Chapter-2

Materials and methods
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This chapter includes the various materials synthesis approaches used for the development of rare earth doped phosphor materials in the nano domain. The developed luminescent materials are characterized by various techniques and instruments employed for characterization have been discussed in detail.

2.1 Materials

For the development of efficient luminescent rare earth nanophosphors the major deciding factors for potential optical performance includes the chemical composition of the material, crystallographic features, crystal dimensions and shape of the crystallites. These features are inherent to the host lattice, dopant ion and any fuel or chelating agent used. These properties get modified by mere presence of any impurity in the sample, thus affecting the luminescence efficacy of the developed nanophosphor. Hence, the prime importance must be given to select impurity free ingredient materials having maximum chemical purity so that luminescent properties of the sample should not be limited by the ingredients purity factor. Therefore, in this context all the chemicals employed as raw materials for synthesis of rare earth doped luminescent nanomaterials described in this thesis were purchased from Sigma-Aldrich or CDH and were of high chemical purity $\geq 99\%$ as listed in Table 2.1.

Table 2.1 Various chemicals used for the synthesis of nanophosphors

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>Chemicals used</th>
<th>Chemical formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Aluminium nitrate nonahydrate</td>
<td>[Al(NO$_3$)$_3$.9H$_2$O]</td>
</tr>
<tr>
<td>2</td>
<td>Europium(III) nitrate hexahydrate</td>
<td>[Eu(NO$_3$)$_3$.6H$_2$O]</td>
</tr>
<tr>
<td>3</td>
<td>Erbium(III) nitrate hexahydrate</td>
<td>[Er(NO$_3$)$_3$.6H$_2$O]</td>
</tr>
<tr>
<td>4</td>
<td>Gadolinium(III) nitrate hexahydrate</td>
<td>[Gd(NO$_3$)$_3$.6H$_2$O]</td>
</tr>
<tr>
<td>5</td>
<td>Lanthanum(III) nitrate hexahydrate</td>
<td>[La(NO$_3$)$_3$.6H$_2$O]</td>
</tr>
<tr>
<td>6</td>
<td>Samarium(III) nitrate hexahydrate</td>
<td>[Sm(NO$_3$)$_3$.6H$_2$O]</td>
</tr>
<tr>
<td>7</td>
<td>Terbium(III) nitrate hexahydrate</td>
<td>[Tb(NO$_3$)$_3$.6H$_2$O]</td>
</tr>
<tr>
<td>8</td>
<td>Yttrium(III) nitrate hexahydrate</td>
<td>[Y(NO$_3$)$_3$.6H$_2$O]</td>
</tr>
<tr>
<td>9</td>
<td>Zinc nitrate hydrate</td>
<td>[Zn(NO$_3$)$_2$.xH$_2$O]</td>
</tr>
<tr>
<td>10</td>
<td>Strontium nitrate</td>
<td>[Sr(NO$_3$)$_2$]</td>
</tr>
<tr>
<td>11</td>
<td>Barium nitrate</td>
<td>[Ba(NO$_3$)$_2$]</td>
</tr>
<tr>
<td>12</td>
<td>Urea</td>
<td>[H$_2$NCONH$_2$]</td>
</tr>
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</table>
2.2 Powder synthesis approaches

In 1990’s, the emergence of blue and UV GaInN emitting diodes promote the rejuvenation in phosphor development field, which had just materialized in the era of 60’s and 70’s for production of fluorescent lighting system and color television displays. This demands the development of simple diodes which offer color high purity along with high efficacy. The high color performance of the diodes depends on the luminescent properties and crystallinity of the host and the dopant ion whereas the high efficacy relates to the absorption and refractive index parameters. This host and the dopant combination result in the occurrence of the luminescence phenomenon.

The phosphor material is developed by the incorporation of dopant or the impurity in the host matrix without creating any perturbation in the lattice of host. These impurities or dopant ions are known as the luminescent centers and are responsible for characteristic luminescence features of the nanophosphor. Most commonly incorporated dopant ions in the host includes the rare earth ion which get dispersed in the host uniformly, causing lesser defects in the lattice. These phosphors are highly recommendable for the optoelectronic application perspective. The stoichiometric control or precision in composition, morphological aspect, surface chemistry, high brightness and quantum efficiency are the major points of concern to develop rare earth doped phosphor for practical application. Moreover, the rare earth doped phosphors grown with reduced dimensionality to nano domain, enmarks the tailored properties in the field of luminescent materials.

