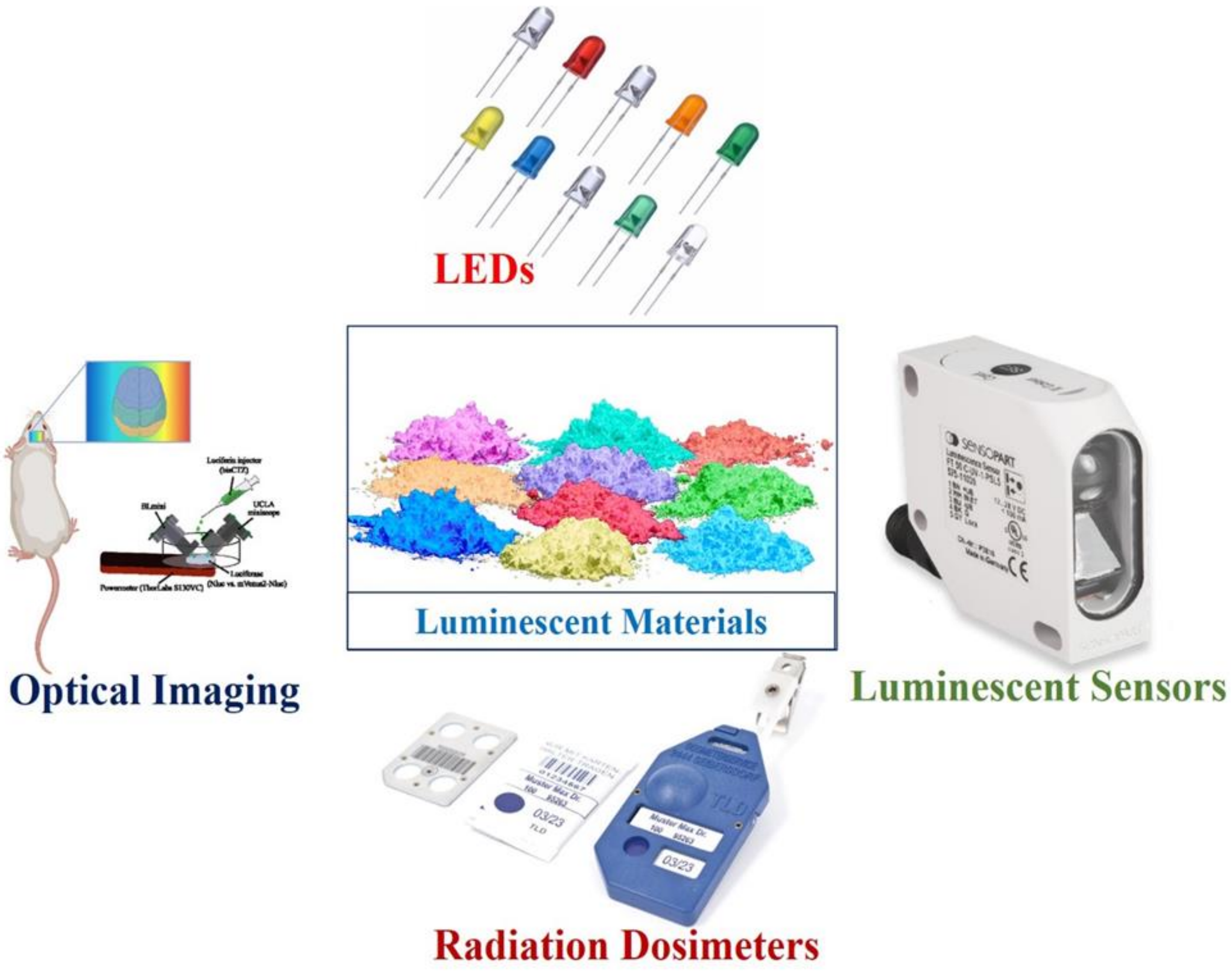
Chapter-1

Introduction

Highlights

This chapter consists of a brief introduction to the luminescence phenomenon, along with its history, luminescence mechanism, and different types of luminescence. The detailed information regarding different perovskites and luminescent perovskites has been briefly discussed. In addition, a brief note on the literature survey on perovskites, rare earths, and rare earth doped perovskites is mentioned. The importance of rare earths as luminescent activators was discussed, along with the basics of lanthanides. In summary, the objective of the thesis is given, followed by the layout of the thesis.



1.1 Luminescence Phenomenon

Luminescence refers to the emission of light in the visible region from a substance like quartz, minerals, semiconductors, and ceramic materials such as phosphors [1-3]. It is a fascinating optical phenomenon observed in several natural and artificially prepared materials. Unlike incandescent light, which is produced by heating an object to high temperatures, luminescence emission occurs when energy is absorbed by a material and later released in the form of visible light. The process of luminescence involves the absorption of energy in the form of photons, or any other term, by the atoms of a luminescent material. If the absorbed energy is high enough to excites the electrons within the material, it causes electrons to move into the higher energy levels of the material. When the excited electrons return to their original states, they release the absorbed energy in the form of visible, ultra-violate (UV), or infrared (IR) light. Instant emission (sustained up to 10^{-8} seconds or for less time) of light on the absorption of energy is commonly defined as fluorescence emission, which ends instantly after the removal of the source of excitation. However, phosphorescence involves a delayed emission of light even after the energy source is removed, as the excited electrons return to their original states more slowly [4,5]. Moreover, bioluminescence is a particular type of luminescence found in living organisms, where chemical reactions within their bodies produce light. The example includes fireflies and 80% of deep-sea creatures. Luminescent materials have numerous applications in various fields. They are used in lighting devices, displays, imaging technologies, TLD, signalling, and sensors. For example, fluorescent dyes are employed in biological research to label and track specific molecules or cells. Phosphorescent materials find applications in glow-in-the dark products, such as watch dials and emergency signs [6-8]. Additionally, bioluminescent organisms have provided invaluable tools for scientific research and have applications in medical diagnostics and environmental monitoring. Overall, luminescence is a fascinating phenomenon that has been harnessed and utilized for a wide range of practical and scientific applications. Moreover, most of the human blood group analysis was done using luminescence technology. Its study continues to advance our understanding of light and matter, leading to new discoveries and innovations in various fields.

