Chapter I

General Introduction

A brief introduction to the solid state lighting technology and different strategies to produce white light are discussed in this chapter. The importance of developing novel RGB emitting single-phase phosphors with broadband excitation in the deep UV region of electromagnetic spectrum, particularly in UV-B and UV-C regions for obtaining high-quality WLED are explained. A brief description about nanophosphors, generally used hosts and activators in phosphors is given. The advantages of molybdate host and rare earth activators such as Tb\(^{3+}\), Sm\(^{3+}\) and Eu\(^{3+}\) are also discussed. The importance of \(\text{R}_2(\text{MoO}_4)_3\) type rare earth molybdates and the sol-gel method, used for the synthesis of samples in this work is also detailed.
1.1 Introduction

The attention of scientific research has now been focused in developing high efficient light source to reduce the electricity consumption. It is well recognized that the widespread replacement of traditional lighting sources by higher efficiency light technology will lead to a considerable reduction of the worldwide energy usage. The history of lighting begins with the invention of incandescent lamp but now they are being phased out due to their low light generation efficiency. The next revolution of lighting was marked by the invention of the fluorescent lamps. Early fluorescent tubes achieved relatively high luminous efficiency, but have low color rendering index and contains mercury which is highly toxic. Hence there is a considerable scope for developing new materials to convert electricity directly to visible light at room temperature without the generation of heat but with high lighting efficiency and CRI.

1.2 Solid state lighting

Solid state lighting (SSL) is emerging as a highly proficient field and a possible substitute to existing lighting technologies. SSL, the next-generation lighting source uses semiconductor materials and devices to convert electricity into light. Lighting applications that use semiconductor light-emitting diodes (LEDs), organic light-emitting diodes (OLED) or polymer light-emitting diodes (PLED) as sources of illumination are commonly referred as solid-state lighting. SSL are now preferred as the light source for many lighting applications and have received incredible research attention in the past decade due to their many advantages when compared to conventional light sources. The advantages include long life, energy savings, better quality light output, intrinsically safe, smaller and flexible light fixtures and durability etc. [1-4]. LEDs technology is much promising, which overcomes the limitations of the fundamental factors
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existed with traditional incandescent and fluorescent lamps. The current attention is the energy saving through efficient conversion of electrical energy to optical energy, reduction of CO$_2$ emission in the atmosphere and the creation of new paradigms in lighting. Thus the SSL sources give an additional boost to the development of LEDs for lighting. In a broad sense SSL covers both organic light emitting diodes (OLEDs) and inorganic light emitting diodes (LEDs). Although the last decade has witnessed an extensive research interest and great progress on organic phosphors for light emitting diodes (OLED) [5-7]. The subject of this thesis centers on phosphors that are novel solid inorganic compounds.

Organic LEDs

OLEDs are organic LEDs, and they use organic materials as their key building blocks. An OLED is an SSL device consisting of a thin, carbon based semiconductor layer that emits light when electricity is applied by adjacent electrodes. Advantage of OLEDs is that it can be configured over larger area with more diffuse light sources, hence becomes practical for general ambient lighting. OLED technology is developing rapidly and is increasingly being used in display applications such as cell phones and personal digital assistant (PDA) screens. However, OLED technology is less mature than LED technology because of their disadvantages like high-cost, aging etc.

Inorganic LED

Inorganic light emitting diodes known as LEDs, are semiconductor devices that produce light when electrical current flows through them. It was Shuji Nakamura who successfully fabricated a blue LED based on InGaN LED chip coated with yttrium aluminum garnet yellow phosphor (Y$_3$Al$_5$O$_{12}$:Ce$^{3+}$, YAG:Ce) [8]. This was the first commercially available white LED and captured scientific attention because of their attractive
properties such as compactness, light weight, and quick response. But the main drawback of YAG-based WLEDs are poor color rendering and serious thermal quenching of luminescence. Up to now the luminescence efficiency of semiconductor based white LEDs has not reached their limit. But based on the current reports, the luminous efficiency of white LEDs can approach 200 lm/W by the year of 2020 which will be far greater than that of incandescent lamps and fluorescent lamps [9].