The development of these rare earth doped phosphor in nano domain by employing reliable routes involves a general mechanism of incorporating dopant ion in the existing host material. The process involves the mixing of starting raw materials; the rare earth ions and the materials constituting host matrix in appropriate ratio. The ratio may considerably differ from the stoichiometric composition of the nanophosphor developed. The raw ingredient materials are mixed mechanically before setup the firing process and are of utmost significance to develop nanophosphors with required composition. Slurring, wet ball milling, dry ball milling, mortaring are some of the useful methods for appropriate mixing of the raw materials. In course of nanophosphor preparation through firing, the unrequisite products are either removed via vaporization during the process or removed from the mixture as by-product. An alternative approach to remove the extra component is to apply
washing treatment on the reaction product after the reaction ceases. In this way, the final reaction product possesses the required nanophosphor stoichiometry [1]. For obtaining the requisite stoichiometrically precised nanophosphor, it is very advisable and necessary to perform the exhaustive experimental analysis on the synthesis and characterization of various doped host matrices with dopant ions.

Numerous synthesis strategies are available to develop phosphors in nano regime with tailored features include the conventional solid state approach [2-7] or wet-chemical approaches (non-traditional strategies) such as hydrothermal technique [8-13], co-precipitation approach [14-17], spray pyrolysis [18-19], microwave synthesis [20-22], sol-gel synthesis [23-37] and solution combustion approach [38-61]. With respect to the global concerns regarding the ecological sustainability, environmental hazards and energy savings, much attention is paid towards the reliable approaches to prepare the nanophosphors at commercial scale. Moreover, the field of luminescent materials displays the room for the improvement in the areas of improved emission color, increased luminous efficacy and reduced cost per lumen output. Thus, the development of nanophosphor for commercialization demands the appropriate selection of synthesis strategy. The various synthetic strategies are briefly explained as follows:

(i) Solid-state method

Solid state approach is most widely utilized traditional synthesis route for phosphor preparation involving high temperature synthesis. The process involves mechanical mixing of the high purity raw materials including host materials dopant or fluxes. The mechanical mixing may be conducted by ball milling, mortaring or other mixing methods followed by the firing treatment at high temperature in the high temperature furnace. The firing process results in formation of the required phosphor in form of large aggregate, which further needs to be properly grounded to remove the coarse particles [62-65]. In the row to obtain fine powdered form the product may also require surface treatment. This method suffers from some drawbacks in the terms of the inhomogeneity of the product form, formation of large lumps of particles, which makes the grounding necessary.

Due to excessive grinding the product synthesized by this solid state method acquire several surface defects. Moreover, the imprecise control over the product stoichiometry, higher processing temperatures and longer time requirement makes this
synthesis process unsuitable for nanophosphor development. This promote the researches to switch to the wet-chemical methods which involves the appropriate molecular level mixing of the starting raw materials, generating the highly uniform, small sized product with larger surface area. Nowadays, the wet-chemical methods are employed for nanophosphor synthesis and overcome the drawbacks of solid state, however, the further sintering may also be required in these methods in order to obtain the product with greater crystallinity.

(ii) Hydrothermal synthesis

The hydrothermal (HT) synthesis route is used for synthesis of some ceramic oxides for which it is difficult to develop single phase crystallinity at their melting point being unstable at the melting point. This process involves the self sustained high vapour pressure generated spontaneously beyond the boiling point of water at relatively low temperatures (100-300°C). This synthesis approach does not require any mechanical mixing of starting materials through milling and calcination procedure [66]. The process starts with dissolution of precursor materials in proper stoichiometric ratio in nitric acid and then the solution is allowed to evaporate up to dryness. The remaining mixture is then transferred inside an autoclave made up of stainless steel lined with teflon possessing filling capacity of 40% distilled water. The mixture is allowed to crystallize within autoclave for few hours, consecutively cooled at room temperature, filtered, washed with distilled water or ethanol and finally, dried in oven at 80°C for some time to obtain the required phosphor. The particle size as well as the shape of the developed nanophosphor is very much influenced by processing parameters like pH setting, temperatures and surfactant addition and pressure. Aqueous medium dissolution/precipitation of the starting materials is helpful in having control over the reaction as well as composition. This process has some limits in terms of the expensive autoclaves which can withstand the high pressure and temperature for prolonged time and is difficult to monitor the nanophosphor development time to time.

(iii) Co-precipitation method

Co-precipitation technique is another soft chemical synthesis tool which is free from any by-product formation except water along with the desired product. This process involves the simple reaction between the stoichiometrically weighed starting
materials and the precipitating reagent. The reaction is very fast, exothermic and instantly results in formation of large amount of precipitates. These precipitates are filtered, centrifuged through centrifugation machine and washed several times using deionized water or ethanol, dried in oven around 80°C. The dried product further needs the heat treatment in favorable atmosphere to collect the desired phosphors. The through mixing of the starting materials affects the nature of the products.