1.1.1 History

The word “Luminescence” comes from the Latin word “Lumen” means light, and was first introduced by the great German scientist Eilhardt Wiedemann in 1888 [1]. Before this, Robert Boyle in 1666 reported luminescence. In 384-322 (BC), a Greek philosopher and scientist named Aristotle observed the light that was coming out of decaying fish. Two thousand years later, a Swiss man named Nicolas Monardes observed an extremely vivid blue color from an aqueous extract of wood called lignum nephriticum [9]. A lot of the phenomenon of light emission was observed to occur due to natural or artificial processes. After such an undefined phenomenon, an English scientist, George Stokes, comes into the picture and studies the cause of light emission with the help of prisms and optical fibres. As per Stoke's observations, the light of a particular wavelength absorbed by the specimen was transformed and reemitted as light with a longer wavelength in comparison with the absorbed one. Later in the nineties, research on luminescence gets triggered. The discovery of light-emitting diodes (LEDs) using luminescence phenomena made a huge impact in the field of electroluminescence [10]. In the beginning of the 20th century, a study on luminescent crystals was carried out for the first time by Lenard and his group. The crystal on which the study of luminescence was made, was then named "Lenard Phosphor" [11]. In addition, the invention of radioactivity by Madam Curie led to the development of the TLD.

During the past few decades, the production and fabrication of white light-emitting diodes (WLEDs) have attracted huge interest worldwide because of their several advantages, including low power consumption, environmental friendliness, cost-effectiveness, and high luminescence efficiency [12]. Consequently, luminescent materials, also called phosphors, with excellent luminescence displays are the key components of commercially available WLEDs. A new generation is working on the luminescence phenomenon, primarily focusing on the luminescence efficiency enhancement and low cost-effectiveness of WLEDs [13]. Since the last six decades, phosphors with excellent displays of several kinds of luminescence have been widely investigated for their practical technological applications in various fields of science and technology. Phosphors doped with different luminescent activators are widely investigated for lighting devices and displays, lasers, and medical purposes [14].

1.1.2 Luminescence Mechanism

The luminescence mechanism is mainly categorized based on the sustained time of luminescence emission, which is mentioned in the following flow chart, Figure 1.1.

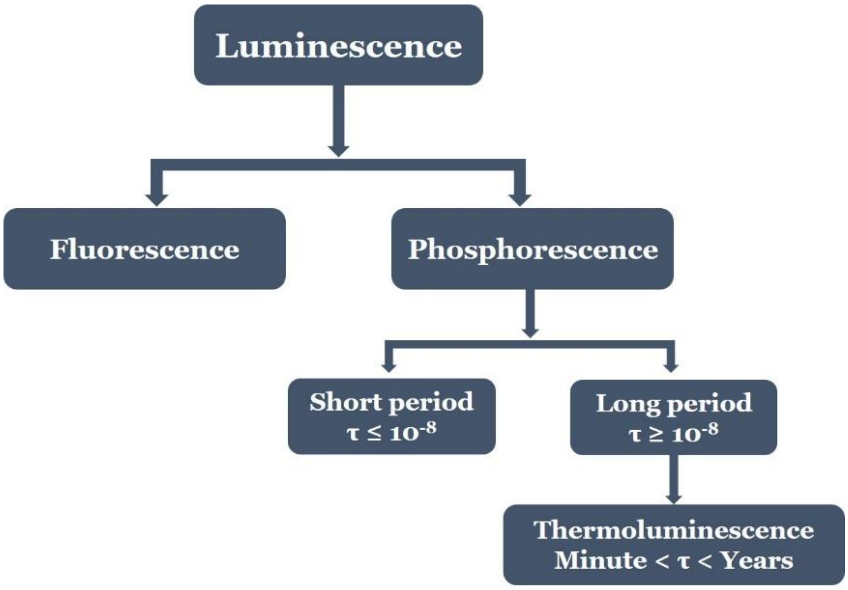


Figure 1.1. Classification of luminescence in term of emission time.

1.1.2.1 Fluorescence

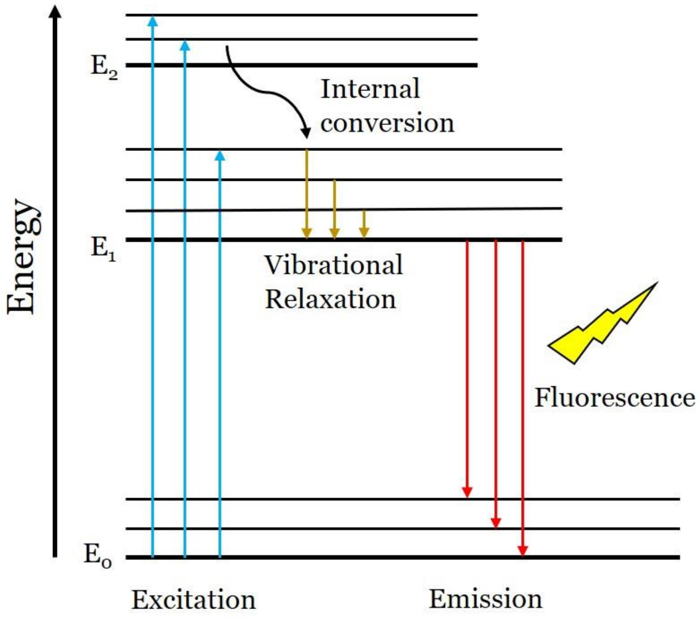


Figure 1.2. Mechanism of fluorescence emission.

