1.1 INTRODUCTION

Since the dawn of civilization, the energy requirement has always remained a burning issue for lighting and display applications and this has not been fulfilled on account of inefficient light sources available to us. In this direction, the first attempt on electric lighting was made in 1880 by Edison and Swan with the development of the incandescent lamp. However, in 1920, the lamp was improved with the addition of a tungsten filament in which the bulb gap was filled with the gas to improve the lifetime of the filament by reducing the filament evaporation (Shinde et al., 2013). After this the fluorescent lamps were developed with improved efficiencies, but the fluorescent lamps have several issues such as the use of mercury in these lamps makes them non-eco-friendly and non-disposable. The other issue is that the lifetime of these lamps is very less i.e. only of the order 1000 h. Around 33% of electricity is utilized in the present lighting system (Shinde et al., 2013) and the remaining goes wasted. Conventional incandescent and fluorescent lamps depend on either heat or discharge of gases. Both processes relate to large energy losses that occur because of the high temperatures and large Stokes shifts involved (Thejo et al., 2012). An incandescent bulb is one of the most inefficient energy sources in daily use because less than 5% of the power consumed by the bulb is converted into light (the rest is lost as heat). These bulbs also have a limited lifetime. Fluorescent lighting is more efficient (50–100 lm/W), but the tubes are fragile and bulky (Xie et al., 2007). The biggest problem with fluorescent lighting is the low color rendering index (CRI). The CRI is a measure of the capability of a light source to reproduce the colors of various objects in comparison to sunlight. The sun is defined as having a CRI of 100, the same as an incandescent bulb. Fluorescent lighting has typical CRI values in the range 80–90 (George et al., 2013).

In comparison to this, the light emitting diodes (LEDs), using the semiconductor, offer an alternative method of light source. Basically, LED is a p-n junction diode, composed of an InGaN alloy that emits wavelengths from 360 nm – 470 nm (near-ultraviolet to blue) depending upon the concentration of Indium content (Kaun et al., 2013). The working of the LED is based on the spontaneous light emission in semiconductors, which is due to the
radiative recombination of an excess of electrons and holes as shown in Figure 1.1. This effect is called electroluminescence and the color of light is obtained by the energy band gap of the semiconductor (Thejo et al., 2012).

The first commercial blue emitting LED based on InGaN was developed in the 1960s. This invention gave rise to the development of white emitting LEDs in 1997 (Nakamura et al., 1997) after the production of blue-emitting InGaN light emitting diode LED in 1993 (Nakamura et al., 1993) after that more and more interest was focused on InGaN/GaN based white-emitting LEDs (W-LED). Green and yellow LEDs were developed by increasing the ‘In’ concentration in the InGaN chips.

**Figure 1.1:** Systematic process of LED showing the process of electron and hole recombination.

### 1.1.1 GENERATION OF WHITE LIGHT

In the last few years, the study on the synthesis and characterization of phosphor materials for the development of white light emitting diodes has gain much attention. Different approaches to the development of white light with a solid-state device and InGaN chip are shown in Figure 1.2 and Figure 1.3. The white light can be obtained by three different methods. First, white light can be produced by combining blue InGaN LED with a broadband yellow-emitting phosphor. This method is based on mixing a longer wavelength of light with a shorter wavelength component. Second, it can be developed by combining an ultraviolet UV-LED with blue, green and red phosphors; and third by using three individual monochromatic LEDs with blue, green and red colors. Among them for white light the use of tricolor (red, green and blue) LEDs has potential high efficiencies and flexible user controlled color. The excitation sources for phosphors in LEDs are ultraviolet (UV) (340–410 nm) or blue light (420–480 nm), whereas those for conventional inorganic phosphors in cathode-ray tubes (CRTs) or fluorescent lamps are electron beams or mercury gas ($\lambda_{em} = 254$ nm) (Thejo et al., 2012). Therefore, the phosphors used in LEDs should have high absorption of UV or blue light. When LEDs are fabricated properly, offers high energy efficiency that results in low power consumption (energy saving), low voltage (generally less than 4 volts) and low current operation usually (less than 700 mA).

**Figure 1.2:** The basic three principals of white-lighting strategies. (a) A three-LED strategy with red, green, and blue (RGB) LED chips. (b) A three-phosphor strategy with a UV LED and RGB phosphors (c) A blue LED with a yellow down-converting phosphor (George et al., 2013).
LEDs can have longer lifetime to 50,000 h with better thermal management than conventional lighting sources (e.g., fluorescent lamps and incandescent lamps) (Poole et al., 2003). In addition, they should also have the following characteristics: (i) high conversion efficiency; (ii) high stability against chemical, oxygen, carbon dioxide, and moisture; (iii) low thermal quenching; (iv) small and uniform particle size (5–20 µm); and (v) appropriate emission colors (Thejo et al., 2012).