The method of mixing and state of stirring has significant effect on the size of aggregates. Homogeneous product formation depends on the appropriate mode of mixing. The co-precipitation technique may sometime face the limitations in terms of co-precipitation of impurities along with the desired product which makes necessary to reprecipitation of the solution for which the sample is again dissolved. Moreover, the nature of flux utilized also has its impact on the morphology of the phosphor particles [17]. When H₃BO₃ is used as a flux in co-precipitation process, it results in formation of spherical shaped particles with size around 300 nm, while Li₂CO₃ or Li₃PO₄ flux are employed separately or in combined form. This results in formation of uniform nearly spherical shaped particles with large size around 5 μm scale. The heat treatment given to the product in presence of double flux at higher temperatures around (1100-1200°C), results in formation of spherical particles, possessing good luminous efficacy.

(iv) **Spray pyrolysis**

With the growing advances in the field of nanophosphor synthesis, spray pyrolysis is a very useful technique mainly useful for the synthesis of oxide materials. This technique involves a sequence of processes either happening simultaneously or in subsequent manner. These sequential processes involve mainly the aerosol generation, their transport, evaporation of solvent molecules, droplet impact and decomposition of precursor materials. The chemical reactants are selected appropriately so that the product formed other than the desired phosphor gets evaporated during the application of temperature. In this process, the aerosol is generated by employing the ultrasonic aerosol generator which atomizes the precursor solution into uniform droplet form. These droplets are then transported to the hot surface of the furnace and undergo thermal decomposition leading to formation of particles which get accumulated within bag filter and given post heat treatment process for crystallization. The solvent molecules in the droplet become volatilize on transportation into hot furnace. The
morphological aspect of particles generated via this strategy is very much influenced by the nature of starting materials as well as the synthetic conditions [18-19]. The phosphor particles produced this way bear advanced characteristics like spherical shape with small size, segregated particles having narrow size distribution.

**(v) Microwave synthesis**

Microwave synthesis is a comparatively progressive and vital technique for development of phosphors having merits in terms of accelerated reaction rates thus saving time, reduced energy utilization and easy reaction conditions [21]. This synthesis technique involves heating process that is typically different from the traditional mode of heating. In traditional mode, the heating starts from the surface to the inside of the material while microwave synthesis involves core heating, a volumetric heating process. The microwave energy is directly absorbed by the reacting materials referred as molecular level heating, which further gets transformed into heat. The energy supplied either in form of low voltage alternating current or high voltage direct current gets transformed and finally converted into the direct current. The energy is directly consumed by the reacting materials, the temperature may rise up simultaneously which can be easily controlled by stabilizing the power input in the microwave machine. This technique works on the principle of rotation of molecules by absorption of energy. The sample gets rotated horizontally along the axis, gets heated up during the process and maintained at required temperature for small duration of time to obtain the desired product.

**(vi) Sol-gel method**

Sol-gel is another efficient wet synthesis technique to develop the phosphors within the nano scaling. Starting with solution phase involving polymerization and polycondensation processes, it gradually gets transformed to sol with solid phase network. Then subsequently undergoes a number of steps like gelling, drying, pressing and casting leading to different structural and phase conversions. All these sequential conversions finally result in formation of powders, fibres, bulk monolithic products or coatings. The selection of precursor materials is very crucial for obtaining the desired sol-gel product. Alkoxides, soluble metal salts, polymers, colloids are most commonly used as starting materials in addition with appropriate solvents and the chelating agents so that the aggregation processes can be controlled to achieve the
solid phase formation. The stoichiometrically weighed high purity precursor materials are dissolved in minimum amount of dilute HNO₃ to obtain a homogeneous solution. The chelating agents are then mixed in this solution in various ratios relative to the metal ions of host matrix to examine their effect on surface area, particle size and optical features exhibited by the synthesized nanophosphors. The final mixture is then continuously stirred at 80°C for 2 h, converting the transparent solution into denser ‘sol’. The sol then gets transformed into gel with continuous heating at 120°C and then the gel is dried to obtain the fluffy powder. The appearance of gel is dependent upon the nature of chelating agent employed such as the chelating agent, tartaric acid results in immediate precipitation whereas citric acid solution precipitation occurs in several hours.

Recently, Pechini-sol-gel method is widely utilized for low temperature material synthesis which involves the esterification processes between the metal ions chelating complexes and ethylene glycol [67-68]. These chelating complexes of metal ions include the metal salts such as nitrates, acetates with complexation agents like L-tartaric acid, EDTA or citric acid. Citric or tartaric acid have good complexation tendency to obtain the nano scaled powder with narrow size distribution, thus provides much easier synthesis route than the other traditional sol-gel methods [69-70]. Due to the presence of carboxylate (-COOH) and hydroxyl (-OH) groups, tartaric acid behave like a bidentate ligand and easily forms polynuclear complexation with metal ions resulting highly homogeneous, small sized particles with greater surface area [71-72]. Although the sol-gel is an effective and simple technique for producing high quality nanoparticles, however, the major drawbacks associated with this method are its expensive starting materials and it is time consuming process [73-77].