A luminescence emission that occurs almost instantly after the absorption of energy and stops after the removal of the external energy is defined as a fluorescence emission [2]. This type of emission occurs in all the chemically stable states of matter: solid, liquid, and gas. Jablonski, in 1952, a French physicist, proposed the following models, which explain almost all of the luminescence process. Fluorescence is caused by photon absorption in the singlet ground state being promoted to the singlet excited state. Therefore, the fluorescence occurs only in the first singlet excited state.

The process involves three steps: absorption, vibrational relaxation, and emission. Figure 1.2 depicts the schematic diagram of the fluorescence emission mechanism. A singlet ground state, the first excited state, and the second excited state are denoted as E_0, E_1 and E_2, respectively. Absorption of energy photons typically belongs to the ultraviolet (UV) or visible range, prompting electrons from their ground (E_0) state to exited state.

Mostly, electrons cannot stay longer in the excited state for more than a few nanoseconds. Hence, as a result, a rapid relaxation of electrons takes place towards the lower energy state, usually in the first excited state (E_1) by losing some of their excess energy through collisions with other molecules in the substance. This process is known as internal conversion. Later, the electron finally returns to its ground state, releasing the excess energy as a photon of longer wavelength than the absorbed photon. This emitted light is what we observe as fluorescence. The emission occurs rapidly, usually within picoseconds to nanoseconds after absorption. Compared to the absorbed light, the fluorescence light emits with lesser energy and has a longer wavelength. The energy loss phenomenon during this process of photon absorption and emission is denoted as a Stokes shift. The occurrence and magnitude of the stokes shift are highly dependent on both the type of substance and its surroundings [2].

1.1.2.2 Phosphorescence

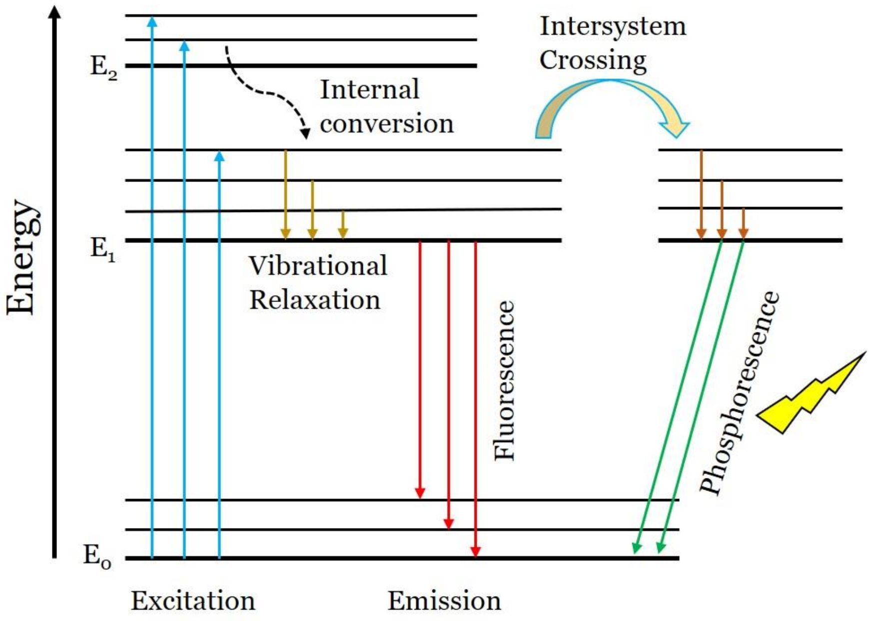


Figure 1.3. Mechanism of phosphorescence emission.

Phosphorescence is like fluorescence but involves a delayed emission of light. The mechanism consists of four steps: absorption, relaxation, intersystem crossing, and emission. Figure 1.3 depicts the schematic diagram of the phosphorescence mechanism. An external energy source, such as UV light, excites an electron in the substance to a higher energy level. The excited electron undergoes internal conversion and vibrational relaxation, like fluorescence. However, in phosphorescent materials, the electron gets trapped in a long-lived excited state known as a triplet state. This state has forbidden transitions to the ground state, resulting in a delay in emissions. Through a process called intersystem crossing, the electron transitions from the triplet state to a metastable excited state, which is also a triplet state. This process is facilitated by the spin of the electron and requires certain conditions, such as specific molecular structures or the presence of heavy atoms. Eventually, the electron undergoes a transition from the metastable triplet state to the ground state, releasing the excess energy as a photon. This emission process occurs over a longer timescale compared to fluorescence, ranging from microseconds to hours, depending on the material [15].

1.1.3 Luminescence Emission

To achieve luminescence emission, a crystalline or amorphous host matrix along with a luminescent activator are the basic components to be needed. Sometimes, the host lattice can be luminescent itself. However, in the case of a non-luminescent host, a slight addition of luminescent activator was intestinally introduced. The base material is the bulk of luminescent phosphor, whereas the doping of activators was responsible for the luminescence phenomenon. Usually, the cause of luminescence and the shade of emitting energy were only because of the activator ions doped in the host matrix, not because of the host itself. Figure 1.4 depicts the diagram of luminescence emission occurring due to the luminescent activator.

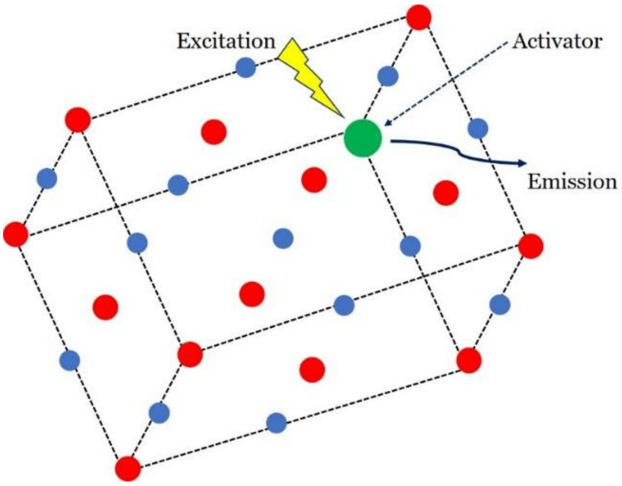


Figure 1.4. Luminescence emission occurring due to the luminescent activator.

