursors. The mixture of corresponding metal oxides/carbonates are ground well and heated typically in temperature range 1000-1600°C. The mechanism of solid-state reactions is diffuse control reaction and hence demands repeated grinding steps and several heating [74-77], in order to obtain well-reacted, small particle size phosphors. To maintain the proper stoichiometry of the crystal lattice and valence of the activator a controlled atmosphere is desirable (e.g. Eu^{2+} or Eu^{3+}). For example, SrGa_{2}Se_{3}:Eu^{2+} (thio-selenide) phosphors are prepared using a solid-state chemical reaction method [14]. The synthesized phosphor displayed a broad excitation band, which is suitable for blue or NUV LED applications and emits green light (528nm). But the disadvantages associated with the solid-state synthesis are prolonged calcination time,
large particle size, high temperature, in homogeneity of the product, presence of
defects that are harmful to luminescence.

The inherent disadvantages of conventional solid-state method can be
overcome by the non-conventional solution-based methods offering molecular level
mixing of the starting materials, which leads to high degree of homogeneity with
small particle size and high surface area. Hence with the development of scientific
techniques several more advanced chemical routes are now adopted.

ii) Sol-gel method

It is a wet-chemical method. This method is based on the phase transformation
of sol obtained, when dilute solutions of metal organics or metal salts react. This sol
which in a solution containing particles in suspension is polymerized at low
temperature to form a wet gel. The advantage of this method is that atomically mixed
powders are obtained with high purity in the as-synthesized conditions. The problems
associated with incomplete reactions are also avoided in this process. However, the
as-synthesized materials must also be heat treated to high temperature to crystallize
the desired phase and to achieve particle size greater than 0.2\(\mu\)m. For example, a
promising red emitting phosphor \(\text{Gd}_2_{x}\text{Eu}_x (\text{MoO}_4)_3\), for white light emitting diodes
was prepared by sol-gel method [31]. The influence of the synthesis method on the
luminescence properties was studied by comparing the optical performances of
samples by sol-gel processing and solid-state reaction. C. Guo et al. found sol-gel
method to be most efficient method to prepare high quality compounds for practical
applications.

iii) Co-precipitation method

This method adopted to prepare the phosphors involves a direct and clean
reaction between the stoichiometric ratio of the desired starting materials and
precipitating reagent chosen. In this process no by-products other than water are
generally produced. The reaction may be vigorous and exothermic in nature, forming
large precipitates immediately at the reaction site, which can be separated by
centrifugation. The resulting precipitates are washed several times by deionized water
and collected in quartz boats and then subjected to thermal treatment in a suitable
atmosphere to give phosphors, which emit-color under a UV source. For example,
\(\text{LaPO}_4\): Ce, Tb phosphor was prepared by firing the \(\text{LaPO}_4\):Ce,Tb precipitate derived
from co-precipitation [34] of aqueous solution of La, Ce, Tb mixed rare-earth nitrate with ammonium dibasic phosphate. Effects of ripening condition of precipitate, flux addition and firing temperature on the morphology and photoluminescence properties of LaPO₄:Ce,Tb phosphor was investigated. Types of flux employed significantly influenced the morphology of the phosphor. When H₃BO₃ was used as flux spherical particles of 300nm were formed. In contrast, when Li₂CO₃ or Li₃PO₄ was employed as flux either separately or a component of double flux, uniform spherical or near spherical particles of 5µm were generated. Firing temperature of 1100°C and 1200°C in the presence of double flux led to the formation of smooth spherical particles.

iv) Hydrolysed colloidal reaction

This colloidal reaction technique is generally carried out at room temperature (<100°C) in atmospheric pressure in presence of deionized water. Hydrolysation takes place yielding the intermediate metastable colloidal mixture from which the phosphors are formed, utilizing a subsequent calcinations and reductive treatment respectively. For example, YVO₄, YPO₄ and YVₓP₁₋ₓO₄ phosphor host materials were synthesized by a special hydrolyzed colloid reaction (HCR) technique [36] from Y₂O₃+V₂O₅+H₂O, Y₂O₃+P₂O₅+H₂O and Y₂O₃+V₂O₅+P₂O₅+H₂O systems at low temperature (T<100°C) and atmospheric pressure. Complex colloidal mixtures with metastable characteristics produced by intensive ball milling were transformed into YVO₄, YPO₄ and YVₓP₁₋ₓO₄ by simple hydrolysis.

v) Spray pyrolysis method

In this method the solution of salts is atomized with ultrasonic spray generators and introduced in to a hot reaction column, where the droplets were dried, decomposed and crystallized in dispersed phase. The prepared particles are collected with a bag filter. The spray solutions are obtained by adding nitrate precursors into distilled water. In some cases a solvent soluble flux can also be used to decrease the defects of particles. Also polymeric precursors such as ethylene glycol or citric acid may be added to spray solutions. The morphology of particles prepared in this method is strongly affected by preparation conditions and type of precursors. Finally, post heat-treatment is done. For example, (Y₁₋ₓGdₓ)₂O₃:Eu (0≤x≤1) phosphor particles are prepared by modified spray pyrolysis process at 900°C [39] and can be applied as a red-emitting phosphor to PDV and fluorescent lamp because of their high efficiency.
Spray pyrolysis is one of the promising processes for the preparation of the improved phosphor particles with spherical shape, fine size, narrow size distribution and non-aggregation characteristics because of its particle formation mechanism.