(vii) Solution combustion synthesis

With the advancement in the research owing to utilization of nanophosphor materials, solution combustion synthesis (SCS) has emerged as an indispensable and versatile synthesis route for developing materials of nano size. It has been continuously employed for the production of more than 1000 types of different nanoscaled oxide powders having applications in fuel cells, catalysts, biotechnology and lighting materials [78]. The synthesis and designing of metal oxide nanocrystalline materials is one among the most crucial step involved in the process of achieving the significant energy conversion and storage at commercial level [79]. SCS
is gaining popularity for synthesis of a wide range of materials due to its simplicity of implementation, time saving, energy saving, possibility to achieve products with desired composition with an ease. At industrial scale, this method is widely employed to synthesize alloy, sulphides, oxide materials and broad range materials including spinels, perovskites, ferrites for diverse and broad range applications. It is broadly acceptable as most convenient way to synthesize simple as well as multicomponent complex oxide materials [1-4].

Solution combustion is an exciting phenomenon based on the redox system which requires heating the solution media to certain moderate temperature and further propagates via self governed highly exothermic reaction; which provides the ample amount of energy for formation of oxide powder. The solution combustion synthesis technique has gone through a lot of research developments. In the year 1967, Merzhano et al. extensively carried out the work regarding the combustion of condensed substances and proposed the theory of self-governed high temperature synthesis (SHS) or combustion synthesis [80]. This concept utilizes the asset of self spreading or self controlled chemical redox reaction by its own to drive the reaction in forward direction and to completion [81]. Although, this type of reaction is having demerits which involves solid reagents as precursors in terms of large sized particles and problems faced to control the SHS mechanism. Due to these drawbacks, the SHS is not found to be viable for development of complex oxide materials [82]. Later on, a further development was carried out in this method by Patil et al. and referred it as solution combustion synthesis by integrating it with the wet chemistry of oxide synthesis [83].

The starting ingredient material for solution combustion synthesis involves the metal salts like nitrates, carbonates, sulphates as the source of metal as well as oxidizing agents and organic fuel as reducing agent in the redox reaction such as urea (CH₄N₂O), acetylacetone (C₅H₈O₂) glycine (C₂H₄NO₂), carbohydrazide (CH₂N₄O), diformylhydrazine (C₂H₄N₂O₂), oxalyl dihydrazide (C₂H₆N₄O₂) sucrose (C₁₂H₂₂O₁₁), starch etc. Depending on the exothermicity of the reaction; the N containing fuels specifically, urea and glycine are widely used as reducing agents due to their greater complexation tendency to form stable complexes with metal. This increases solubility and checks selective precipitation of metal ions in the solution and also functions as fuel for the reaction. If the precursor materials are used as metal chlorides; then it
further requires some combustion igniting materials such as nitrate ions in form of ammonium nitrate, which are used to initiate the process. In pursuit of environment concerns, the most widely used solvents for SCS are the water and ethanol but some organic solvents like acetonitrile and 2-methoxymethanal are also employed for oxide production.

![Fig.2.1 Muffle furnace](image)

The SCS process involves the homogeneous mixing of starting materials in minimum amount of solvent such as water in pyrex beaker and then introduced into a muffle furnace (Fig.2.1) maintained at a temperature around 500°C. Hot plate may also be utilized for the ignition process. When the resulting solution in the furnace, attains the ignition temperature, the self spreading exothermic reaction begins which further does not require the external energy source. During this combustion process, the organic fuel is oxidized by the nitrate ions present in the solution and thus lead to release of heat of the reaction which meets the requirement of energy to carry out the formation of oxides. Within minutes the reaction may attain the temperature as high as 1600°C and in some cases may rises or exceed 3000°C [9]. The process begins with boiling, ignites to burn with flame, evolution of gases like N₂, CO₂, H₂O which finally lead to the formation of foamy, oxide product which may spread to the top of the beaker. The whole process consumes 3-5 minutes. The key merit of this process is high efficiency in terms of time and energy. Hence, once the reaction mixture is
ignited; within minutes the precursor materials get transformed into respective oxides governed by the self generated exothermic reaction without demanding further continuous supply of external energy.

There are certain parameters which controls the growth of nano-crystalline oxide powder with high homogeneity, purity, small or nano- agglomerated particles at low cost. Some of these combustion parameters include the type of precursor material or its composition, type of fuel, oxidant-fuel ratio and generation of gases during the process. The chemical composition of precursor materials exerts pronounced effect on the features of the resulting oxide. The precursor materials that are intimately mixed, resulting in homogeneous product formation, involving use of metal nitrates as oxidant and fuel such as urea when dissolved in water as solvent. The nitrogen containing fuels like urea/glycine tend to formation of powders with nano sized range due to their easy availability, low cost, high exothermicity and high coordinating tendency with metal nitrates. It is worth mentioning that the amount of gases generated during the combustion process has great impact on the morphology, particle size and surface area of powder produced. By using different fuels, the difference in particle size is acknowledged depending on number of moles of gaseous product generated during the process. The influence of gases on the morphology, crystallite size, degree and nature of agglomeration can be controlled by tuning the oxidant-fuel ratio.