![Image](http://dba.med.sc.edu/price/irf/Adobe_tg/models/rgbcmy.html)

**Figure 1.3:** The generation of white lighting by combining three different colors.

[Table 1.1: Classification of different LED materials](http://dba.med.sc.edu/price/irf/Adobe_tg/models/rgbcmy.html)

<table>
<thead>
<tr>
<th>S. No</th>
<th>Materials (LEDs)</th>
<th>Wavelength (nm)</th>
<th>Emission color</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>InGaN</td>
<td>450-500, 500-570</td>
<td>Blue, Green</td>
</tr>
<tr>
<td>2.</td>
<td>GaN based blue LEDs</td>
<td>465</td>
<td>Blue</td>
</tr>
<tr>
<td>3.</td>
<td>GaAs</td>
<td>&gt; 760</td>
<td>Infrared</td>
</tr>
<tr>
<td>4.</td>
<td>GaP: N</td>
<td>570-590</td>
<td>Green</td>
</tr>
<tr>
<td>5.</td>
<td>GaP</td>
<td>570-590</td>
<td>Yellow, Green</td>
</tr>
<tr>
<td>6.</td>
<td>AlGaInP</td>
<td>625, 610, 590</td>
<td>Red, Orange, Yellow</td>
</tr>
<tr>
<td>7.</td>
<td>InGaN/YAG</td>
<td>400-450</td>
<td>Violet</td>
</tr>
<tr>
<td>8.</td>
<td>GaAlAs</td>
<td>610-760</td>
<td>Red</td>
</tr>
<tr>
<td>9.</td>
<td>GaAsP</td>
<td>610-760</td>
<td>Red</td>
</tr>
<tr>
<td>10.</td>
<td>GaP</td>
<td>610-760</td>
<td>Red</td>
</tr>
</tbody>
</table>
The classification of different LED materials with their emission color and wavelengths is shown in Table 1.1. The LEDs chips are mostly developed by combining elements from group III and V of the periodic table. The elements of group III are aluminum (Al), gallium (Ga) and indium (In) and group-V elements are phosphorus (P), arsenic (As) and nitrogen (N). These LEDs give light from n-UV to blue, green, yellow, red and infrared regions. Some of the LEDs emit light more than one or two colors such as InGaN and AlGaInP. The emission color of these LEDs depends on the concentration of aluminum and indium.

1.1.2 APPLICATIONS OF LIGHT EMITTING DIODES

The LEDs can be used in LCD backlights, displays, transportation equipment, lighting, and general lighting. LEDs are also used as a light source for LCD backlights in products such as: mobile phones, cameras, portable media players, notebooks, monitors, and TVs. Display applications include LED electronic scoreboards, outdoor billboards, and signage lighting, such as LED strips and lighting bars. Examples of transportation lighting areas are passenger vehicle and train lighting (e.g., meter backlights, tail and brake lights) (Chang et al., 2012) and ship and airplane lighting (e.g., flight error lighting and searchlights). General lighting applications are divided into indoor lighting (e.g., LED lighting bulbs, desk lighting, and surface lighting) (Shibata et al., 2009), outdoor lighting (e.g., decorative lighting, street/bridge lighting, and stadium lighting), and special lighting (e.g., elevator lighting and appliance lighting) (Huang et al., 2010). The use of LEDs in general lighting has increased, beginning with street lighting in public areas and moving on to commercial/business lighting and consumer applications.

1.2 LUMINESCENCE

Light is a form of energy. To produce light, another form of energy must be required. There are two general methods to produce the light, incandescence and luminescence. Incandescence is light from heat energy. If you heat some material to a high enough temperature, it will begin to glow. For example, when a metal rod is heated at a high temperature, it begins to glow “red hot” that is incandescence. When the tungsten filament of incandescent light bulb is heated by applying electricity, it glows brightly “white hot” by the same means. Luminescence is a form of cool light energy, i.e., light emitted by sources other than a hot, incandescent body, such as a black body radiator (Kitail et al., 2008).

Generally, Luminescence is defined as the emission of light by a substance in the visible or near visible region. It occurs when an electron returns to the electronic ground state from an excited state and loses its excess energy as a photon. It occurs by the movement of
electrons within a substance from more energetic states to less energetic states. This phenomenon was identified by G.K. Stokes in 1852 and formulated his law of luminescence by the name of Stoke's law, which states that the wavelength of the emitted light is greater than that of the exciting radiation. After that, the term “Luminescence” was introduced into the literature by the German physicist Eilhard Wiedemann, in 1888 which means “weak glow” (Vij et al., 1998). It may be caused by chemical reactions, electrical energy, subatomic motions, or stress on a crystal. The process of luminescence is basically a two step process which involves (a) the excitation of the material by the absorption of energy and (b) the subsequent emission of light. Luminescence is in contrast with the incandescence which is the production of light by heated materials.

1.2.1 CLASSIFICATION OF LUMINESCENCE

Luminescence phenomenon can be classified on the basis of (i) the characteristic time ‘τc’ of the excited state and (ii) on the basis of mode of excitation. The family tree of the luminescence is shown in Figure 1.5.

1.2.1.1 ON THE BASES OF CHARACTERISTIC TIME ‘τc’:

After the absorption of radiation, emission of light takes place at characteristics time ‘τc’, on the bases of ‘τc’ the process of luminescence can be classified into fluorescence and phosphorescence.

Thus, if the characteristic time ‘τc’ is less than $10^{-8}$ sec, then it is known as Fluorescence and if the characteristics time ‘τc’ is greater than that of $10^{-8}$ sec, then it is known as Phosphorescence.
1.2.1.2 **ON THE BASES OF MODE OF EXCITATION:**

The other classification of the luminescence is made on the basis of the type of source used to excite the material which is also shown in Table 1.2. The brief divisions of luminescence phenomena on the basis of mode of excitation are as:

(a) **Triboluminescence**: The prefix ‘tribo’ is a Greek word meaning “to rub”. In triboluminescence the emission of light occurs due to the mechanical actions such as scratching, crashing, rubbing or grinding of the solid material. A large number of materials emit light on mechanical stress. Grinding to sugar crystal in a mortar is an example of triboluminescence.