vi) Hydrothermal method

It is a chemical method, to obtain high purity phosphors, as well as to control the microstructure. In this method stoichiometric amounts of precursors are dissolved in nitric acid. The solutions are evaporated until dryness. The residual mixture is then sealed in Teflon-lined stainless steel autoclave with a filling capacity of 40% distilled water and allowed to crystallize at low temperature for a few hours. The phosphor powders prepared are filtered washed with distilled water and dried in an oven at 80°C. This processing has great advantages, such as low processing temperature at high pressure, better metal ions distribution that produce fine, well crystallized powder. These powders must also be heat treated to high temperature to extract maximum luminous efficiency. For example, nanosized long-persistent phosphors SrS:Eu$^{2+}$, Dy$^{3+}$ were prepared by the hydrothermal method [46]. Duan et al. found that the afterglow intensity of SrS:Eu$^{2+}$, Dy$^{3+}$ was higher than that of SrS:Eu$^{2+}$ prepared at the same temperature, but the afterglow of SrS:Eu$^{2+}$, Dy$^{3+}$ decayed more quickly with the increase of sintering temperature.

vii) Microwave method

Microwaves are a form of electromagnetic energy, like light waves or radio waves, and occupy a part of the electromagnetic spectrum ranging from as long as one meter to as short as one millimeter or equivalently with frequencies between 300 MHz and 300GHz [78]. Originally, microwaves were principally used for communication. In 1950, the use of microwave energy to heat materials was discovered. Now a days, it finds application in industries such as vulcanization of rubber, ceramics, organic, inorganic compounds synthesis and phosphor synthesis. The most prominent characteristic of microwave heating is volumetric heating, which is quite different from conventional heating where the heat must diffuse in from the surface of the material. Volumetric heating means that materials can absorb microwave energy directly and internally and convert it to heat. It is this characteristic that leads to advantages using microwaves to process materials.
In microwave the electrical energy, in the form of low-voltage alternating current and high-voltage direct current, is transformed and converted into direct current. A magnetron uses this direct current and generates microwaves with a frequency of 2450 megacycles per second or 2.45 GHz (gigahertz). The microwaves are directed by an antenna at the top of the magnetron into a waveguide. The waveguide channels microwaves to a fanlike device called a stirrer which disperses them inside the oven cavity. The microwaves are then reflected off from the metal walls of the oven’s interior and are absorbed by molecules. Because each wave has a positive and negative component, the molecules in the materials are jostled back and forth at twice the rate of the microwave frequency, namely 4.9 billion times a second.

Microwave heating finds many advantages over the conventional heating as it is environmental friendly, time and energy saving, provides rapid heating and requires less processing, hence it is used in the synthesis of phosphors. For example, YVO₄:Eu³⁺, Sm³⁺ red phosphor has been synthesized by microwave assisted sintering [49].

viii) Combustion method

Combustion synthesis is a novel technique that has received great attention in the past few years. This method was discovered in Patil’s laboratory in India in 1988 [79]. It is also known as self-propagating high temperature synthesis. K.C. Patil serendipitously synthesized fine particles of α-alumina and related oxide materials using this method in his laboratory. Since the preparation of α-alumina foam by rapidly heating a solution of aluminium nitrate and urea [50] quite a number of advanced materials have been prepared by means of combustion synthesis [51]. For example, a variety of useful oxides such as yttria [52-53], ceria [53-54], zirconia [53, 55-56], zinc oxide [57-58], iron oxide [59], thoria [60], aluminates [61-64], chromites [65-68], ferrites [69-70], manganites [68,71], titanates [72-73] etc. has been obtained using this technique.

This method involves a highly exothermic reaction which occurs with the evolution of heat and light as shown in Fig. 2.1.4, when the mixture of fuel and oxidizer are ignited. The common fuels employed for the combustion process are urea (CH₄N₂O), Carbohydrazide (CH₂N₄O), Oxalyl dihydrazide (C₂H₆N₄O₂), glycine (C₂H₅NO₂), diformyl hydrazine (C₂H₄N₂O₂) etc. All these fuels contain nitrogen but
differ in the reducing power and amounts of gases that generate, which obviously affects the characterization of the reaction products. The nitrate salts are favoured as oxidizer because they serve as water-soluble low temperature nitrogen source for the synthesis.