1.2.1 White light generation approaches using LEDs

LEDs emit nearly monochromatic light, making them highly efficient for colored light applications such as traffic lights and exit signs. However, to be used as a general light source, white light is needed. SSL based on white light emitting diodes (WLEDs) possess potential as well as many advantages over conventional light sources such as high color rendering index (CRI), long lifetime, high luminescence efficiency, low power consumption, environment friendliness etc. [10, 11]. Two primary approaches are generally used to obtain a white light in LEDs which are the RGB-LED and phosphor converted LED (pc-LEDs) method and are schematically shown in Figure 1.1.

![Figure 1.1 White light generation different approaches.](image-url)
In RGB-LED method three LED chips simultaneously generating primary colors and are employed to produce RGB-generated white light. It eliminates the conversion losses associated with the use of phosphors and are relatively expensive but continuously tunable. RGB mixing is the most efficient way to make white light from LEDs since there is no quantum deficit arising from the Stokes shift characteristic of photonic energy down-conversion of the phosphor [12]. The major disadvantage is that it requires independent output power control on each LED and the instability in color temperature due to the differential aging of the RGB LED with variations of driving current.

In Phosphor converted LEDs (pc-LEDs), light from an LED is allowed to pass through a phosphor material. The phosphor material absorbs light and emits light of different wavelength. This is a method in which phosphor is the necessary part and it determines the emission color. Generally, pc-LED uses two techniques which are the Blue LED with a yellow phosphor and UV LED or nUV with RGB phosphor. Blue LED with yellow phosphors (blue LED + YAG: Ce³⁺) is the most common pc-LED based white light source and is still the principal device found in the market. But the pc-WLEDs made by means of blue LED + YAG: Ce yellow phosphors suffer some weaknesses, such as poor color rendering index and low stability of color temperature [13].

UV LED or n-UV +RGB phosphor method consists of converting UV radiation from a UV LED into red, green, and blue lights by using three suitable phosphors in measured amounts or a single RGB emitting phosphor, thereby combining the light of three colors together to produce white light [14, 15]. The UV-LED chips emit light with different wavelength ranges, such as UV-A (320–400 nm), UV-B (280–315 nm) and UV-C (180–280 nm) respectively [16-18]. Commonly used RGB WLEDs are
fabricated by exciting with UV-A LED sources, but deep UV LEDs with UV-B and UV-C regions of the electromagnetic spectrum are also developed to fabricate the RGB based WLEDs. Among the UV-LEDs which are currently used, UV-B or UV-C based WLEDs exhibits improved performance in lighting technology [19, 20]. The great advantage of UV-B and UV-C LED chips is its invisible emission and these devices provide a wide range of colors and controlled CRI [21].

n-UV LEDs with RGB phosphors represent one of the best white light assemblies in terms of both high luminous efficiency and high CRI. Moreover, the electrical to optical power conversion is more efficient in UV than in blue LEDs and the emission spectrum can be more stable with respect to the driving current and the temperature of the LED chip. n-UV LEDs exhibits greater photon density at higher currents than the blue LEDs to compensate for the Stokes loss thereby allow to design high brightness white light sources with suitable phosphor systems [22]. Here, the blue portion of the spectrum is generated with phosphors instead of LEDs which allows more flexibility in the design. The phosphors have tunable peak locations which are important for CRI and lumen equivalence. But RGB phosphors obtained by mixing three phosphors with primary colors sicken from problems of complex mixing of different phosphors, lack of efficient red phosphors, and self-absorption etc. Thus, for obtaining high quality WLED it is important to develop novel RGB emitting single-phase phosphors with broadband excitation in the UV region, particularly in UV-B and UV-C regions.