When the material is excited with some kind of energy, the energy absorption by the activators is dominant in comparison with the host. A radiative transition occurs in the activators' energy states, resulting in luminescence. Which is the direct emission of light for which the activator is only responsible. The emission intensity is strongly dependent on the absorbed energy. In some cases, the luminescent activators have poor absorption of exciting energy, and due to that, the luminescence intensity gets compromised. To overcome such difficulty, another foreign dopant called a sensitizer with excellent energy absorption characteristics can be incorporated into the host matrix in addition to activator ions. Subsequently, the process of light emission will take place in the following manner:

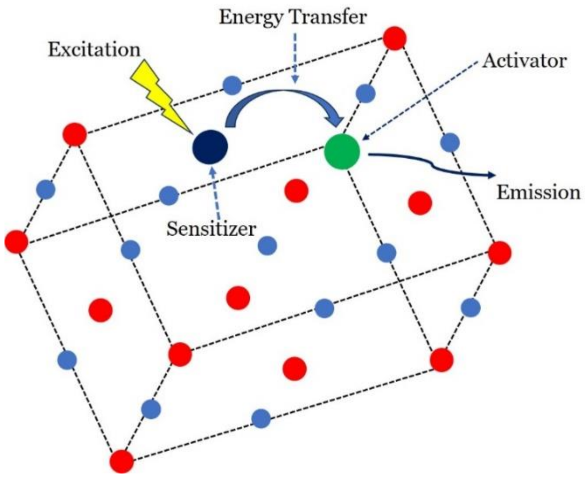


Figure 1.5. Energy transfer mechanism and occurrence of luminescence phenomenon.

Figure 1.5 depicts the energy transfer mechanism between the sensitizer and the luminescent activator, and the occurrence of luminescence. Initially, the sensitizer absorbs energy from the source of excitation and transfers it to the parent luminescent activator. The process is called an energy transfer mechanism. As a result, the emission of parent activator ions was enhanced, and high-quality luminescence can be achieved.

1.1.4 Types of Luminescence

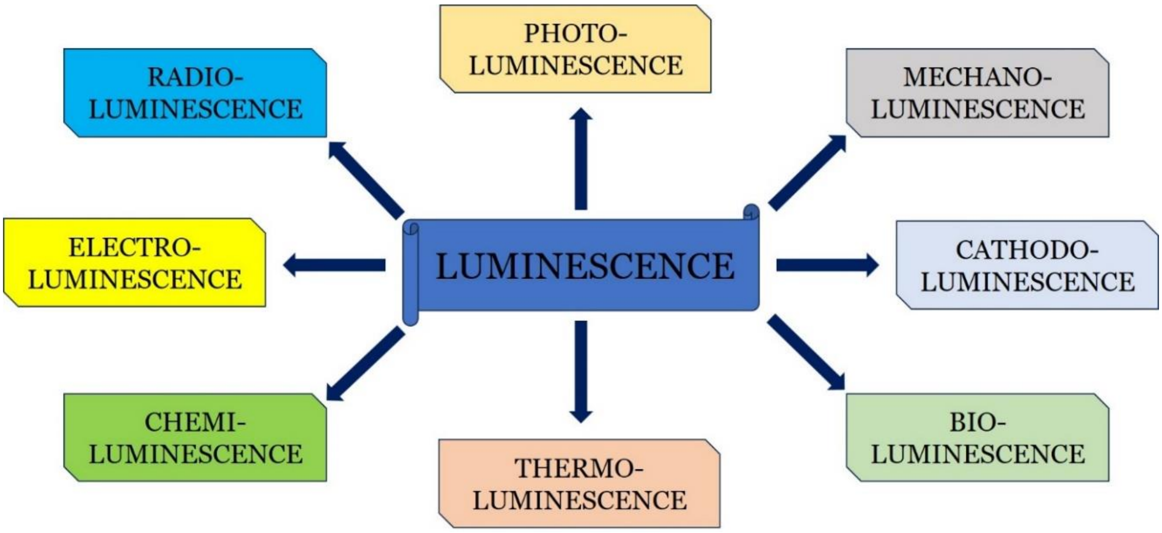


Figure 1.6. Schematic classification of luminescence.

Based on the source of excitation, luminescence is categorized into many kinds. Figure 1.6 depicts the schematic classification of luminescence types.

1.1.4.1 Photoluminescence

The luminescence process takes place upon the absorption of an energy photon belonging to UV, visible, or IR light, which is defined as photoluminescence. It may either fluorescence or phosphorescence and always obey the Stokes rule. In contrast, sometimes the Stokes rule is overruled in the case of up-conversion luminescence, which means that the emitted light has a lower wavelength in comparison to the absorbed one. Upon energy absorption, the electron jumps to an excited state; the process is called photo-excitation, and then comes back to its original state by radiating the absorbed energy in terms of visible light. In detail, the electron in an excited state undergoes an intersystem crossing process, which means that the electron is moving towards a triplet excited state from a singlet excited state. Later, a radiative relaxation of electrons takes place, which is termed photoluminescent emission. The outcome of the PL process is the plot of PL intensity as a function of wavelength. The plot of electron excitation is called the excitation spectrum, and the plot of light emission as a function of wavelength is called the emission spectrum.