As a low cost and energy efficient synthesis the SCS is extensively explored; however, the complex mechanism of the combustion reaction is still unclear. In the literature, the three probable mechanistic routes which vary in explanation about type and progress of reaction are available. Kingsley et al. describes the simultaneous thermal degradation of urea into biuret and ammonia initially and then to cyanic acid trimer (HCNO) at elevated temperature while aluminium nitrate to alumina and nitrogen oxide. The final phase of the reaction proceeds via reaction between the combustible species (such as ammonia and cyanic acid) and the nitrogen oxide yielding flame generation. The above concept is well favoured by the researches like Chandramouli et al. and Lie et al. Whereas, Segadaes et al. are of the opinion that the comprehensive combustion reaction is a summation of partial reactions of thermodynamic significance and the heat requirement of the system is accomplished by reaction between the fuel and the oxygen, which in turn produced by
decomposition of nitrate ions [39, 45] Suresh et al. viewed that on ignition, the self catalyzed redox reaction between fuel and metal nitrates propagate to completion making full expenditure of fuel without further requirement of heat [46]. The calorimetric and thermal-gravimetric techniques have been exhaustively utilized to examine the solution combustion propagation as reported in literature [47, 53, 84], whereas the experimental data of gaseous products are not accessible in the literature. Actually, the calorimetric and thermal gravimetric analysis and gaseous evolution phase of the reaction can be probed simultaneously to better understand the solution combustion reaction progress.

Currently, a large number of nanophosphors of significant application such as aluminates [86], zirconates [57, 85], oxides [41-42], phosphates [55-56], vandates [87] etc. have been synthesized by using this SCS route. The homogenously mixed precursor solution and high temperature evolved during the reaction ensure the formation of highly pure, uniform well developed particles in nano dimension. In pursuit of environmental concerns with time and energy efficiency; the SCS method is highly exploited by the researchers than the conventional and other wet chemical methods of nanophosphor synthesis.

As a part of the thesis work, on capitalizing the merits of SCS; the author has employed the solution combustion approach using urea as an organic fuel to develop various oxide phosphors in nano domain.

2.3 Nanophosphor characterization techniques

The synthesized nanophosphors can be characterized by employing spectroscopic and microscopic techniques including X-ray diffraction spectroscopy (XRD), photoluminescence spectroscopy (PL) and transmission electron microscopy (TEM) all these techniques are described in details as follows:

2.3.1 X-ray diffraction spectroscopy

X-rays are the high energy electromagnetic radiations possessing much higher frequency than the visible light. These high energy rays having the wavelength range 0.5-2.5 Å are employed for diffraction and have much more penetrating power than the UV or visible light. These electromagnetic rays when interact with matter get scattered to generate a diffraction pattern. This specific diffraction pattern makes the
basis of X-ray diffraction spectroscopy, which is perhaps most widely utilized nondestructive analytical tool to characterize the materials, to draw information about the quantitative phase identifications, unit cell dimensions and structural imperfection existing in the sample, preferred crystal orientations, crystallinity, grain size.

These X-rays has a very revival history and came into existence in 1895; discovered by German physicist W. C. Roentgen who was working with a cathode ray tube. In the year 1912, another scientist Max von Laue, proved wave like nature of X-rays through his experiments and discovered that the crystalline materials behave like three dimensional diffraction grating for the interacting X-ray wavelengths just like the planar spacing in a crystal lattice. In the same time period (20th century), the Nobel laureates W.H. Bragg and his son W.L. Bragg has successfully established the derivation of the conditions for diffraction from a three dimensional periodic arrangement of atoms. It became possible to locate the absolute distribution of atoms within a crystal by examining the nature of scattered or diffracted X-rays by the crystal and hence, established the crystal structure [88].