1.3 Phosphors

The phosphor is a solid luminescent material that emits light when excited by an external energy source. Depending on the duration of persistence of emission of light luminescence is subdivided into
fluorescence and phosphorescence. Fluorescence is the spin-allowed ($\Delta S = 0$), the radiative transition from the lowest excited level to the ground state and it occurs only in the presence of exciting radiation. Phosphorescence is spin-forbidden transitions ($\Delta S = 1$), the radiative transition from the excited triplet state to the ground state and is a slow process ($10^{-4}$ to 10 seconds), persists even after the removal of absorbed radiation.

All light emission processes consist of promotion of an electron in an atom, molecule or ion from its ground state to a higher energy quantum state. The atom, molecule or ion after excitation is said to be in its excited state, then the relaxation from the higher energy state to ground state occurs and the energy difference between the two states is released in the form of photons observed as emission. Depending upon different kinds of excitation source such as ultraviolet radiation, X-ray, a beam of energetic electrons, electric current, there are different types of luminescence occurs corresponding to photoluminescence, X-ray luminescence, cathodoluminescence, electroluminescence etc. This thesis focus on the photoluminescence properties of the phosphor and it is the processes of spontaneous light emission from a material under optical excitation.

1.3.1 Nanophosphors

Nanophosphors are nanostructured high purity inorganic crystalline materials that are intentionally doped with a small amount of activators which efficiently emit light under photon excitation. To meet the demands for various applications, nanophosphors are usually in the form of powders with specific requirements on particle size distribution and morphology [23]. As compared to the existing bulk phosphors, nano-sized phosphor particles exhibit improved electrical, optical and structural properties due to the quantum size effect. Also, nanophosphor exhibit
reduced scattering of the emitted light photons, hence resulting in enhanced luminescence efficiency [24]. With the rapid advances in nanotechnology there has been growing interest in the synthesis, characterization and luminescence features of rare earth doped nanophosphor.

An inorganic nanophosphor consists of a host crystal and an activator. In a crystalline host, a relatively small amount of activators is intentionally doped. The host materials constitute the major part of the phosphor while activators are primarily responsible for the characteristic luminescence in phosphors. The host materials are chosen in such a way that it will absorb the emitted radiation without affecting the excited lattice vibrations, for that material with large band gap and stability are opted. An activator is a foreign ion which gives rise to a luminescent center when introduced into a host lattice and generates the desired emission after absorption of excitation energy. Most often the activator may absorb the excitation energy directly, thereby promoting an electron from the ground state to excited states or the energy may be transferred from the host to the activator. In many luminescent materials, the exciting radiation is not absorbed by the activator directly. In such cases, it is possible to excite the activator by indirect means where sensitizers play the role. Sensitizers are ions or ionic groups incorporated in the host lattice which absorb the exciting radiation and subsequently transfer it to the activator or defects through energy transfer. Thus, the proper choice of host lattice and an activator ion are the demanding requirements to obtain an efficient phosphor material.

1.4 Activators in Phosphors

In a phosphor material, the activator needs to be optically active and capable of absorbing energy, without dissipating it before the emission
process. There are only a few elements in the periodic table which can be considered as optically active centers in crystals. Transition metals, complex ions and rare earth ions are considered to be a preferable activators in luminescent materials.