(b) **Chemiluminescence and Bioluminescence**: It is the process of luminescence, in which the emission of light takes place due to the chemical reaction and occurs in the biological systems during biological decay of organic materials and some chemical reactions, especially those involving oxidation-reduction mechanisms. Glowworms, fireflies and various fungi and bacteria found on rotting wood or decomposing flesh are the examples of Chemiluminescence and bioluminescence.

(c) **Sonoluminescence**: It is the emission of light from the imploding bubbles in a liquid when excited by the sound.

(d) **Radioluminescence**: It is the emission of light from a material which takes place due to the bombardment of high energy particles such as α-particles, β–particles, as well as high energy radiations such as x-rays, γ-rays, accelerated protons and neutrons. Radioluminescence can be used for emergency exit signs, in medical field and radiation dosimetry etc.

(e) **Electroluminescence**: It is the emission of light from a material generated by the action of an electric field. This effect is really observed in the semiconductors and light emitting diodes (LEDs). Electroluminescence (EL) is classified into two forms, i.e. injection electroluminescence and high field electroluminescence. In injection EL, light is emitted due to the recombination of electrons and holes that meet together in the band gap of the material or on a border between n-type and p-type semiconductors (p-n-junction). In high-field EL light is emitted due to the excitation of luminescence centers by majority of electron and holes accelerated under the action of strong electric fields of the order of 1 \( \text{--} 2 \) MeV/cm. The applied electric filed either be AC or DC.

(f) **Cathodoluminescence**: In Cathodoluminescence, high energy beam of electron is used as an exciting source to produce the light. These beams are generated from the electron gun
and then put on the phosphor materials to emit the light in visible light. Cathodoluminescence has applications in the field of biology, medicine, screen of the television using cathode ray tubes etc.

**(g) Thermoluminescence:** Thermoluminescence (TL) is the emission of light from a material after exposure by using the ionization radiations such as (gamma rays, UV-rays, X-rays etc.) when it is heated. In other word, heat frees the trapped charge carriers which give the light. In thermoluminescence, heat is used as a simulated agent. Radiation dosimetry, archeological and geological dating are the main application of thermoluminescence studies.

<table>
<thead>
<tr>
<th>Luminescence process</th>
<th>Excitation source</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photoluminescence</td>
<td>Light energy commonly UV or Visible light.</td>
<td>Widely used in material science techniques for characterizing dopants and impurities and is also used in light technology as fluorescent lamps.</td>
</tr>
<tr>
<td>Thermoluminescence</td>
<td>Photons, charged particles, stimulate by heat</td>
<td>Used to determine defects in solids, used for radiation dosimetry.</td>
</tr>
<tr>
<td>Radioluminescence</td>
<td>Nuclear radiation</td>
<td>Used in scintillator for nuclear particle detection.</td>
</tr>
<tr>
<td>Cathodoluminescence</td>
<td>Energetic electrons</td>
<td>Used in cathode ray tubes for television sets and computer monitor.</td>
</tr>
<tr>
<td>Electroluminescence</td>
<td>Electric current</td>
<td>Neon lamps, for panel lighting used in liquid crystal display and in LEDs.</td>
</tr>
<tr>
<td>Chemiluminescence</td>
<td>Chemical reaction</td>
<td>Glow sticks, luminal</td>
</tr>
</tbody>
</table>

**Table 1.2: List of different luminescence processes.**

**1.3 MECHANISM OF LUMINESCENCE**

The basic mechanism of luminescence can be explained by using the (i) Jablonski diagram and (ii) Configurational Coordination model.

**1.3.1. JABLONSKI DIAGRAM**

To explain the processes occurring between the absorption and emission of light can be explained by using a Jablonski diagram as shown in Figure 1.6. The lowest and darkest horizontal line in the ground, first and second electronic energy states represent the singlet state shown by $S_0$, $S_1$ and $S_2$, and $T_1$ represents the triplet electronic state respectively. There are several vibrational levels that can be associated with each electronic state as shown in Figure 1.6 by the thinner blue lines (1, 2,… 5). Absorption can occur from the ground singlet state ($S_0$) to various vibrational levels in the singlet excited vibrational levels i.e. $S_1$ and
After the absorption of energy, the excited electrons come to the ground state by following several processes which described below:

**Figure 1.6: Jablonski diagram.**

### 1.3.1.1 Absorption:
A material can emit the energy only when the excited energy is absorbed. After absorbing the energy it arises the electrons from ground state to the excited energy state. So, absorption is the incident energy that is absorbed by the material. The materials can be excited by using ultraviolet or visible radiation, X-rays etc. The transition from the singlet electronic ground state $S_0 \rightarrow S_1, S_2$ in Figure 1.6 represents the absorption.

### 1.3.1.2 Non radioactive relaxation process:

**(a) Vibrational relaxations:** After the absorption of energy, the electrons jump toward the excited state, this energy can be dissipated by vibrational relaxation processes. It is a non radiative process. In this process, the energy absorbed by the electron is given away to the other vibrational modes within the same electronic state. These processes are very fast so that the lifetime of a vibrational excited state lies between $(10^{14} \text{ s to } 10^{11} \text{ s})$ which is less than the lifetime of the electronically excited state.

**(b) Internal conversion:** It is also a non-radiative process between the two electronic states of same spin multiplicity. This process takes place due to the overlap of vibrational energy levels of one electronic state to the vibrational levels of the lower electronic state. Relaxation from $S_1$ or $S_2$ in Figure 1.6 shown by dotted arrow is an internal conversion. It normally occurs on a time scale of $(10^{14} \text{ s to } 10^{11} \text{ s})$.