1.1.4.2 Thermoluminescence

Thermoluminescence (TL) is a phenomenon in which certain materials emit light when heated after being exposed to ionizing radiation. The process of thermoluminescence involves the absorption of ionizing radiation, such as X-rays, beta rays, UV rays, and gamma rays, by a material. This radiation excites electrons within the crystal lattice structure of the material, promoting them to higher energy levels. After some time, these excited electrons try to return to their original energy levels and get trapped within the crystal structure. The light emission is not immediate but rather occurs when the material is heated. Figure 1.7 depict the TL mechanism steps involved.

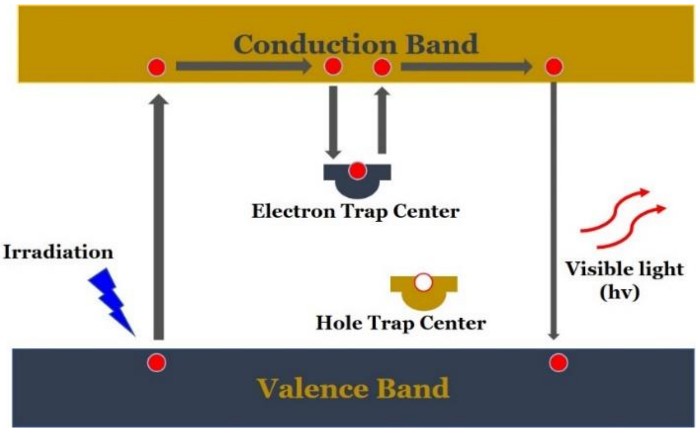


Figure 1.7. Thermoluminescence mechanism.

When the irradiated material is subjected to controlled heating, the trapped electrons are provided with additional thermal energy. This energy enables the electrons to overcome the energy barriers that prevent their recombination, and as a result, they return to their original energy levels, releasing the stored energy as visible light. The emitted light can be detected and measured using appropriate instruments, such as photomultiplier tubes or photodiodes. The intensity of the thermoluminescence light emitted is directly proportional to the amount of ionizing radiation to which the material was exposed. This property forms the basis of thermoluminescence dating, a technique used in archaeology and geology to determine the age of objects or geological formations by measuring the accumulated radiation dose. TL materials, such as phosphors or crystals, are employed as thermoluminescence dosimeters (TLDs) to monitor radiation exposure.

1.1.4.3 Electroluminescence

Electroluminescence is a phenomenon in which a material emits light when an electric current passes through it or when it is subjected to an electric field. It is a type of luminescence, which refers to the emission of light from a substance not resulting from high temperatures. In electroluminescent devices, such as light-emitting diodes (LEDs), a voltage is applied across a semiconductor material or an organic compound. This voltage excites the movement of electrons and holes within the material. When the electrons recombine with the holes, energy is released in the form of photons, resulting in the emission of light. The color of the emitted light depends on the properties of the material and the energy levels involved in the electron transitions. By selecting different materials or modifying the composition, it is possible to produce electroluminescent devices that emit light across a wide range of color, including red, green, and blue. Electroluminescence is widely used in various applications, such as display, and LEDs. Electroluminescence provides advantages like energy efficiency, fast response, compactness, and durability, making it a potential choice for many lighting and display technologies.

1.1.4.4 Chemiluminescence

Chemiluminescence is a process in which light is emitted as a result of a chemical reaction. It occurs when certain chemical compounds, called luminophores, undergo a reaction that releases energy in the form of light instead of heat. The reaction typically involves the excited state of a molecule or atom returning to its ground state, resulting in the emission of photons. Unlike fluorescence or phosphorescence, which require external energy sources such as light or heat to excite the molecules, chemiluminescence reactions are self-induced and do not require external energy. They are often triggered by the mixing of two or more chemicals, such as an oxidant and a reductant, which react together to produce light. Chemiluminescence has various applications in fields such as analytical chemistry, biomedical research, and forensic science. Chemiluminescent reactions are also employed in light-sticks, glow sticks, and other novelty items that produce light without the need for electricity or heat.

1.1.4.5 Cathodoluminescence

Cathodoluminescence is a phenomenon where light is emitted from a material when it is bombarded with high-energy electrons, typically produced by an electron beam. When the electrons strike the material, they transfer energy to the atoms or molecules, bringing them to higher energy levels. As these excited states decay, the material emits photons of light. Cathodoluminescence is commonly used in various scientific and technological applications. It provides valuable insights into the properties and structures of materials at the nanoscale, allowing researchers to study their composition, defects, and optical properties. It has applications in semiconductor characterization, device fabrication, and even in the analysis of geological samples, among others.

1.1.4.6 Radioluminescence

Radioluminescence refers to the phenomenon of light emission caused by the interaction between ionizing radiation and certain materials. When high-energy radiation, such as alpha particles, beta particles, or gamma rays, interacts with a substance, it excites the atoms within those materials. As the excited atoms return to their lower energy states, they emit light in the process, which is known as radioluminescence. Radioluminescence has found applications in areas such as radiation detection, medical imaging, and various industries where luminous indicators are needed in low-light or no-light conditions.

1.1.4.7 Bioluminescence

Bioluminescence is a natural phenomenon where living organisms produce light. It occurs when certain chemicals, known as luciferins, react with enzymes in the presence of oxygen to generate light. This light emission is often seen in various organisms, such as fireflies, deep-sea creatures, and certain fungi. For some, it serves as a form of communication, enabling them to attract mates. Fireflies, for example, use their bioluminescent flashes to find and attract their mates. The light produced by bioluminescent organisms is typically cold, meaning it emits very little heat compared to other sources of light.

1.1.4.8 Mechanoluminescence

Mechanoluminescence is a phenomenon where the substance emits light when subjected to mechanical stress or deformation. When pressure or stress is applied to the materials, such as by bending, or crushing, the crystal structure of the material undergoes changes, causing the release of stored energy in the form of visible light. This process generates excited states or vacancies within the crystal lattice, which then relax by releasing photons of light. Mechanoluminescent materials have practical applications, such as in stress sensors, impact detectors, and structural health monitoring.