Transition metal ions are frequently used as optically active centers in commercial phosphors. They have an electronic configuration of \(1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^n\ 4s^2\), where \(n\) means the number of 3d electrons \((1 < n < 10)\). These 3d electrons are valence electrons and are responsible for the optical transitions. Ti\(^{3+}\), V\(^{4+}\), V\(^{3+}\), Cr\(^{4+}\), Cr\(^{3+}\), Cr\(^{2+}\), Mn\(^{4+}\), Mn\(^{3+}\), Mn\(^{2+}\), Fe\(^{3+}\), Fe\(^{2+}\), Fe\(^{+}\), Co\(^{3+}\), Co\(^{2+}\), Co\(^{+}\), Ni\(^{3+}\), Ni\(^{2+}\), Ni\(^{+}\), Cu\(^{2+}\) etc. are the most commonly used transition metal activators in phosphors. Complex ions, such as molybdate (MoO\(_4^{2-}\)), vanadate (VO\(_4^{3-}\)), and tungstate (WO\(_4^{2-}\)), are widely used luminescence centers in practical phosphors. The luminescence center of MoO\(_4^{2-}\)-complex ion consists of a central Mo metal ion, coordinated by four O\(^2-\) ions in tetrahedral symmetry. Other analogous complexes are tungstate (WO\(_4^{2-}\)) and vanadate (VO\(_4^{3-}\)) which comes under the scheelite type compounds [25]. The intrinsic luminescence of these complex ions is often observed in the blue to green spectral regions due to the spin-forbidden \(^1T_1 \rightarrow ^1A_1\) transition. Also, scheelite phosphors exhibit efficient absorption of blue or near-ultraviolet light due to strong broad charge-transfer band enabling them to have an efficient energy transfer from the complex ions to rare earth ions which finds potential application in white LED.

### 1.4.1 Rare Earth Ions

Rare earth ions in inorganic host matrices form an important class of phosphors as they possess a few interesting characteristics such as excellent chemical stability, high luminescence efficiency, and flexible emission colors with different activators [26, 27]. The electron contribution of a lanthanide ion can be written as follows: \(1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\)
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$4d^{10} 4f^{n} 5s^{2} 5p^{6} 6s^{2}$ where $n$ is an integer from 2 to 14. Rare earth ions are usually doped in crystals in the trivalent or divalent state. Trivalent ions show a $4f-4f$ intra configurational optical transition, whereas divalent ions show a $4f-5d$ intra configurational optical transition. The $4f$ electrons that are involved in the optical transitions of trivalent ions are well shielded by the outer $5s^{2}$ and $5p^{6}$ electrons so that the energy levels of $4f$ electrons are not much affected by the ligands in the host crystals. The luminescence of divalent ions are due to the $4f^{n} \rightarrow 4f^{n-1}5d$ transitions and are parity allowed, leading to intense broad absorption and emission spectra. With this abundant f-orbital configuration lanthanide ions are widely used as emitting species in many phosphors.

Mechanism of light emission in rare earth activated phosphor materials include $4f-4f$, $4f-5d$ and charge transfer transitions. In the $4f-4f$ transitions, electrons are transferred between different energy levels of the $4f$ orbital of the same rare earth ion. The energy levels within the $4f$ orbital have same parity and are forbidden as per the parity selection [28]. But these parity rules are relaxed due to a perturbation such as electron vibration coupling and uneven crystal field effect from host lattice [29]. In the case of trivalent lanthanide ions, $4f$ electrons are well shielded from external fields by the $5s$ and $5p$ electrons, hence the crystal field effect from host lattice is very small. Moreover, $4f$ emission spectra of RE$^{3+}$ ions exhibit narrow lines with high color purity due to this shielding effect. Unlike the strictly forbidden intra-$4f$ transitions, $4f-5d$ transitions are dipole allowed transitions [30]. Hence, $4f-5d$ transitions are strongly dependent on the host and vary over the spectral range from the deep UV to far-infrared region. In charge-transfer state transition, $2p$ electrons from the neighboring anions are transferred to a $4f$ orbital. These transitions are allowed and result in broad and intense absorptions.
Different rare earth elements exhibit different emission colors, for example, Eu$^{3+}$ ions show red emission, Tb$^{3+}$ emit green light, Sm$^{3+}$ orange light and Tm$^{3+}$ blue light. Yb$^{3+}$, Nd$^{3+}$ and Er$^{3+}$ are well-recognized for their near-infrared luminescence and Pr$^{3+}$, Sm$^{3+}$, Dy$^{3+}$, Ho$^{3+}$ and Tm$^{3+}$ exhibits transitions in the near-infrared region. Gd$^{3+}$ is a well-known sensitizer which provides intermediate levels for energy transfer from the host to the activator ions and shows emission in the UV region. Also, the rare earth ions exhibit color tunability within a single phased host by simply varying the doping concentration without adding another dopant in the lattice. Although rare earth based phosphors are costly their excellent performance justifies their benefit in phosphor synthesis.