**(c) Intersystem crossing:** It is also a non-radiative process between the two electronic states of different spin multiplicity. It is a transfer of energy from the singlet excited state to the triplet excited state. The relaxation from $S_1$ to $T_1$ in Figure 1.6 shown by the red arrow is an example of intersystem crossing. It is a slow process normally occurs on a time scale of $(10^{7} \text{ s to } 10^{9} \text{ s})$

### 1.3.1.3 RADIATIVE PROCESSES:

**(a) Fluorescence**
Fluorescence is the emission of light from excited electronic state that has the same spin multiplicity as the ground electronic state. The radiative transition from $S_1 \rightarrow S_0$ (singlet-singlet) in Figure 1.6 represents fluorescence.

**(b) Phosphorescence**
Phosphorescence refers to the emission of light associated with a radiative transition from an electronic state that has a different spin multiplicity from that of the ground electronic state. The radiative transition $T_1 \rightarrow S_0$ (triplet-singlet) in Figure 1.6 represents phosphorescence.

1.3.2 CONFIGURATIONAL COORDINATION MODEL

The configurational coordination model is also used to explain the luminescence mechanism. This model was given in 1936 by Von Hippel and used by Seitz in 1939 to explain the luminescence process. The energy absorbed by the luminescent material from the incident radiation may be dissipated by non radiative transition in the form of heat or in the form of emission of light. The process is explained by using the potential energy curves of both the ground and the excited state shown in Figure 1.7. These curves show the potential energy of the absorbing centre as a function of the distance between an impurity atom and the next nearest neighbour in a crystal lattice.

Figure 1.7: Configurational Coordinate model.

The ground state A and the excited state B of the two curves do not occur for the same value of R. After the excitation i.e. absorption of energy, the centers from the ground state A will rise to the excited state B (transition A → B). Since the transition state is not stable, the carriers make a non radiative transition to the stable state C. The excess energy is given to the
impurity atoms and nearest neighbour in a crystal lattice in the form of heat. When de-
excitation takes place, the carriers undergoes a transition from the stable state C to the upper
excited state D (C → D) by an emission light (photon). With the occurrence of transition (C
→ D), the centers again gain a stable configuration in the ground state (A) from an unstable
state (D) by non-radiative loss of energy. This model explains the Stoke’s law, according to
which the emission normally takes place at a longer wavelength than that of the absorption.

1.4 PHOSPHORS

Phosphor is a Greek word which means light bearer. Generally, phosphors are the
luminescent materials that emit photons when excited by an external energy source, such as
an ultraviolet light (photoluminescence), electron beam (Cathodoluminescence) etc. Basically
phosphors are composed of an inert host lattice which is transparent to the excitation
radiation and an activator, which acts as a luminescent center. These activator ions create
defect or luminescent center in the host lattice which are responsible for the luminescence.
When the activator ions show too weak absorption, a second kind of impurities can be added
(sensitizers), which absorb the energy and subsequently transfer the energy to the activators.
Luminescence process mainly occurs in three steps, namely absorption of energy at the
activator site, relaxation, and return to the ground state with the subsequent emission of a
photon. The efficiency of a phosphor depends on the amount of relaxation that occurs during
activation and emission. The luminescence properties of a phosphor can be characterized by
its emission spectrum, brightness, and decay time. The excitation and emission spectra of
phosphors provide additional information pertaining to both the basic luminescence
mechanisms and their practical application.

The luminescent materials used as phosphors are categorized according to their use in
the application or according to the chemical forms. According to the method of synthesis,
phosphors are classified on the basis of their chemical forms are as:

1.4.1 Inorganic materials: The inorganic luminescent materials are made up of a host lattice
and activator ions doped in it with very small concentrations, typically a few mole percent or
less. The activator ions create artificial energy levels in the host material that can be
populated by absorption of energy or by energy transfer, and are responsible for the
luminescence. Generally, two types of activator ions are well known. In the first type, the
energy levels of the activator ion involved in the emission process show only weak
interaction with the host lattice. For examples many of the rare earth ions RE$^{3+}$, where the
optical transitions take place only between the 4f – 4f transition that are well shielded from
their crystal field effects of the host lattice by the $5s^2$ and $5p^6$ orbitals. As a result characteristics line emission spectra can be found. The second types of activator ions strongly interact with the host lattice. This is the case when 5d electrons are involved in the emission. For example, in Mn$^{2+}$, Eu$^{2+}$, and Ce$^{3+}$, as well as for s$^2$ ions like Pb$^{2+}$ or Sb$^{3+}$. Host materials show good optical, mechanical and thermal properties. There are many host materials used for inorganic phosphors such as:

Aluminates, Borates, Phosphates, Vanadates, Titanates, Tungstates, Carbonates, Chlorides, Fluorides, Ferrites, Germanates, Gallates, Mangnates, Nitrides, Oxides, Silicates, Sulphides, Sulphates, Tantalates, Zirconates, halo-phosphates, and apatite structures.

1.4.2 Organic materials: These include polymers or low molecular weight materials which are usually aromatic compounds and find their application in thin films or solid solutions. Most recently, their two types of classes have been developed – main chain polymers with isolated chromophores and side chain polymers having linked chromophores. They are used as an emissive electroluminescent layer in organic light emitting diodes (OLEDs).