![Combustion reaction occurring with evolution of heat and light](image)

**Fig. 2.1.4 Combustion reaction occurring with evolution of heat and light**

Stoichiometric compositions of metal nitrates and fuels are calculated based upon propellant chemistry. Thus, heat of combustion is maximum for O/F ratio 1 [50]. Based on the concepts used in propellant chemistry [50], the elements C, H, V, B or any other metal are considered as reducing elements with valencies 4+, 1+, 5+, 3+ (or valency of the metal ion in that compound), respectively and oxygen is an oxidizer having the valency of 2-. The valency of nitrogen is taken as zero because of its conversion to molecular nitrogen during combustion. Accordingly, the oxidizing (O) and reducing (F) valencies for M(NO$_3$)$_3$ and urea can be calculated as follows.
$M(N\text{O}_3)_3$ Urea, $CH_4N_2O$

1M = 3+ C = 4+
9O = 18- 4H = 4+
3N = 0 O = 2-
15- 2N = 0 6+

Where M = Y, Gd, La, Al, Tb, Ce.

The oxidizing and reducing valencies of metal nitrates and fuels used in the combustion synthesis of oxide phosphors are summarized in Table 2.1.1.

Table 2.1.1 Oxidizing and reducing valencies of metal nitrates and fuels

<table>
<thead>
<tr>
<th>Compound</th>
<th>Oxidizing/Reducing valencies</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M(N\text{O}_3)_2$</td>
<td>10-</td>
</tr>
<tr>
<td>$M(N\text{O}_3)_3$</td>
<td>15-</td>
</tr>
<tr>
<td>$M(N\text{O}_3)_4$</td>
<td>20-</td>
</tr>
<tr>
<td>$NH_2NO_3$</td>
<td>2-</td>
</tr>
<tr>
<td>Urea, $CH_4N_2O$</td>
<td>6+</td>
</tr>
<tr>
<td>Glycine, $C_2H_5N_2O_2$</td>
<td>9+</td>
</tr>
<tr>
<td>Carbohydrazide (CH), $CH_4N_4O_2$</td>
<td>8+</td>
</tr>
<tr>
<td>Oxalyl dihydrazide (ODH), $C_2H_3N_4O_2$</td>
<td>10+</td>
</tr>
<tr>
<td>3-Methyl Pyrazole 5-One (3MP50), $C_4H_6N_2O$</td>
<td>20+</td>
</tr>
<tr>
<td>Diformyl hydrazine (DFH), $C_2H_4N_2O_2$</td>
<td>8+</td>
</tr>
<tr>
<td>$NH_4VO_3$</td>
<td>3+</td>
</tr>
</tbody>
</table>

Hence, for any combustion synthesis, the mixture of metal nitrates (as an oxidizer) and a proper organic fuel are dissolved in a minimum amount of water in a Pyrex vessel and introduced into a muffle furnace maintained at temperature of 500°C or less Hot plate can also be used for the process. The combustion reactions are carried out at low temperature initially below the phase transition of the target product. The solution boils, foams and ignites to burn with flame or sometimes only smouldering is noticed, to yield voluminous, foamy powder in 3-5 minutes occupying the whole volume of the reaction container as shown in Fig. 2.1.5. The chemical energy released during this exothermic process rapidly heat the system to high temperatures (>1600°C) without any external heat source, such a high temperature leads to formation and crystallization of phosphors.
A key feature of this technique is that the heat required to drive the synthesis is provided for the main part by an exothermal reaction occurring among the reagents, thus greatly reducing the amount of heat that has to be supplied by an external source. Actually, metal nitrates can also be decomposed by simple calcination into metal oxides, upon heating to or above their decomposition temperature; afterwards these oxides can further react together giving new substances. But, in this case, a constant external heat supply is necessary, to maintain the system at the high temperature required accomplishing the appropriate reaction. On the contrary, the combination of nitrates with a sacrificial fuel causes the ignition of this mixture of precursors at a rather low temperature as well as the advance of an exothermal reaction that provides itself the heat necessary for the synthesis. In this way the system is not forced to stay at high temperature for a long period of time, thus preventing particles sintering.

In addition, as the reagents are mixed in an aqueous solution, this method enables a good chemical homogeneity of the system, which leads to a nearly instantaneous reaction. Thus, combustion synthesis provides an interesting alternative to other elaborate techniques because it offers several attractive advantages such as simplicity of experimental set-up, surprisingly short time between the preparation of reactants and the availability of the final product, cheapness due to energy saving.

If on one hand the combustion synthesis is an efficient, quick and straightforward method for the preparation of oxide materials, on the other hand the mechanism of the process in terms of reactions involved is quite complex. Besides, it
has been shown that the properties of the resulting oxide powders (crystalline or amorphous structure, crystallite size, purity, surface area, particle clustering and agglomeration, etc.) strongly depend on the processing parameters adopted [80].

Most of previous investigations reported in the literature dealt with the properties of final products and were aimed at evaluating the influence exerted by the composition of the reactant mixture on both phase composition and microstructure of the oxides obtained. For example, product characteristics were observed to depend on the kind of sacrificial fuel used [61-63] as well as on the adoption as precursors of acetates instead of nitrates [62]; these characteristics were also found to change with both the nitrates/fuel ratio and the concentration of precursors in the water solution [52, 54 and 65].