Among the rare earth ions Tb$^{3+}$, Sm$^{3+}$ and Eu$^{3+}$ have attracted considerable attention in phosphor research as their energy level spectra contain several metastable multiplets. These metastable multiplets offer the possibility of simultaneous emission at a characteristic wavelength in different crystalline host materials. For the present work Tb$^{3+}$, Sm$^{3+}$ and Eu$^{3+}$ were used as the activator ions and their characteristics are detailed here.

**Terbium**

Trivalent Terbium (Tb$^{3+}$) is one of the most investigated rare earth ions during the past decade. Tb$^{3+}$ ion has eight $4f$-electrons (with half-filled $4f^7$ and one electron) and it exhibits excitation bands owing to the allowed transition from $7F_6$ ground state of $4f^8$ configuration to the levels of $4f^7 5d^1$ configuration. This absorption often falls in deep UV or V-UV region of the spectrum. From the excited state, the ion relaxes to $5D_j$ levels of $4f^8$ configurations via several steps resulting in sharp emission corresponding to the intra configurational $f-f$ transitions. These narrow emission lines are observed in the blue- green spectral region due to $5D_3 \rightarrow 7F_j$ ($J = 6, 5, 4$) and $5D_4 \rightarrow 7F_j$ ($J = 6, 5, 4, 3, 2$) transitions. The relative intensities of blue
emission and green emission get slightly affected by the concentration of terbium ions. At low concentration blue emission is dominant, while for high concentrations, these emissions are quenched by cross relaxation and the green emission becomes prominent [31, 32]. The most intense lines around 490 and 545 nm are ascribed to $^5D_4 \rightarrow ^7F_6$ and $^5D_4 \rightarrow ^7F_5$ transitions in the blue and green region respectively.

**Europium**

$\text{Eu}^{3+}$ ions emit bright red light due to intraconfigurational transitions in $4f^6$ energy level and widely used as one of the promising red emitters. Eu doped phosphors produce single phased white light emission due to red emission from the $^5D_0$ and the blue and green emissions from the higher $^5D$ states i.e. $^5D_1, ^5D_2$ and $^5D_3$ of europium under excitation at 395 nm ($^7F_0 \rightarrow ^5L_6$) [33]. The transition at 395 nm matches well with commercially available near UV LED chips. The spectra of $\text{Eu}^{3+}$ ion usually comprise of emission lines corresponding to $^5D_0 \rightarrow ^7F_4,^5D_0 \rightarrow ^7F_3,^5D_0 \rightarrow ^7F_2,^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_0$ transitions in 575-700 nm range. $\text{Eu}^{3+}$ ions usually occupy the sites with no inversion symmetry in the host crystals. The strong red emission line at around 610 to 630 nm is due to the electric dipole transition of $^5D_0 \rightarrow ^7F_2$. But when $\text{Eu}^{3+}$ ions occupy sites with inversion symmetry, the emission line at 592 nm due to the $^5D_0 \rightarrow ^7F_1$ magnetic dipole transition becomes relatively stronger and dominates.

**Samarium**

$\text{Sm}^{3+}$ ion produces intense orange-red emission originating from the intraconfigurational transitions in $4f^6$ energy level and is a potential activator for use in warm-white light emitting diodes. In the case of $\text{Sm}^{3+}$ ions, the host crystal lattices have little effect on the emission and excitation spectra because of its characteristic $f-f$ transitions. It possesses several absorption bands at wavelengths below 500 nm and efficient
fluorescence is obtained from the $^4G_{5/2}$ excited level [34, 35]. The emission bands are mainly observed due to transition from $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$, $^4G_{5/2} \rightarrow {}^6H_{9/2}$, and $^4G_{5/2} \rightarrow {}^6H_{11/2}$ in the range 550-700 nm. The Sm$^{3+}$ ion offers high luminous efficiency due to the narrow emission bands.