1.4.3 Hybrid compounds: Hybrid materials are those in which organic molecules are introduced into a silica matrix have the properties of an inorganic matrix and the functionality of the organic component and are called as organically modified silicates (ORMOSIL). They also include organic-inorganic complexes of Eu$^{3+}$ and Tb$^{3+}$ in hybrid form or their complexes with aromatic carboxylic acids, β- diketones and heterocyclic ligands like 2,2-bipyridine and 1,10-phenanthroline incorporated into various matrices..

1.5 ALKALINE EARTH BORATES MATERIALS

Borate compounds are a family of boron containing element that are formed by the combination of boron and oxygen (B - O) Atoms. The crystal structure of borate compounds is formed by the framework of tetrahedral BO$_4$ and triangular BO$_3$ units as shown in Figure 1.8. In these compounds, boron always maintains its valence state of +3, so the tetrahedral bonding has a negative charge and seeks attachment to a cation which helps to make its structures more stable. A large number of metal borate families are known to us till now. Among these families, alkaline earth borates are considered as the most stable compounds. When the alkaline earth metals such as magnesium (Mg), calcium (Ca), strontium (Sr) and barium (Ba) combine with tetrahedral BO$_4$ and triangular BO$_3$ units of borate alkaline borate materials were formed. Alkaline earth metals are known to have two electrons in their outer electronic shell which form cation with 2+ and an oxidation state or oxidation number of +2 which makes them more stable element.
The alkaline earth borate compounds are divided into number of sub families of different phases: in single phase as: $\text{MB}_2\text{O}_4$, $\text{M}_2\text{B}_2\text{O}_5$, $\text{MB}_2\text{O}_7$, $\text{M}_3(\text{BO}_3)_2$ (where $\text{M} = \text{Ba, Ca, Sr and Mg}$) and in mixed phase as $\text{A}_2\text{B}(\text{BO}_3)_2$ (where $\text{A} = \text{Ba, Mg and Sr}$ and $\text{B} = \text{Ca and Mg}$). From the luminescence materials point of view, these materials can be considered as the best host lattices for phosphors because they have the characteristics of an insulator and semiconductors, wide energy band gap, low sintering temperature, excellent chemistry, high stability.

### 1.6 ROLE OF RARE EARTH IONS IN LUMINESCENCE

Rare earth (RE) ions are widely used as activators for the development of phosphor materials. The characteristic properties of RE ions are due to the gradual filling of 4f subshells, which is well shielded by 5s$^2$ and 5p$^6$ orbits (Liu et al., 2002). RE ions are usually found in trivalent (3+) state. The RE ions are consists of the 17 elements, starting from Sc. (At. no. 21), Y (At. no. 39) La (At. no. 57) to Lu (At. no. 71). The electronic configurations of these ions are shown in Table 1.3.

Among, these RE ions, 4f$^0$ (La$^{3+}$), 4f$^7$ (Gd$^{3+}$) and 4f$^{14}$ (Lu$^{3+}$) are stable ions and other elements exchange their electrons to acquire the stable configuration. RE ions from Ce$^{3+}$ to Lu$^{3+}$ contain one to fourteen 4f electrons in their inner shell configuration and the ions from Ce$^{3+}$ to Lu$^{3+}$ are incompletely filled 4f orbitals as shown in Table 1.3, which help in producing luminescence in the UV, visible and infrared region.

These lines show emission either from the 4f-4f transitions or from the 5d-4f transitions. RE ions with an emission from 5d-4f transition has an emission wavelength that changes from one host to another, because such transitions are symmetry dependent (Reid et al., 2013, Marius et al., 2013). For understanding the luminescent properties, it is important to have the knowledge of energy levels of rare earth ions. The energy levels of these ions are divided into three states, i.e. (a) 4f- 4f transitions, (b) 4f - 5d and (c) transitions arises from the charge transfer (CT) band.

### Table 1.3: Electronic configurations of different trivalent rare-earth ions in the Ground state.

<table>
<thead>
<tr>
<th>Atomic No.</th>
<th>Ions</th>
<th>Elements</th>
<th>4f Electrons</th>
<th>S</th>
<th>L</th>
<th>J-</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>Sc$^{3+}$</td>
<td>Ar</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>Y$^{3+}$</td>
<td>Kr</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>57</td>
<td>La$^{3+}$</td>
<td>Xe</td>
<td>↑</td>
<td></td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>Ce$^{3+}$</td>
<td>Xe</td>
<td>↑, ↑</td>
<td>1/2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>Pr$^{3+}$</td>
<td>Xe</td>
<td>↑</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The energy levels in the 4f - 4f configurations are forbidden, because these states have the same parity. All the elements among the rare earths ions show 4f-4f transitions except Ce$^{3+}$, Gd$^{3+}$ and Yb$^{3+}$. The 4f - 4f transitions are almost similar in all host materials. If there is any change, then it is very small, such transitions are not symmetry dependent. This is due to the shielding of the electrons in the 4f shell by the outer 5s, 5d and 6s shells which are completely filled. The electrons in 4f shell are not affected by the outer environment, which leads to the electron de-excitation from one state to another without losing energy to the environment, which leads to the sharp peaks in the luminescence spectra. The 4f- 5d transitions are also found in the rare earth ions, in spite of 4f-4f transitions. These transitions occur, when an electron from the 4f orbital is raised to the higher 5d level.