When the fast moving electronically charged particle like electron possessing sufficiently high kinetic energy is allowed to decelerate it results in generation of X-rays. The adequate kinetic energy possessing electron when bombarded on an appropriate metal target, nearly 1% of its kinetic energy is interconverted into X-rays while the rest of the energy is liberated as thermal energy. The X-ray generated constitutes a continuous spectrum of a range of wavelength and entitled as white radiation. The minimum wavelength end of this continuous spectrum which is having zero intensity up to a specific wavelength is referred as short wavelength limit ($\lambda_{SWL}$) [89]. The $\lambda_{SWL}$ is related to the applied voltage in a reciprocal manner, the later is needed to accelerate the electrically charged particle and this reciprocal dependency can be expressed via equation as:

$$\lambda_{SWL} = 12.40 \times 10^3 \text{ V}$$

The intensity increases rapidly to a maximum beyond short wavelength region and then decreases without making sharp demarcation towards the longer wavelength region. The maximum extent of energy is achieved through acceleration of electron which is stopped via a single collision and has wavelength corresponding to the short wavelength limit. However, if the electron continues to undergo a number of collision to decelerate then it yield only a fraction of energy possessing longer wavelength limit
is emitted as radiation. These entire wavelengths $\lambda_{SWL}$ and wavelength beyond $\lambda_{SWL}$ are integrated to form the continuous spectrum [90]. The intensity of the X-ray emitted (total continuous spectrum) per second shows direct dependency on the atomic number of the target nuclei which is expressed via equation (2.3.2).

$$I_{\text{Continuous spectrum}} = A \cdot I \cdot Z \cdot V^m$$ \hspace{1cm} (2.3.2)

Where $A$ corresponds to constant of proportionality, $I$ is the electric current, $Z$ denotes the atomic number of target nuclei and $m$ is a constant having value equal to 2. The nature of target material has a great influence on intensity of the X-rays emitted while the wavelength distribution of continuous spectrum remains undisturbed by the type of target nuclei used under consideration. Moreover, the adequately high voltage applied during acceleration of charged particle yields certain high intensity radiations along with the continuous spectrum which possess specific wavelengths and correspond to the metal target. These metal based radiations are associated with narrow wavelength range appear in different sets of increasing wavelength as K, L, M etc. The K set further composed of different components as $K_\alpha (K_{\alpha1}, K_{\alpha2})$ and $K_\beta$. $K_{\alpha1}$ is preferred over $K_{\alpha2}$ for obtaining the diffraction pattern from array of crystal planes because it is having shorter wavelength and double intensity as possessed by $K_{\alpha2}$. Copper lists among the most widely used target material for single crystal diffraction associated with Cu $K_\alpha$ radiation (1.5418 Å).

(i) Principle of diffraction

Fundamentally X-ray diffraction technique is focused on to resolve structural information in the crystal lattice of any material by directing X-ray beam towards the target material. Generally, materials lattice are comprised of uniform array of equidistant crystal plane. The reflection of X-rays from such planes results in production of a particular diffraction pattern portraying the information about the lattice acquisition. The reflected rays within same phase difference reinforce each other and integrate to form constructive interference while out of phase rays constitute destructive interference. Fig.2.2 demonstrates the array of equidistant atomic plane displayed by the horizontally placed dotted line. The X-ray beam associated with wavelength $\lambda$ is allowed to strike the crystal plane making an angle $\theta$ at some point. The planar system of crystal exhibit semi-transparent nature thus allowing some of the X-rays to transmit through it and others get reflected by the atoms in the plane.
Fig. 2.2 Diffraction of X-rays by a crystal following Bragg’s Law.

The figure depicts that the incident beams P and Q get reflected through the path AP’ and CQ’ after striking the crystal plane at point A and C respectively. The path difference executed by the incident ray P and Q is determined via equation (2.3.3).

\[ BC + CD = d \sin \theta + d \sin \theta = 2d \sin \theta \]  

(2.3.3)

The condition for obtaining the constructive interference of the reflected rays should be such that the path difference (d sin\( \theta \)) must be an integral multiple of wavelength \( \lambda \) of the incident X-ray beam expressed through equation (2.3.4).

\[ 2d \sin \theta = n\lambda \]  

(2.3.4)

The above expression is universally expressed as Bragg’s expression where \( n \) relates to order of reflection, \( d \) is interplanar spacing while \( \theta \) corresponds to the Bragg’s angle at which maximum intensity is obtained owing to constructive interference of reflected rays [91-93]. A little deviation from this Bragg’s angle leads to destructive interference as a consequence of it, no diffraction pattern is obtained.

\[ \sin \theta = n\lambda / 2d \leq 1 \]

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

The interplanar or \( d \) spacing of the crystal planes should be of the order of the magnitude of the X-ray wavelength used. So, to obtain the first order Bragg’s
reflection, the X-ray wavelength should be of the magnitude less than or equal to 2d. Therefore, via first order reflection, the d spacing of the crystal plane can be measured by making use of Bragg’s angle. From each crystallographic parallel set of planes, with characteristic d spacing and associated Bragg’s angle or the reinforced constructive reflection, the diffraction pattern will be obtained.

By taking considerations of Bragg’s law, the average crystallite size of any crystalline sample can be evaluated via equation better known as Scherrer’s equation as:

\[ D = \frac{0.941 \lambda}{\beta \cos \theta} \]  \hspace{1cm} (2.3.5)

Where, D denotes the average crystallite size, λ is wavelength of X-ray used, θ is Bragg’s angle for constructive reflection and β is the full width of half maximum (FWHM, in radian).