1.5 Molybdate as a suitable host lattice

The host lattice strongly influences the luminescence properties of the phosphors. The main requirements for the host lattice of phosphors include chemical stability, strong covalent chemical bonds and large crystal field splitting. There are many phosphor hosts which are currently used in SSL include silicates, nitrides and oxynitrides, aluminates, sulfides, oxysulfides, phosphates and oxides etc. Among the different hosts, oxide matrices are most suitable host materials for the development of advanced phosphors due to their ease of synthesis and low manufacturing costs together with excellent thermal and chemical stability [36, 37]. Among different oxide hosts, inorganic compounds with the scheelite structure, such as molybdates have gained much attention due to their self-activated luminescence and strong charge transfer band in the UV region.

Molybdate phosphors for LED applications have attracted much attention due to the high chemical and physical stability, low synthesis temperature and environmentally friendly characteristics [38]. A good phosphor candidate for WLED should have a wide excitation band, which overlaps the emission wavelength of the LED chips and also able to convert the excitation energy into efficient emission [39]. According to these requirements, a large number of compounds have been suggested to be host lattices for phosphors, among which molybdates have received considerable attention because of their high stability and outstanding properties [40, 41].
Rare earth activated molybdate phosphors exhibit high intensity for the forbidden 4f-4f transitions of rare earth ions. The two key factors that contribute to the increase in the intensity of the 4f-4f transitions are the covalent nature of MoO$_4^{2-}$ groups in the lattice and the possibility to have high activator concentrations in host lattices with MoO$_4^{2-}$ ions. The molybdate host lattice have many advantages over other host lattices such as, the excitation band is broad due to the charge transfer band (CTB) in UV or near-UV wavelength range, which efficiently transfer the excitation energy to trivalent lanthanide ion [42]. The charge transfer band in O → Mo can easily absorb the emission from a GaN-based LED very efficiently [43]. Also, the heavy Mo-atom increases the probability of parity-forbidden transitions resulting in comparatively strong absorption and excitability of the material. Many molybdates, especially the scheelite structure are being investigated for decades because of their interesting luminescence and structural properties and are widely used as electro-optical materials, acousto-optic modulators, ionic conductors, anode material for Li-ion Batteries and at low temperatures as scintillators in radiology [44, 45].

Rare earth molybdates exist in different crystal phases with the same or different valences of molybdenum. The formation of different phased structures depends on the preparation method, pH value of the reaction system, and stoichiometric ratio of the starting materials etc.

1.5.1 Rare earth Molybdates

Molybdate is a potential lattice in which 14 trivalent rare earth ions can be incorporated in combination with each other, leading to a variety of different applications. Due to the difference in the coordination environment of Mo, they show obvious diversity in the spectral character. For example, materials containing tetrahedrally coordinated Mo have the MoO$_4$ excitation band centered at 275–330 nm, while those with
octahedrally coordinated Mo have the MoO$_6$ excitation band centered at 385–400 nm [46].