Despite these extensive investigations, the mechanism of the combustion synthesis is still not well understood, probably owing to the short synthesis times and the great number of parameters that influence the process. At any rate its knowledge entails great importance in order to control the characteristics of the final products. Three main possible mechanisms, which differ in kind and succession of chemical reactions involved in this complex process, were expounded in the literature. Kingsley et al. [50] suggested that during the first step of combustion synthesis the thermal decomposition of urea and aluminium nitrate occur simultaneously. Urea decomposes initially to biuret and ammonia and, at higher temperatures, to cyanic acid (HCNO) trimer, while aluminium nitrate decomposes to amorphous alumina and nitrogen oxide. According to these authors, afterwards, final gas phase reactions between combustible species (like ammonia and cyanic acid) and oxides of nitrogen occur, causing the appearance of a flame. Li et al. [61] and Chandramouli et al. [60] also support this theory. On the contrary, Segadaes et al. [57, 64 and 72] suggested that the overall combustion reaction could be dismembered into partial reactions of thermodynamic significance, among which a combustion reaction between the fuel and the oxygen produced in the decomposition of the nitrates supplied the heat needed for the synthesis reaction. Suresh et al. [59] suggested that a direct reaction between a metal nitrate and a sacrificial fuel occurs during combustion synthesis. This last reaction results in the complete fuel consumption and, being exothermal and
autocatalytic once ignited, goes to completion without taking any heat from external sources.

Some attempts of investigating, in an indirect way, the progress of combustion synthesis reactions by using calorimetric and thermal-gravimetric techniques are reported in literature, [60, 63, 69 and 73] while experimental results about the gases developed during the advancement of the process are not yet available.

Actually, the combination of calorimetry and thermal-gravimetry with the simultaneous analysis of gaseous reaction products is a powerful tool, suitable for better understanding the mechanism of combustion synthesis.

The combustion synthesis technique proves to be a simple, efficient, quick and straightforward route to synthesize phosphors. This method provides high purity, high crystallinity and high homogeneity even at low firing temperature, thus this route proves to be better than the conventional method. Hence in the present study author has adopted combustion synthesis for the preparation of phosphors.

2. INSTRUMENTATION

In material characterization, basically the synthesized materials are characterized by variety of techniques to assure that the appropriate materials with suitable properties are synthesized. Some of the techniques and instruments utilized for the characterization of phosphor are given below:

A) LUMINESCENCE SPECTROSCOPY

i) Principle

The photoluminescent spectrum is obtained by plotting the relationship between the wavelength and the intensity of emitted light from a sample excited by an appropriate excitation source of constant energy. The source of excitation can be UV and visible light such as tungsten lamp, discharge lamp, xenon discharge lamp, mercury discharge lamp, laser [81-82], excimer lamp [83], electron beam excitation etc. The spectrum is obtained using a monochromator equipped with an appropriate light detector. In an excitation spectrum, the relationship is obtained by observing changes in the emitted light intensity at a set wavelength while varying the excitation energy. When the excitation source is light, single-frequency light produced by a monochromator impinges on the sample and the emitted light intensity is recorded as the excitation wavelength is varied.
In a spectrum, intensity of light at a particular wavelength is expressed along the ordinate and the wavelength along the abscissa. The units of the ordinate are either irradiance \(E\) (W.m\(^{-2}\)) or number of photons \(E_p\) (photons.m\(^{-2}\)). The units of the abscissa are expressed in terms of wavelength \(\lambda\) (nm) or wave number \(\tilde{\nu}\) (cm\(^{-1}\)).

Using these units, the spectrum irradiance is expressed as

\[
E(\lambda) = \frac{dE}{d\lambda} \text{ (W.m}^{-2}.\text{nm}^{-1})
\]

Or
\[
E(\tilde{\nu}) = \frac{dE}{d\tilde{\nu}} \text{ (W.m}^{-2}.\text{(cm}^{-1})^{-1})
\]

and the spectral photon irradiance is expressed as

\[
E_p(\lambda) = \frac{dE_p}{d\lambda} \text{ (photons.m}^{-2}.\text{nm}^{-1})
\]

Or
\[
E_p(\tilde{\nu}) = \frac{dE_p}{d\tilde{\nu}} \text{ (photons m}^{-2}.\text{(cm}^{-1})^{-1})
\]

Depending upon the type of the experiment, the units are selected. For quantum efficiency, photon irradiance is employed whereas for energy efficiency, irradiance is employed. The luminosity of a phosphor is expressed in terms of irradiance, which is obtained by integrating the spectral data, \(E(\lambda)\), multiplied by the relative photopic spectral luminous efficiency, \(V(\lambda)\), divided by the light equivalence value, [84-85] \(K_m = 673 \text{ lm.Watt}^{-1}\) i.e.