<table>
<thead>
<tr>
<th>Atomic no.</th>
<th>Ground state</th>
<th>Excited states</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$^{3+}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ce$^{3+}$</td>
<td>$^2F_{5/2}$, $^2F_{7/2}$</td>
<td>$^5d_1$</td>
</tr>
<tr>
<td>Pr$^{3+}$</td>
<td>$^3H_4$</td>
<td>$^3H_6$, $^3F_2$</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>$^4I_9/2$</td>
<td>$^3G_{5/2},^2G_{7/2},^4G_{7/2}$</td>
</tr>
<tr>
<td>Pm$^{3+}$</td>
<td>$^5I_4$</td>
<td>$^5G_{12},^3G_3$</td>
</tr>
<tr>
<td>Sm$^{3+}$</td>
<td>$^6H_{5/2}$</td>
<td>$^4H_{7/2},^6F_{1/2},^6F_{3/2}$</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>$^7F_{1}$, $^7F_0$</td>
<td>$^7F_2$</td>
</tr>
<tr>
<td>Gd$^{3+}$</td>
<td>$^8S_{7/2}$</td>
<td>$^6I_{11/2},^6I_{9/2},^6I_{7/2}$</td>
</tr>
<tr>
<td>Tb$^{3+}$</td>
<td>$^7F_6$</td>
<td>$^7F_5$</td>
</tr>
<tr>
<td>Dy$^{3+}$</td>
<td>$^5H_{15/2}$</td>
<td>$^6F_{11/2},^6H_{13/2},^7H_{11/2}$</td>
</tr>
<tr>
<td>Ho$^{3+}$</td>
<td>$^5I_8$</td>
<td>$^5G_{6},^3H_6$</td>
</tr>
<tr>
<td>Er$^{3+}$</td>
<td>$^4I_{15/2}$</td>
<td>$^3H_{11/2},^4G_{11/2}$</td>
</tr>
<tr>
<td>Tm$^{3+}$</td>
<td>$^3H_6$</td>
<td>$^3F_6,^3H_4,^3H_5$</td>
</tr>
<tr>
<td>Lu$^{3+}$</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

In 4f-5d transitions, the emission wavelength changes from one host to another (Reid et.al., 2013, Marius et al., 2013) because such transitions are symmetry dependent. This is due to the interaction of the 5d-electrons with the ligands of the host than the 4f orbital,
which leads to the splitting of the 5d states into number of energy levels. In this transitions the bonding strength changes upon 4f–5d excitation giving raise to broad emission bands. The CT band mostly occurs in the ultraviolet and characterize by the broad and strong absorption which is due to the charge transfer from ligands to metal ions. In case of rare earth ions, Eu$^{3+}$ shows strong CT band than other ions. Table 1.4 shows the different transitions of rare earth ions.

1.7 REVIEW OF LITERATURE

From last few decades, extensive attention has been given to develop the rare earth doped alkaline earth borates phosphor. They have been considered as very good hosts for the development of luminescent materials (Ramasamy et al., 2011). A variety of borate host materials doped with rare earth and other ions have been reported as phosphor materials for a variety of applications (Chen et al., 2002; Li et al., 2009; Kim, at el. 16). Luminescent studies of rare earth (RE) doped MB$_2$O$_4$, M$_2$B$_2$O$_5$, MB$_4$O$_7$, M$_3$(BO$_3$)$_2$ (where M = Ba, Ca, Sr and Mg) and in mixed borates as A$_2$B (BO$_3$)$_2$ (where A = Ba, and Sr and B = Ca and Mg) phosphors for LED have been studied.

The crystal structure of Ba$_2$Ca (BO$_3$)$_2$ borate has been reported by (Akella et. al,. 1995) and found that Ba$_2$Ca (BO$_3$)$_2$ compound has monoclinic structure with space group C2/m (12) with a = 9.362(2) Å, b = 5.432(2) Å, c = 6.635(2) Å, β = 119.38(1), and V = 302.6(1) Å$^3$. The luminescent properties and site occupancy of Ce$^{3+}$ activated Ba$_2$Ca (BO$_3$)$_2$ phosphor was reported for the applications of LED (Lin et al., 2007). They synthesized the phosphor by using Ce$^{3+}$ and Na$^+$ by using solid state reaction method followed by calcinations at 950 °C for 6 h in CO reducing atmosphere. From the spectroscopic studies they observed excitation and emission bands of Ce$^{3+}$ are due to Ce$^{3+}$ on two different lattice sites, i.e., Ba$^{2+}$ and Ca$^{2+}$ sites in Ba$_2$Ca(BO$_3$)$_2$. The emission spectra of Ba$_2$Ca (BO$_3$)$_2$:Ce$^{3+}$, Na$^+$ shows a broad band extending from 350 nm to 650 nm under 341nm and 395 nm. The excitation peak at 180nm is due to the host-related absorption due to the [BO$_3$]$^{3-}$ groups are observed. Both the spectra for Ce$^{3+}$ sites of Ca$^{2+}$ and Ba$^{2+}$ shows stoke- shift. Ce$^{3+}$ and Mn$^{2+}$ co-doped Ba$_2$Ca(BO$_3$)$_2$ phosphors for white light emitting diode have been reported. (Guo et al., 2008). They obtained white light by varying the content of Mn$^{2+}$ ion in co- doped Ba$_2$Ca(BO$_3$)$_2$: Ce$^{3+}$, Mn$^{2+}$ phosphors excited with UV or violet light. To improve the luminescent properties of blue emitting Ba$_2$Ca (BO$_3$)$_2$:Ce$^{3+}$ phosphor, the effect of charge compensator K$^+$ on Ba$_2$Ca (BO$_3$)$_2$:Ce$^{3+}$, Na$^+$ phosphor reported (Lin et al., 2009).When Ba$_2$Ca (BO$_3$)$_2$:Ce$^{3+}$, Na$^+$ is co-doped with K$^+$, they observed no influence on Ce$^{3+}$ 5d state energies, crystal field splitting and the Stokes shift. They reported this phosphor as an intense bluish – green LED phosphors
with near-ultraviolet (n-UV) InGaN chips ($\lambda_{em} = 395$ nm). After that, a lot of different approaches such as synthesize methods, study of new host materials were used to improve the luminescent properties of alkaline earth borates were carried out by using different rare earth ions. The studies of a new host Ba$_2$Mg (BO$_3$)$_2$ doped with Ce$^{3+}$, Eu$^{2+}$ synthesized by solid state method were reported (Lin et al., 2006). Under the excitation of UV light of 296 nm, a broad blue emission band centering at 416 nm corresponds to the 5d$^1 \rightarrow$4f$^1$ transition of Ce$^{3+}$. After this, similar studies for the same host were reported by (Zaifa et al., 2012). The effect of Na$^+$ metal ion on Ba$_2$Mg (BO$_3$)$_2$ : Ce$^{3+}$, Eu$^{2+}$ phosphor. They observed that luminescent intensity for Ba$_2$Mg (BO$_3$)$_2$: Ce$^{3+}$, Eu$^{2+}$, Na$^+$ phosphor was much stronger than Ba$_2$Mg (BO$_3$)$_2$: Ce$^{3+}$, Eu$^{2+}$ phosphor.