(ii) Procedure and instrumentation

![Fig.2.3 Rigaku Ultima IV diffractometer.](image)

The sample whose diffraction pattern is to be analyzed is grounded to fine powder and spread uniformly on the sample holder. The evacuation conditions are not needed for this process. The sample is then allowed to interact with X-rays inside the instrument and diffraction data is collected between the 2θ range of 10-80° at scan speed of 2° min⁻¹. X-ray diffractometer comprise mainly of three units as X-ray tube, a sample holder and an X-ray detector. The X-rays are generated inside the X-ray
tube. A collimator is inserted between the X-ray source and the sample holder to direct the X-ray towards the sample. The detector detects and processes the X-ray diffraction signal which is then transferred to the output device. The powder X-ray diffraction analysis of the synthesized nanophosphors are performed by assessing Rigaku Ultima IV diffractometer (Fig.2.3) equipped with Cu Kα radiation at 40 KV tube voltage and 40 mA tube current setting.

2.3.2 Photoluminescence (PL) spectroscopy

(i) Principle

Photoluminescence spectroscopy is a versatile and non-destructive powerful optical tool for probing the electronic arrangement of materials. It involves the analysis of events that includes the emission of light from a sample not as a result of thermal process or excitation but via photoexcitation. A plot between the intensity of emitted light and wavelength of light used results in the photoluminescence spectrum. The excitation spectrum in turn is obtained by rooting a specific and fixed emission band in a certain range of excitation wavelengths while the observed band in excitation spectrum will be further employed to record the emission spectrum. Thus the photoluminescence spectrum is composed of excitation and emission spectra. The state of photoexcitation of any material may be achieved by applying various routes of photonic source like xenon discharge lamp, tungsten lamp, mercury discharge lamp, discharge lamp, excimer lamp, laser or electron beam as excitation source [94-96]. In both type of spectrum, the photoluminescence intensity is plotted along the ordinate while wavelength changes are displayed along the abscissa. The ordinate is expressed in units of irradiance E (W.m⁻²) or in terms of photons absorbed/emitted (photons.m⁻²) while the abscissa is expressed in terms of unit of wavelength as nm. Usually abscissa may also be expressed in terms of wavenumber ¯v with unit cm⁻¹. Therefore, the spectrum irradiance can be illustrated in terms of the units utilized as:

\[ E (\lambda) = \frac{dE}{d\lambda} \left( W.m^{-2}.nm^{-1} \right) \]  \hspace{1cm} (2.3.6)

or

\[ E (\bar{v}) = \frac{dE}{d\bar{v}} \left( W.m^{-2}.cm^{-1} \right)^{-1} \]  \hspace{1cm} (2.3.7)

Whereas, the spectral photon irradiance can be represented as:
\[ E_p(\lambda) = \frac{dE_p}{d\lambda} (\text{photons.m}^{-2}\text{nm}^{-1}) \quad (2.3.8) \]

or

\[ E_p(\bar{\nu}) = \frac{dE_p}{d\bar{\nu}} (\text{photons.m}^{-2}\text{cm}^{-1})^{-1} \quad (2.3.9) \]

Usually the units in which the abscissa and ordinate are expressed are based on the requirement of experiment performed. Quantum efficiency which relates the number of photons emitted as per the number of photons absorbed by any sample is always expressed in terms of photon irradiance while irradiance unit is employed to represent the energy efficiency. The photopic luminous efficiency function \( V(\lambda) \) is multiplied with spectral data \( E(\lambda) \) and integrating the whole function within the limits zero to infinity results in mathematics of luminosity of the phosphor or the amount of light emitted which is illustrated as follows:

\[ L = K_m \int_0^\infty V(\lambda)E(\lambda)d\lambda, \text{ lm.m}^{-2} \quad (2.3.10) \]

where \( K_m \) relates to the constant with value 673 lm.watt\(^{-1}\).

(ii) CIE chromaticity system

CIE chromaticity system is an international standard for the existing primary color established in the year 1931. It permits all the other subsidiary colors to be properly weighed addition of the three basal colors. The Commission International de l’Eclairage an illumination based on the mathematical relationships, introduced the most widely explored concept of chromaticity index to designate the color coordinates of a system through the specific points \( x \) and \( y \) [97-98]. The CIE color coordinate diagram is represented through Fig.2.4. The mathematically derived chromaticity system comprise of RGB color space and RGB tristimulus system depending on the fact of perception by human eye. The response of human eye can be explained in terms of three tristimulus values.