1.2 Role of the Rare Earths

Lanthanide (Ln)	Atomic Number	Electronic configuration (Ln^{3+})	Ground state	Excited state	Emission region
Lanthanum (La)	57	[Xe] $4f^0$	$^1S_0$		
Cerium (Ce)	58	[Xe] $4f^1$	$^2F_{5/2}$	$^2F_{7/2}$	NIR
Praseodymium (Pr)	59	[Xe] $4f^3$	$^3H_4$	$^1G_4$, $^1D_2$, $^3P_0$	NIR
Neodymium (Nd)	60	[Xe] $4f^4$	$^4I_{9/2}$	$^4F_{3/2}$	IR
Promethium (Pm)	61	[Xe] $4f^5$	$^5I_4$	$^5F_1$	IR
Samarium (Sm)	62	[Xe] $4f^6$	$^6H_{5/2}$	$^4G_{5/2}$	Orange
Europium (Eu)	63	[Xe] $4f^7$	$^7F_0$	$^5D_0$, $^5D_1$, $^5D_2$	Red
Gadolinium (Gd)	64	[Xe] $4f^7$	$^8S_{7/2}$	$^6P_{7/2}$	UV
Terbium (Tb)	65	[Xe] $4f^9$	$^6F_6$	$^5D_3$, $^5D_4$	Green
Dysprosium (Dy)	66	[Xe] $4f^{10}$	$^6H_{15/2}$	$^4F_{9/2}$	Blue, Yellow
Holmium (Ho)	67	[Xe] $4f^{11}$	$^5I_8$	$^5F_5$, $^5S_2$	NIR, Green
Erbium (Er)	68	[Xe] $4f^{12}$	$^4I_{15/2}$	$^4S_{3/2}$, $^4F_{9/2}$, $^2H_{11/2}$, $^2H_{5/2}$	Green, NIR
Thulium (Tm)	69	[Xe] $4f^{13}$	$^3H_6$	$^1G_4$, $^1D_2$	NIR
Ytterbium (Yb)	70	[Xe] $4f^{14}$	$^2F_{7/2}$	$^2F_{5/2}$	NIR
Lutetium (Lu)	71	[Xe] $4f^{14}$	$^1S_0$		

Table 1.1. Lanthanides and their luminescence colors.

Rare earth elements play a crucial role in the luminescence properties of various materials. Luminescence refers to the emission of light from a substance when it absorbs energy. Rare earths are known for their unique electronic configurations, which give rise to distinct energy levels and transitions, making them excellent candidates for luminescent applications [16,17]. The electronic configuration of rare earths provides energy levels with specific quantum numbers, which determine the wavelengths of light they can absorb and emit. The transitions between these energy levels result in luminescence. Different rare earth ions exhibit specific energy level structures, leading to a broad range of colors and emission spectra

[18]. Moreover, rare earth elements are widely used in phosphors, which are materials that convert absorbed energy into visible light. Phosphors doped with rare earth ions exhibit luminescence through various mechanisms, such as fluorescence, phosphorescence, and up-conversion luminescence.

Table 1.1 summarises the lanthanides from the periodic table, along with the electronic transition states responsible for the emission of different colors in the visible range. Rare earths have efficient luminescent properties, including high quantum yields and long luminescence lifetimes. These characteristics make them suitable for applications requiring bright and long-lasting luminescence, such as lighting, displays, and imaging technologies. In addition, the rare earth ions offer the ability to tune and control luminescence properties by selecting specific rare earth ions and adjusting their concentrations in different host materials. This flexibility enables the creation of materials with desired emission colors. Rare earths can act as sensitizers in luminescent systems. They can efficiently transfer energy to other luminescent centres, enhancing the emission of other elements or materials. This phenomenon is important in applications like white light-emitting diodes (LEDs), where rare earths enable the generation of a broad visible spectrum by combining multiple emissions [19].

Not only the luminescence emission, but the other phenomenon's resulting due to the rare earth incorporation making it more fascinating to investigate.

Down-conversion and Up-conversion luminescence: Down-conversion and up-conversion luminescence are the phenomena of light emission that define the conversion of light from one wavelength to another wavelength. These phenomena of light emission can easily be achieved via rare earth doping. Almost all the rare earth shows down-conversion emission, in which the high-energy light excitation is converted into lower-energy light emission. This process involves the absorption of photons of shorter wavelengths and the emission of a single photon of longer wavelength. However, very few of the rare earths demonstrate the phenomenon of up-conversion, the conversion of lower-energy excitation into high-energy light emission, including erbium (Er^{3+}) and ytterbium (Yb^{3+}) [20]. The up-conversion involves the absorption of photons of longer wavelengths re-emitting a single photon of shorter wavelength.

Persistent luminescence and Long-lasting luminescence: The persistent luminescence and long-lasting luminescence were defined closely same, but they were not exactly the same. Both of this type of luminescence from the materials continue to emit light after the removal of source of excitation. The persistent luminescence is the phenomenon, in which a material continues to emit light for a minute to hours under optical excitation [21].

Whereas long-lasting luminescence is a luminescence that continues for an extended duration. Long-lasting luminescence, which might extend beyond hours to days or even longer. To achieve these phenomena, cerium (Ce^{3+}), europium (Eu^{3+}), and terbium (Tb^{3+}) are widely incorporated as luminescent centres.

Energy transfer mechanism: Energy transfer mechanisms play a critical role in rare earth induced luminescence. The rare earth ions are very popular for their characteristic luminescence and energy transfer mechanisms for triggering the emissions. The energy transfer processes resulting in rare earth induced luminescence involve energy transfer between two active centres, namely the sensitizer and activator. The sensitizers are first excited upon the absorption of longer-wavelength photons and then transfer their energy to the activators, leading to the enhanced luminescence emission intensity. Understanding the energy transfer mechanism between two active centres reduces the high energy consumption. Erbium (Er^{3+}), ytterbium (Yb^{3+}), and Neodymium (Nd^{3+}) are commonly incorporated as sensitized elements in order to achieve the energy transfer mechanism.