\[
L = K_m \int_0^\infty V(\lambda)E(\lambda)d\lambda, \quad \text{lm.m}^{-2}
\]

ii) CIE colorimetric system

In the study of color perception, one of the first mathematically defined color spaces was the CIE colorimetric system [86] established by the CIE in 1931. This is the most important concept used these days. The CIE chromaticity diagram is shown in Fig. 2.2.1. This system consists of the RGB and the XYZ colorimetric systems. The XYZ system, which will also be explained below, was laid down as an extension of the RGB system for practical applications.
The RGB system was derived from results of psychophysical experiments. In the experiments, the observers viewed a circular field with an angular diameter of 2°. The circular field consisted of two identical half circles adjacent to each other. The color of the two identical half circles was independently variable. One of the two half circles was used as the reference field and another was used as the test field. Colors of the test field were made to match those of the adjacent reference field. During the observations, it was found that in some wavelength ranges mixtures of three primary colors could not match the reference colors. In these wavelength ranges, matches were
established if an amount of one of the three primary colors was added to the monochromatic reference colors.

This implies that matches can be established by the subtracting one of the primary colors from the mixtures. In other words, there are some wavelength ranges where the stimulus of the primary colors is negative. In this way, the mixture ratio of the primary colors to match all the spectral colors over the entire visible range was obtained. It was assumed, when a match was established, that the reciprocals of the energy ratio of each primary color of the test field corresponded to the relative strength of the stimuli of the respective primary colors at the wavelength of the reference with which the color was matched. Based on the above assumption, three spectral distribution curves of the relative strength of the stimulus for each of the three primary colors (red, green and blue) over the entire visible range were obtained. The curves are called the spectral tristimulus values or the color matching coefficients. They are \( r(\lambda) \), \( g(\lambda) \), and \( b(\lambda) \), respectively. \( \lambda \) in the parenthesis is the wavelength.

As, the sum of the three tristimulus values at each wavelength is always 100%, the mixture ratio of the three primary colors can be obtained by any two of the three tristimulus values. The RGB color metric system is based on this and all colors are indicated on the \( r(\lambda) \) and \( g(\lambda) \) coordinates.

To overcome difficulties associated with the negative stimulus of the primary colors, based on the above mentioned color matching experiments, three imaginary reference color stimuli \([X]\), \([Y]\), and \([Z]\) were introduced. By employing the imaginary reference color stimuli, the original tristimulus values were converted mathematically into positive values and all colors could be composed by mixing (not subtracting) these three stimuli. This is the basis of the XYZ colorimetric system. \( Y \) has been chosen to correspond with the lightness stimulus. Based on the similar idea with that of the RGB colorimetric system, all colors are indicated by these coordinates.

Test light source colors are specified below. The tristimulus value \((X, Y \text{ and } Z)\) for a test light source, which has a spectral energy distribution \( P(\lambda) \), are calculated with the following formulae.
\begin{align}
X &= K \int_{380}^{780} P(\lambda) \overline{x}(\lambda) d\lambda \\
Y &= K P(\lambda) \overline{y}(\lambda) d\lambda \\
Z &= K \int_{380}^{780} P(\lambda) \overline{z}(\lambda) d\lambda
\end{align}

Where

\[ K = \frac{1}{P(\lambda)Y(\lambda) d\lambda} \]

and \( x(\lambda), y(\lambda), \) and \( z(\lambda) \) are the spectral stimulus values for 2°. These quantities are written as \( x_{10}(\lambda), y_{10}(\lambda), z_{10}(\lambda) \) for 10.

The chromaticity coordinates of the color of the light sources \( x \) and \( y \) are calculated with the following formulae.

\begin{align}
x &= \frac{X}{X + Y + Z} \\
y &= \frac{Y}{X + Y + Z}
\end{align}

The colors of light sources on the XYZ colorimetric system are specified with \( Y \) calculated with Eq. 7 and \( x \) and \( y \) calculated with Eq. 9 and 10 respectively.

**Specification of the nonluminous object colors**

The tristimulus values [87] \( (X, Y, \) and \( Z) \) of the object for which the spectral reflectance (or spectral transmittance) is \( \rho(\lambda) \) and \( \tau(\lambda) \) are given by

\begin{align}
X &= \frac{1}{K} \int_{380}^{780} P(\lambda) \rho(\lambda) \overline{x}(\lambda) d\lambda \\
Y &= \frac{1}{K} \int_{380}^{780} P(\lambda) \rho(\lambda) \overline{y}(\lambda) d\lambda \\
Z &= \frac{1}{K} \int_{380}^{780} P(\lambda) \rho(\lambda) \overline{z}(\lambda) d\lambda
\end{align}

Where \( K = \int_{380}^{780} P(\lambda) \overline{y}(\lambda) d\lambda \)

\( P(\lambda) \) is the spectral power distribution of the light source which illuminates the object, and \( x(\lambda), y(\lambda), \) and \( z(\lambda) \) are the CIE spectral trichromatic stimuli for...
fields of 2° or 10°. The chromaticity co-ordinates of the color of the objects can then be calculated, as with the light sources, using Eq. 9 and 10.