The crystal structure of calcium and strontium orthoborate M$_3$(BO$_3$)$_2$, where M= Ca, Sr) were first time reported by (Vegas et al.,1975). In 1992, the luminescence properties of Ca$_3$B$_2$O$_6$ doped with Eu$^{3+}$, Tb$^{3+}$ and Ce$^{3+}$have been reported by Van der Voort and found that Eu$^{3+}$ ion shows maximum emission. An energy transfer from Bi$^{3+}$ to RE (RE = Eu$^{3+}$, Dy$^{3+}$, Sm$^{3+}$, Tb$^{3+}$) in alkaline earth borates under the charge compensator has been reported (Zhiwu et al., 1993). An enhancement in the luminescence intensity under the charge compensator Na$^+$, and Li$^+$ for Ca$_3$B$_2$O$_6$:Dy$^{3+}$ phosphor has been reported for the applications of LEDs (Sun et al., 2011, Sun et al., 2012). (Lu et al., 2006) synthesized Ca$_3$B$_2$O$_6$: Er$^{3+}$ by Czochraski method and its application for the development of laser operation has been explored. The effect of calcining temperature on (Sr, Ca)$_3$B$_2$O$_6$: Eu$^{2+}$ has been reported and found that at 850 it starts to crystalline, also with the increase in calcining temperature the particle size increase (Xue et al., 2011). The effect to Eu$^{2+}$ ion concentration on the emission intensity for Sr$_{3(1-x)}$B$_2$O$_6$:xEu$^{2+}$ has been studied by (Song et al., 2009) and found the maximum concentration at $x = 0.07$ of Eu$^{2+}$ ion. Recently, Liu et al., 2014) has reported the effect of alkali metal ions (Li$^+$, Na$^+$ and K$^+$) luminescent properties of Ca$_3$B$_2$O$_6$:Sm$^{3+}$ by using the as a charge compensator for the application of white light emitting diodes (wLEDs) synthesized by solid state method. (Liu et al., 2013) reported the crystal structure and luminescent properties of Sr$_2$B$_2$O$_5$:Eu$^{2+}$ blue emitting phosphor for the LED application.

After that, a new class of borates doped with Ce$^{3+}$ doped Ba$_3$B$_2$O$_5$ phosphor has been reported (Li et al., 2014). The CIE coordinates of Ba$_3$B$_2$O$_5$:Ce$^{3+}$ are (0.1531, 0.0726), which falls in the blue emitting region of the CIE diagram enabling this blue phosphor to be excited efficiently by UV or NUV LEDs. Similar has been reported by (Liu et al., 2014). They found highest concentration quenching on 5 mol % with intense blue peak at 423nm upon 350nm excitation. This material also shows good thermal stability at 200°C.
Fujimoto et al., 2015 reported the photoluminescence, photo-stimulated luminescence and thermoluminescence properties of CaB$_2$O$_4$ crystals activated with Ce$^{3+}$. They observed that PL spectrum under excitation at 325 nm showed an intense emission band in the 350 – 370 nm wavelength range due to the Ce$^{3+}$5d (t$_{2g}$) state to the 4f ground-state levels ($^2$F$_{5/2}$ and $^2$F$_{7/2}$). Luminescence studies and energy transfer properties of Sr$_2$B$_2$O$_5$:Ce$^{3+}$, Tb$^{3+}$ phosphors was reported (Sun et al., 2015). Under the excitation of 317 nm, Sr$_2$B$_2$O$_5$:Ce$^{3+}$, Tb$^{3+}$ phosphors emit blue emission Ce$^{3+}$ ions and green emission bands due to the f–f transition of Tb$^{3+}$ ions, respectively. They reported that phosphor Sr$_2$B$_2$O$_5$:Ce$^{3+}$, Tb$^{3+}$ might be used as one of double emission phosphor for n-UV excited white light emitting diodes. A new blue emitting SrB$_2$O$_4$:Eu$^{2+}$ phosphor with high color purity for near-UV white light-emitting diodes has been reported by (Zheng et al., 2015). They observed a strong excitation band from 270 nm -350 nm due to the Eu$^{2+}$ ion from 4f ground state to 5d excited state. The broad blue band emission from 350 to 520 nm with a peak wavelength of 448 nm originates from the lowest relaxed 4f$^6$5d$^1$ level to 4f$^7$ ($^8$S$_{7/2}$) level of Eu$^{2+}$ ions.