RGB system is developed experimentally through observation made on the circular field possessing an angular diameter of 2°. The circular field is occupied by adjoining two half circles; presented as reference field in the left and test field as the right half circle. The reference field color is invariable and remains unaltered in terms of intensity over the entire visible range wavelength. While the color composition of the test field comprising of a mixture of three basal colors red, green and blue can be made variable by disturbing the ratio of these primary (RGB) colors.
The color composition of the test field through variable RGB ratio was then compared with the adjacently located reference field color. In case of non-compatible or unmatching color situation, a variable quantity of any of the RGB color is introduced or subtracted to the reference color to achieve similar color presentation. If the subtraction of any of the primary color of mixture is carried out then it will lead to an assumption that the negative stimulus for primary color is induced at some wavelength ranges. All the spectral color over the entire visible range can be well matched by fixing the appropriate ratio of the three primary basal colors. The inverse energy ratios of primary test field color correlate with the stimulus strength of the respective reference primary color wavelength with which the color matching is established. The CIE color coordinates are specially designed to represent the photoluminescence spectrum of a nanophosphors in terms of two coordinates x and y. The color coordinates are usually calculated automatically through the spectrophotometer assessed for optical analysis or via making utilization of MATLAB software using software data.

(iii) Procedure and Instrumentation

Photoluminescence spectral analysis of nanophosphors were measured by introducing the finely powdered sample into the sample holder and subjected to irradiation with UV light. The excitation and emission spectra were recorded by
selecting the wavelength scan mode at a scan speed of 1200 nm min⁻¹, excitation and emission slit width 2.5 nm and 400 V PMT voltage setup. The decay analysis is carried out in time scan mode.

**Fig.2.5 Hitachi F-7000 fluorescence spectrophotometer**

The spectrophotometer primarily consists of three basic units, excitation source, sample holder and detector. The source of excitation employed should give continuum spectrum in place of line spectra. Usually, xenon lamps are useful due to their high intensity at all wavelengths beyond 250 nm. A monochromator is associated with the assembly which allows only selected wavelength of light. The photomultiplier tubes are utilized as detector which detects and process the signals. In the present work, the optical features of the prepared nanophosphors are measured by employing Hitachi F-7000 fluorescence spectrophotometer assembled with xenon lamp as an excitation source as depicted in Fig.2.5.

**2.3.3 Transmission electron microscopy**

Transmission electron microscopy (TEM) is an advanced microscopic technique which offers information about the morphology, composition and crystallographic features of the sample. The transmission electron microscope is a very impressive and powerful instrument which displays the maximum magnification most likely over the one million times or more, high quality 2D images with detailed description about the surface features, shape and size of the nanophosphors material [99]. TEM is different from ordinary microscope in terms of application of lenses and light. The ordinary microscope utilizes glass lenses to direct the light on the sample while TEM utilizes the high quality electromagnetic lenses to direct the electrons into a very thin beam
over the sample. The electron beam is allowed to transmit through the utilization specimen; interaction with the specimen results in formation of image which is ultimately devised by imaging device. It is possible to achieve the imaging at very high resolution as compared to light microscope because TEM utilizes smaller de-Broglie wavelength of the electron beam. The basic requirement to obtain a TEM analysis is that the specimen under consideration must possess minimum thickness so that the electron beam can pass through the sample or may be treated as electron transparency.

(i) Principle

TEM is basically based on the principle of interaction of energetic electrons with the ultra-thin specimen. It comprises of three types of powerful electromagnetic lenses such as condenser lenses, objective lenses and the projector lenses. The condenser lenses are employed to generate shorter wavelength bound electron beams while the objective lenses directs the electron beam on the spectrum. The electron thus passes through the specimen and finally projected by the projector lens towards the photographic plate where they are converted into light to form an image. During the transmission of energetic electrons, the electron wavelength is directly related to speed of interacted electron. The faster moving electrons possess shorter wavelength and hence the image processed will be of higher quantity and detailed description. The density of the specimen under analysis has a great influence on the TEM examination. A porous material or less denser material permits more electrons to transmit through it which appear as lighter areas of image while the denser materials permits less electrons to pass through it. Thus these differences furnish information about the structure, shape and size of the materials possessing non-uniform density.

(ii) Procedure and instrumentation

For obtaining the TEM images the ultra-thin materials are required. The process involves the dispersion of sample into an appropriate solvent which is then applied on the carbon coated grids by using micro tipped dropper. The sample is allowed to evaporate the extra solvent. The grid is dried and injected inside the microscope column to obtain the high quality detailed images. TEM instrument essentially comprises of three systems as: electron gun which produces the high energy electrons, the electromagnetic lenses and the image recording system, which processes the electron image to some form of image which is perceptible to the human eye.
Fig.2.6 Technai-G² transmission microscope

The image recording system comprises of fluorescent screens and digital camera. Technai-G² transmission microscope depicted in Fig.2.6 is employed to examine the morphological aspects of the synthesized nanophosphors.

References