CIE co-ordinates are powerful concept because they facilitate representing an entire luminescent spectrum by two numbers and the simplicity of the visual method for obtaining the color gamut of phosphors is quite attractive. The main drawback of CIE co-ordinate system is that it involves complexity in calculation but the spectrophotometer used by us automatically calculated the CIE co-ordinates.

**iii) Procedure**

Photoluminescence (PL) spectra were taken in solid powder form of complexes. For photoluminescence measurements, 0.05g powder samples were pressed into pellets (10mm diameter and 1mm thickness), then exposed to a ultraviolet rays of suitable wavelength using xenon arch lamp. All measurements were carried out at room temperature. The emission color was analyzed and confirmed with the help of *Commission de I Eclairage* (CIE) chromaticity coordinate diagram.

**iv) Instrument**

Photoluminescence (PL) spectra and color coordinates were recorded with a Minolta spectroradiometer CS-1000 shown in Fig. 2.2.2.

![Minolta spectroradiometer CS-1000](image)

**Fig. 2.2.2 Minolta spectroradiometer CS-1000**

**B) X-RAY DIFFRACTION STUDIES**

In 1895, German Physicist W.C. Roentgen 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 analysed the same experiment and derived the conditions for diffraction from a 3d-periodic arrangement of atoms.
X-rays are electromagnetic radiation of very much shorter wavelength compared to that of light. The X-rays used in diffraction have wavelengths in the range of 0.5-2.5 Å and thus lie in between gamma and ultraviolet rays. X-rays carry energy and the rate of flow of this energy through unit area perpendicular to the direction of motion of the wave is proportional to the square of the amplitude of the wave and known as intensity (I) of the radiation.

X-rays are produced when an electrically charged particle (e.g. electrons) of sufficient kinetic energy is rapidly decelerated. When electrons moving at high speeds are directed to a metal target, a very small percentage of their kinetic energy is converted into X-rays. Most of the kinetic energy of the electrons striking the target is converted to heat, less than 1% being transformed into X-rays. The X-rays emitted by the target consist of a continuous range of wavelengths and is called the white or continuous radiation. The minimum wavelength in the continuous spectrum is inversely proportional to the applied voltage which accelerates the electrons towards the target. The intensity is zero upto a certain wavelength, called the short wavelength limit ($\lambda_{SWL}$). It increases rapidly to a maximum and then decreases with no sharp limit on the long wavelength side. The continuous spectrum gets generated due to the emission of energy as a result of declaration of electrons heating the target. Electrons which are stopped in a single impact give rise to maximum energy. The corresponding wavelength, [88] known as short wavelength limit, is given by Eq. 14.

$$\lambda_{SWL} = 12.40x 10^3/V \quad (14)$$

If an electron is not completely stopped in one encounter, it undergoes a glancing impact which only partially decreases its velocity, then only a fraction of its energy is emitted as radiation; the corresponding X-ray has a wavelength longer than $\lambda_{SWL}$. The totality of these wavelengths, ranging upward from $\lambda_{SWL}$ constitutes the continuous spectrum. The total X-ray energy emitted per second, i.e. intensity is given by Eq. 15.

$$I_{\text{continuous spectrum}} = A i Z V^m \quad (15)$$

Where A is proportionality constant, m is a constant of about 2, i is the current and Z is the atomic number of the target [89]. The material of the target affects the intensity but not the wavelength distribution of the continuous spectrum.
When the applied voltage is sufficiently high, in addition to the white radiation, a characteristic radiation of a specific wavelength and high intensity is also emitted by the target. However, these are narrow and their wavelengths are characteristics of the target metal. These radiations fall into several sets, K, L, M, etc in the order of increasing wavelength. Ordinarily K lines are useful in X-ray diffraction because longer wavelengths lines are being easily absorbed. Several lines are possible in the K set i.e. Kα₁, Kα₂, and Kβ₁. Among these Kα₁ is preferred for X-ray diffraction.

i) Basic Principles of Diffraction

X-ray diffraction can be explained in simple terms by the reflection of an X-ray beam from a stock of parallel equidistant atomic planes. The diffracted beam is thus composed of a large number of scattered rays mutually reinforcing each other. Diffraction essentially is a scattering phenomenon. When X-ray interacts with atom, it gives rise to scattering in all directions; in some of these directions the scattered beams will be completely in phase and so reinforce each other to form diffracted beams.