Verstegen in 1974 reported the luminescent properties of Tb$^{3+}$ in the borate X$_2$ Z(BO$_3$)$_2$ (X = Ba, Sr, Ca; Z = Ca, Mg) compounds. In the emission spectra they observed the transitions $^5$D$_4$ → $^7$F$_6$, $^5$D$_4$ → $^7$F$_5$, $^5$D$_4$ → $^7$F$_4$ and $^5$D$_4$ → $^7$F$_3$ of Tb$^{3+}$ ion with the strongest transition at $^5$D$_4$ → $^7$F$_5$ one. The splitting in the energy level were also observed for both host lattices, indicating that the 4f levels are only slightly affected by minor changes of the crystal field. To improve the efficiency they used K$^+$ ion as a charge compensator and its quantum efficiency being twice as high as that of the non-compensated material. The luminescent properties and energy transfer between Eu$^{3+}$ and Tb$^{3+}$ in BaB$_2$O$_4$ matrix and found the presence of Eu$^{2+}$ and Eu$^{3+}$ in BaB$_4$O$_7$ matrix studied (Gao et al., 1996). They reported BaB$_4$O: Eu$^{3+}$, Tb$^{3+}$ as a new phosphor for the application of lamp phosphor. Wang et al., 2012) reported a green strontium borate Sr$_2$B$_2$O$_5$: Tb$^{3+}$, Li$^+$ phosphor. They observe excitation spectrum composed of different peaks of 303 nm ($^7$F$_6$ → $^3$H$_6$), 318 nm ($^7$F$_6$ → $^5$D$_0$), 340 nm ($^7$F$_6$ → $^5$L$_7$), 351 nm ($^7$F$_6$ → $^5$L$_5$), 369 nm ($^7$F$_6$ → $^5$G$_5$), and 376 nm ($^7$F$_6$ → $^5$G$_4$). The strongest emission peak is observed at 545 nm corresponding to the $^5$D$_4$ → $^7$F$_5$ transition of Tb$^{3+}$ ion. They reported Sr$_2$B$_2$O$_5$: Tb$^{3+}$, Li$^+$ phosphor as promising green phosphor. The optical absorption and luminescence studies of Yb$^{3+}$ and Tb$^{3+}$ co-doped BaB$_2$O$_4$ ($\beta$ and $\alpha$) phase has been reported by (Solntsev et al., 2012). A broad emission peak centered at 360nm for both un-doped and RE $^{3+}$ doped BaB$_2$O$_4$ phosphor has been observed on excitation at 250nm. This emission is due to the native defects of BaB$_2$O$_4$ phosphor. The narrow peaks for Tb$^{3+}$ were observed in 400- 700nm range with main excitation peak 550 nm. A group of lines in the 960–1100nm range were
associated with the $^2\text{F}_{5/2} - ^2\text{F}_{7/2}$ transitions in the Yb$^{3+}$ ion. They also observed that the incorporation of Tb$^{3+}$ ion does not influence the wavelength position of Yb$^{3+}$, Yb$^{2+}$ ions in the BaB$_2$O$_4$: Yb, Tb phosphor.

1.8 MOTIVATION

Luminescent materials are considered as good materials because of their potential applications in solid state lighting. These materials are being used in modern lighting, display fields, radiation dosimetry etc. The borate-based phosphors have been of great interest for usage in practical application because of their large band-gap, low cost and excellent physical and chemical stability. Alkaline earth based oxide phosphors doped with rare earth ions have been explored as one of the good luminescence materials in the past few years. Thus, the main objective of this work is to synthesize the rare earth doped alkaline borate based oxides nanophosphors/phosphors and to explore these materials for their potential applications in solid state lighting and dosimetry etc.

1.9 OBJECTIVES

The main objectives of this work are:

1. To synthesize the alkaline earth based borate nanophosphor doped with different rare earth metal ions by using combustion.
2. To synthesize bulk alkaline earth based borate phosphor by solid state reaction method.
3. A systematic comparison will be done between different properties of bulk and nanophosphors.
4. To characterized the above synthesized phosphor for their structural and morphological properties.
5. To study the effect of different rare earth ion’s concentration on the photoluminescent and thermo-luminescent properties of the synthesized phosphors.
6. To study the surface and spectral properties of the synthesized phosphors.

1.10 SIGNIFICANCE OF PRESENT WORK

In the present work, the luminescence properties of some alkaline earth based oxides nanophosphors have been investigate for the applications of light emitting diodes. Rare earth doped alkaline borate phosphors are considered as the best candidates in the field of lightning because of their large band gap, high melting point and chemical stability. Due to large band gap we can tailor the luminescent properties of host material by using different rare earth metal ions in the range of visible spectra. Now, nanophosphors are replacing the traditional phosphors, which are in use since last decade as they are portable as well as provide high
resolution with increased luminescence efficiency. Future use of nanophosphors will result in the reduction of cost of making high-resolution display devices and will bring a revolution in the industry.

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