Tunable luminescence: The rare earths exhibited their characteristic luminescence emission color upon optical excitation, which corresponds to an electronic transition occurring within 4f states of it. The choice of rare earth ions and appropriate host lattice can exhibit a range of emission wavelengths in the visible, UV, and IR regions. In some cases, the color tunability can be obtained by varying the doping concentration, and the co-doping of other rare earth may also give fine color tunability. Europium (Eu^{3+}), terbium (Tb^{3+}), erbium (Er^{3+}), holmium (Ho^{3+}), dysprosium (Dy^{3+}), praseodymium (Pr^{3+}), and cerium (Ce^{3+}) show visible emission; however, gadolinium (Gd^{3+}) is a good choice for UV light, and to achieve IR emission, neodymium (Nd^{3+}) is widely incorporated in the host lattice. The color tunability expands the range of phosphor applications, including in displays, diodes, and lasers.

In summary, their unique electronic configuration, energy levels, and efficient luminescent properties make them valuable for a wide range of applications, including lighting, displays, imaging, radiation dosimetry, and optical devices.

1.3 Introduction to Perovskite

The history of perovskite is quite fascinating, as it includes both the mineral and the perovskite materials used in various industrial applications. Perovskite gets its name from the Russian mineralogist Lev Perovski, who discovered a new mineral ($CaTiO_3$-Calcium Titanate) with a unique crystal structure in the Ural Mountains of Russia in 1839 [22]. The mineral was then named "perovskite" in his honor. In the 1920s, the crystal structure of perovskite was thoroughly studied by the Ukrainian mineralogist Victor Goldschmidt. He identified the crystal structure as a cubic arrangement of oxygen atoms with larger cations occupying the corners and smaller cations in the centre of the unit cell. In early of 20th century, perovskite oxides gained significant attention due to their remarkable properties. These materials exhibit properties like high-temperature superconductivity, colossal magnetoresistance, and ferroelectricity. Scientists explored their potential applications in various fields, including electronics, magnetism, and energy. The structural classification of inorganic perovskites is based on the composition and arrangement of their constituent atoms. In general, the structure of an inorganic perovskite can be described as ABX_3, where A and B represent cations, and X represents an anion, such as oxygen or any halide [23]. The A cation is typically larger and is located at the corners of a regular octahedron, while the B cation occupies the centre of the octahedron. The X anion is positioned at the face centres of the octahedron. The following Figure 1.8 represents the family of perovskites.

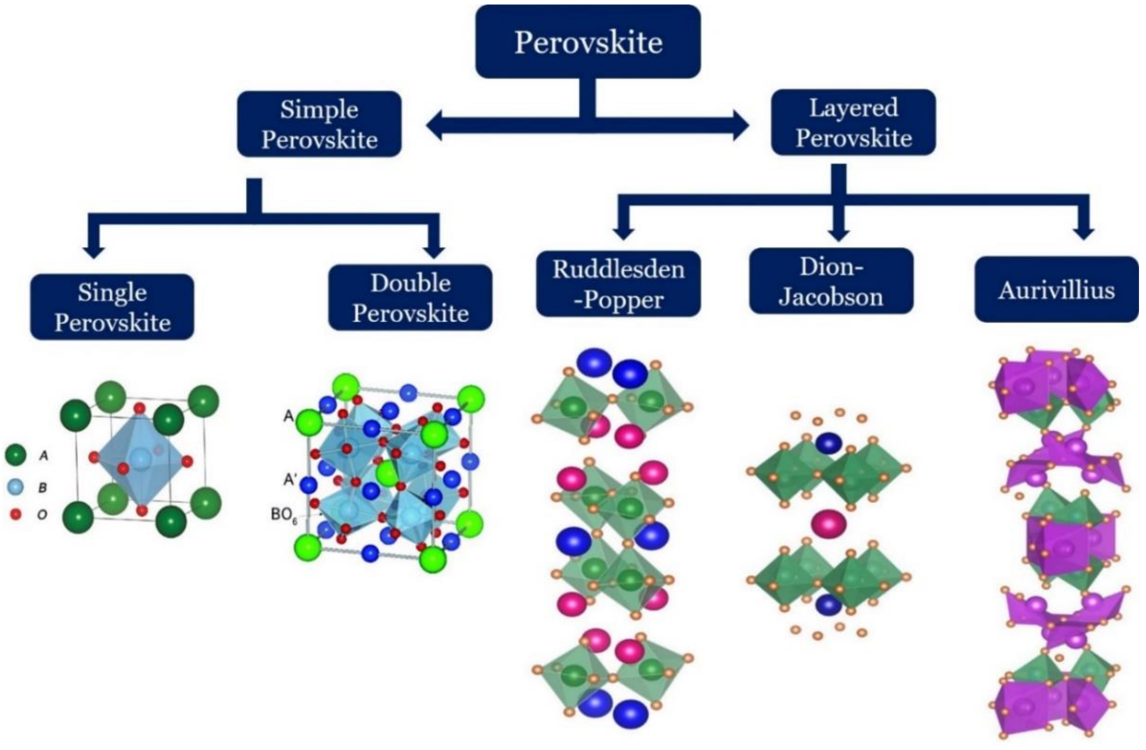


Figure 1.8. Classification of perovskite structure.

Based on the arrangement of the B cations, inorganic perovskites can be further classified into the following categories:

Double Perovskite: Double perovskites contain two different types of the B cations. If half of the B site is replaced by B' cation, then the resultant perovskite is called a double perovskite. They have the general formula $A_2BB'O_6$, where A is typically a larger cation, B and

B' are different cations, and O is the anion [24]. To identify the crystal structure of the double perovskite, Goldschmidt introduced the concept of the "tolerance factor" by considering the ionic radii balance of the constituent elements. The formula for the same is as follows:

$$T_f = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)}$$

where, R_A = ionic radii of A cation

R_B = ionic radii of A cation

R_O = ionic radii of oxygen.