Fig. 2.2.3 Diffraction of X-rays by a crystal

Fig. 2.2.3 shows a set of parallel planes in a crystal. A beam of X-rays of wavelength \( \lambda \) is directed towards the crystal at an angle \( \theta \) to the atomic planes. The
atomic planes are considered to be semi-transparent, i.e. they allow a part of the X-rays to pass through and reflect the other part. Considering rays $1, I_a$ in the incident beam, they strike the atom at K and P in the first plane of atoms and are scattered in all directions. However, only $I_1$ and $I_a$ out of all scattered rays are completely in phase and so capable of reinforcing one another. Rays 1 and 2 are scattered by atoms K and L, and the path difference for rays is given in Eq. 16.

$$ML+LN = d \sin \theta + d \sin \theta = 2d \sin \theta$$  (16)

The two scattered rays will be completely in phase if this path difference is equal to an integral multiple of wavelengths, i.e.

$$n\lambda = 2d \sin \theta$$  (17)

Eq. 17 is known as Bragg Law and $\theta$ is known as the Bragg angle [90-91] where maximum intensity occurs and $n$ is the order of diffraction. At other angles, there is little or no diffracted intensity because of destructive interference.

$$\sin \theta = \frac{n\lambda}{2d} \leq 1$$

$$\lambda \leq 2d \text{ for } n=1$$

Thus, first order Bragg reflection can occur only for wavelengths $\lambda \leq 2d$. Since the lattice spacing $d$ is of the order of angstroms, X-rays (wavelength in Å) are well suitable for diffraction studies. This means that spacing $d$ can be easily evaluated from measurements of first order Bragg angle $\theta$ using Bragg’s law with $n=1$. If the regular arrangement of atoms in a crystal is considered, stacks of parallel lattice planes are found with different characteristic spacings. Therefore, each crystallographic phase shows a characteristic set of d-spacings which yields a diffraction pattern with intensities at the corresponding Bragg angle $\theta$ [92].

The average crystalline size in phosphors powders can be estimated using the scherrer equation based on diffraction peak broadening. This scherrer equation (Eq. 18) has been drawn from Bragg’s Law.

Scherrer equation,

$$D = \frac{0.941\lambda}{\beta \cos \theta}$$  (18)
Where,

\[ D \] is the average crystallite size

\[ \lambda \] is the x-ray wavelength

\[ \theta \] is the diffraction angle.

\[ \beta \] is the full width at half maximum (FWHM) in radian.

Sample identification can be easy by comparing the experimental diffraction pattern to that in the JCPDS files. Sample preparation is relatively simple; powders can be pressed into a disc, film, or smeared onto a substrate and the experiment does not require vacuum. The particle size and its crystalline behavior were analysed by observing the peak broadening and noise in diffraction pattern.

ii) Instrument

Rigaku D/Max 2000-Ultima plus diffractometer as shown in Fig. 2.2.4 was used to analyse XRD pattern.

![Fig. 2.2.4 Rigaku D/Max 2000-Ultima plus diffractometer](image)

C) ENERGY DISPERSIVE X-RAY ANALYSIS

Energy dispersive X-ray analysis is an experiment that determines the amount in weight percent of various elements present in a compound. By EDAX technique a quantitative analysis can be made of elements with atomic number of 6 (carbon) or greater. This type of analysis is useful for organic as well as inorganic compounds. Combining the EDAX spectrum with the SEM allows the identification, at micro structural level, of compositional gradients at grain boundaries, second phases, impurities, inclusions, and small amounts of material. In the scanning mode, the
SEM/EDS unit can be used to produce maps of element location, concentration, and distribution.

i) Principle

One of the instruments most commonly used in conjunction with the SEM is the Energy Dispersive X-ray Spectrometer (EDS). The X-ray spectrometer converts a X-ray photon into an electrical pulse with specific characteristics of amplitude and width. A multi-channel analyzer measures the pulse and increments a corresponding "energy slot" in a monitor display. The location of the slot is proportional to the energy of the X-ray photon entering the detector. The display is a histogram of the X-ray energy received by the detector, with individual "peaks," the heights of which are proportional to the amount of a particular element in the specimen being analyzed. The locations of the peaks are directly related to the particular X-ray "fingerprint" of the elements present. Consequently, the presence of a peak, its height, and several other factors, allows the analyst to identify elements within a sample, and with the use of appropriate standards and software, a quantitative analysis can be made of elements with atomic number of 6 (carbon) or greater.

ii) Instrument

The energy dispersive X-ray analyses were performed by EDAX-PV 99.

D) SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy also known as SEM, can generate impressive physical and structural details. The scanning electron microscope is based on scanning a finely focused electron beam across the surfaces of a specimen. The latter reflects the beam into two directions X and Y. These reflection signals are collected, and their intensities are displayed on a cathode-ray-tube screen by brightness modulation. As already indicated, the method allows specimen magnifications to more than 100,000 while maintaining a large depth of focus. The ease of sample scanning of a SEM over large distances is quite appealing, in that a large sample scanning-viewing area is first surveyed at generally low magnifications to seek out particular areas of interest, followed by high magnification of those specific areas for subsequent detailed investigations. Hence, specific surfaces irregularities, for example, known to be present or noted at low magnifications can be identified and further investigated at significantly higher magnifications. Such studies can highlight unexpected
geometrical configurations, unique shapes of particulates, or the degree of deficiency. The SEM is also extensively employed for the generation of dimensional and spatial relationship details of structure elements.