R$_2$MoO$_6$ compounds have been widely studied, owing to their broad and intense CT bands in the near-UV wavelength and excellent thermal as well as chemical stability [47]. R$_2$MoO$_6$ compounds are found to crystallize in three polymorphs, with monoclinic, cubic and tetragonal symmetries [48]. La$_2$MoO$_6$ preferentially adopts the tetragonal form whereas Pr$_2$MoO$_6$ and Nd$_2$MoO$_6$, adopts pseudo-cubic structure at low temperatures [49]. At high temperature, these two compounds crystallize in the tetragonal form [50]. The smaller and heavier lanthanide (Sm-Lu and Y) crystallizes in the monoclinic modification of scheelite structure [51]. R$_2$Mo$_2$O$_9$ compounds are notable due to their high oxide-ion conductivity property [52]. The O$^{2-}$ ions exhibit good conductivity and are often used as solid electrolytes [53]. The Pr$_2$Mo$_2$O$_9$, Ho$_2$Mo$_2$O$_9$ find potential application in color pigments, because of their interesting optical properties and low toxicity [54]. R$_2$Mo$_2$O$_9$ generally crystallizes in cubic and monoclinic systems.

In 1965, Nassau et al. published a detailed report on the conditions for the formation of trivalent rare earth molybdate with the general composition R$_2$(MoO$_4$)$_3$ (R = La-Lu). Lanthanide ions such as La$^{3+}$, Pr$^{3+}$ and Nd$^{3+}$ are found to crystallize in a monoclinic structure and the heavier lanthanides, Er-Lu and Y crystallize in the orthorhombic phase [55]. These classes of materials are well-known for their potential application in the area of phosphors, display devices and lasers etc. [56]. Moreover, they act as promising host candidates for luminescent materials owing to the special properties of the MoO$_4^{2-}$ group. In R$_2$(MoO$_4$)$_3$ lanthanide ions usually occupy a lattice sites without centrosymmetry, hence these compounds always exhibit excellent luminescence properties. These
compounds are also proven to be a potential host for the doping of other rare earth ions because due to the comparable ionic radii and chemical valency the doped rare earth ions can substitute the crystallographic sites of another rare earth ion with equal probability, without disturbing the lattice. In recent years, there has been a renewed interest in investigating molybdate with the general composition \( \text{R}_2(\text{MoO}_4)_3 \) and has resulted in a large number of publications on account of their practical applications [57-60]. The synthesis, structural, and spectroscopic characterization of pure and \( \text{Sm}^{3+}/\text{Eu}^{3+} \) doped \( \text{Tb}_2(\text{MoO}_4)_3 \) nanophosphors are systematically investigated in this work.

1.6 Synthesis Techniques

Various chemical methods have been developed for the synthesis of advanced phosphor and ceramic materials for a wide variety of applications. Among which sol-gel method, wet chemical method, solid state reaction method, co-precipitation method, hydrothermal synthesis, solvothermal synthesis, spray pyrolysis, combustion method and polymer precursor method are the most common methods used for the synthesis of phosphors [61, 62]. A brief account of the sol-gel process which has been employed for the synthesis of phosphor samples presented in this thesis is given below.

1.6.1 Sol-gel process

Sol-gel method is one of the most important techniques for the synthesis of various functional materials because it offers many advantages over conventional solid-state method such as higher uniformity in particle size distribution, non-agglomeration and fine powders etc. The surface area of powders produced from sol-gel is very high and higher surface area phosphors have better thermal conductivity when excited with high-
energy photons which are favorable to the lifetime of UV GaN-based WLEDs [63].

Sol-gel process for the synthesis of phosphors often uses chelating agents for metal cations. The functional groups of chelating agent form a chelate with cations in the sol. The chelating agent distributes the cations atomistically through the polymer structure and prevents segregation and precipitation [64]. Heating of the sol to moderate temperature causes a condensation reaction via dehydration and the sol turns into gel. The gel can be either cross-linked or non-cross-linked depending on the stoichiometry of the reactants. The high viscosity of the gel causes low cation mobility which prevents the different mixed cation from segregation. So during calcination, there is a little segregation of various cations takes place. Calcination of the gel in air or other gases cause breakdown of the gel and subsequently the cations are oxidized to form crystallites of mixed cation oxides. The major advantages of the sol-gel route are that it uses relatively low temperature and it can produce very fine high purity product. This method is a simple, economic and effective way to produce high-quality nanomaterials.

References


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