i) Fundamental electron-material interactions

SEM tools rely on the generation of electrons accelerated through an electric field to acquire sufficient kinetic energy. These energized electrons are then directed onto the material to be investigated. The electron interaction with the material results in a number of different energy dissipation modes. The particular type of released energy depends on the energized electron interaction with the various orbital electrons of the material. If the ejected orbital electron is weakly bound, it emerges with only a few eVs of energy. These are termed secondary electrons. Secondary electrons generated sufficiently deep within the material are reabsorbed by that material before they can reach the surface, whereas those generated near the surface can escape and therefore are detectable. Secondary electrons created at topographic peak areas in a material will have a greater chance to escape than those generated in topographic troughs. Furthermore, since the greatest density of secondary electrons is created by the primary beam of energized electrons before they spread into the material to undergo other possible energy signals. The ability to capture both the topographic sensitivity and the spatial resolution forms the basic for high-resolution microscopy of the material surfaces as measured by a SEM tool. As long as a material surface exhibits some degree of surface irregularities, it generates a SEM micrographic image.

The ultimate spatial resolution of a SEM image is proportional to the tool’s ability to generate an electron current density. The development of the field mission gun Crewe in 1968 greatly advanced the resolution of a SEM. The gun creates extremely high electron current densities by forcibly emitting electrons from a needle-pointed metal tip under an intense electric field and ultra-high-vacuum conditions.

ii) SEM Analysis

SEM photo microscopy tends to be the preferred means to obtain any initial high-resolution data of a particular sample. It is quite useful for the most dimensional and structural shape information, including feature-to feature comparisons to evaluate consistencies or abnormalities.
iii) Instrument

Philips XL30 instrument shown in Fig. 2.2.5 was used for SEM analysis of the phosphors.

Fig. 2.2.5 The Philips XL30, Fully computer-controlled scanning electron microscope

E) TRANSMISSION ELECTRON MICROSCOPY

TEM is a microscopy technique where by a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a CCD camera. TEMs are capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument to be able 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. TEM forms a major analysis method in a range of scientific fields, in both physical and biological sciences.

i) Schematic outline of a TEM

A TEM contains four parts: electron source, electromagnetic lens system, sample holder, and imaging system. Fig. 2.2.6 shows a schematic outline of a TEM.
**Electron source**

The electron source consists of a cathode and an anode. The cathode is a tungsten filament which emits electrons when being heated. A negative cap confines the electrons into a loosely focused beam (Fig. 2.2.7). The beam is then accelerated towards the specimen by the positive anode. Electrons at the rim of the beam will fall onto the anode while the others at the center will pass through the small hole of the anode. The electron source works like a cathode ray tube.
Electromagnetic lens system

After leaving the electron source, the electron beam is tightly focused using electromagnetic lens and metal apertures. The system only allows electrons within a small energy range to pass through, so the electrons in the electron beam will have a well-defined energy.

1. Magnetic Lens: Circular electro-magnets capable of generating a precise circular magnetic field. The field acts like an optical lens to focus the electrons.

2. Aperture: A thin disk with a small (2-100 micrometers) circular through-hole. It is used to restrict the electron beam and filter out unwanted electrons before hitting the specimen.

Sample holder

The sample holder is a platform equipped with a mechanical arm for holding the specimen and controlling its position.
Imaging system

The imaging system consists of another electromagnetic lens system and a screen. The electromagnetic lens system contains two lens systems, one for refocusing the electrons after they pass through the specimen, and the other for enlarging the image and projecting it onto the screen. The screen has a phosphorescent plate which glows when being hit by electrons. Image forms in a way similar to photography.

ii) Working principle

TEM works like a slide projector. A projector shines a beam of light which transmits through the slide. The patterns painted on the slide only allow certain parts of the light beam to pass through. Thus the transmitted beam replicates the patterns on the slide, forming an enlarged image of the slide when falling on the screen.

TEMs work the same way except that they shine a beam of electrons (like the light in a slide projector) through the specimen (like the slide). However, in TEM, the transmission of electron beam is highly dependent on the properties of material being examined. Such properties include density, composition, etc. For example, porous material will allow more electrons to pass through while dense material will allow less. As a result, a specimen with a non-uniform density can be examined by this
technique. Whatever part is transmitted is projected onto a phosphor screen for the user to see.

For preparation of samples for TEM analysis, the nanophosphors were dispersed well in an appropriate solvent. Then with the help of a micro tipped dropper the fine particles were applied on thin glass film and allowed to stand for some time to allow the solvent to evaporate. After drying the specimen was transferred in the microscope column for imaging at different magnification and the electron diffraction patterns were recorded.

iii) Instrument

JEOL JEM-2100F instrument as shown in Fig.2.2.9 was used for TEM analysis of the inorganic phosphors.

Fig. 2.2.9 JEOL JEM-2100F Transmission Electron Microscopy
REFERENCES