The tolerance factor for perovskite structures was concluded to be in the range of $T_f = 0.99$ to $T_f = 0.77$. In the geometry of double perovskite, a tolerance factor (T_f) less than unity indicates either a monoclinic or orthorhombic structure of the material, while a T_f nearly equal to unity denotes a cubic double perovskite [25].

Ruddlesden-Popper Perovskite: Ruddlesden-Popper perovskites have a layered structure with alternate layers of perovskite-like units. They have the general formula $A_{n+1}B_nX_{3n+1}$, where n represents the number of perovskite-like layers. A well-known example of Ruddlesden-Popper perovskite is $SrTiO_3$ simple perovskite based $Sr_3Ti_2O_7$.

Dian-Jacobson Perovskite: The chemical composition $A'A_{n-1}B_nX_{3n+1}$ was categorized as a perovskite family member. This type of perovskite is widely investigated for the optoelectronics devices applications, including $A'A_{n-1}Pb_nI_{3n+1}$.

Aurivillius Perovskite: The Aurivillius phase belongs to layered perovskite with chemical formula $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$. In this type of perovskite $(A_{n-1}B_nO_{3n+1})^{2-}$ layer of perovskite were located in between $[Bi_2O_2]^{2+}$ layers.

These classifications provide a framework to categorize and understand the structural diversity of inorganic perovskites. Moreover, the crystal structure, structural tunability, wide range of chemical and physical properties, ability to emit visible emission, and energy storage capacity make perovskite special in comparison with other materials.

1.4 Luminescent Perovskites and Concerned Literature Review

In the field of luminescence investigation and its applications, many phosphors were explored for their excellent display of luminescence. Herein, the author of the thesis proposes luminescence studies on perovskite-based luminescent phosphors and activated perovskite phosphors to functionalize them for various applications. During the initial stages of the research, a brief literature review on luminescent phosphors and rare earth-activated perovskite phosphors was carried out. As per the literature survey, several luminescent perovskites were previously reported for their diverse luminescence phenomena, such as photoluminescence, thermoluminescence, persistent luminescence, optically stimulated luminescence, up- and down-conversion luminescence, etc. A survey of the literature in accordance with the presented thesis is mentioned below:

The present day's research on luminescence materials was triggered because of their various technological applications, including in WLEDs and in various types of dosimetry. Research on phosphor-converted LEDs is in high demand because of their high color rendering profile and low color corelated temperature in comparison with incandescence lamps. Several rare-earth doped double perovskite phosphors with the ability to emit white light were previously reported. Meijiao Liu et al. [26] reported a highly efficient europium doped red phosphor Ca_2YSbO_6 for WLED applications. They found excellent quantum efficiency about 92.1 % in addition to high thermal stability. Also, they proposed an excellent color rendering profile of 82.6 by fabricating it with the commercial phosphor InGaN and $Y_3Al_5O_{12}$:Ce^{3+}. Yongbin Hua et al. [27] proposed a new double perovskite structure Sr_3MoO_6 by doping Eu^{3+}. As per the results, a very high color purity of the order of 94.78 % was obtained, which can be very good number for the phosphor to be incorporated in WLEDs. Later in 2020, Xiaoyong Huang et al. [28] synthesized a novel composition of double perovskite Ca_2YTaO_6 activated with trivalent lanthanide Eu^{3+}. Upon UV excitation, they found excellent red down-conversion luminescence, including a high color purity of about 97.4 %. With outstanding color coordinates and an excellent color rendering index of about 92.1 with 21.76 lm/W luminous efficiency, they proposed a suitable candidate for warm white light-emitting diodes. Shaoying Wang et al [29] introduced a high-performance Ca_2GdTaO_6:Eu^{3+} red phosphor for WLED application. As per the study, the phosphor shows internal quantum efficiency around 83%, which is a very good number, in addition with high thermal stability of the order of 82%. The studied phosphor can serve as a promising red phosphor component for WLEDs. K. Dabre et al. [30] synthesized Ca_2ZnWO_6 double perovskite by doping three different rare earth elements, which are Eu^{3+}, Sm^{3+}, and Pr^{3+}. For all three doping elements, Ca_2ZnWO_6 exhibited red spectral emission upon UV-blue excitation. Moreover, several single rare earth activated perovskite with CIE color coordinated in white spectral region were reported, including, Ca_2YTaO_6:Bi^{3+}\Eu^{3+} [31], and Ca_3WO_6:Dy^{3+} [32]. Le Zhang et al. [33] reported a layered Ruddlesden-Popper perovskite $Sr_3Ti_2O_7$ for its luminescence characteristics. Also, they reported the charge compensation study in the same formula by doing additional doping of Li^{+} with the primary dopant Eu^{3+}.

Not only in LED applications, but also the perovskite chemical family is widely investigated for their illuminating device applications such as lighting displays and plasma displays by activating via rare earth elements. Yuntong Li et al. [34] prepared a novel europium activated Ba_3WO_6 nanowires using a solid-state reaction. In the report, the studied phosphor was prepared at different sintering temperatures to examine the effect of heating temperature on the crystal structure. Moreover, the same phosphor was co-doped with different charge compensating ions, primarily Li^+, Na^+, and K^+. As a result, they proposed the high applicability of the phosphor in lighting applications. Yongbin Hua et al. [35] reported the multifunctional double perovskite Sr_2LaNbO_6 which was studied for cathodoluminescence and photoluminescence. The Judd-Ofelt study on the phosphors was carried out. From the obtained results, phosphor's applicability in flexible luminescence film, displays, and field emission displays were revealed. A yellow-emitting novel $NaLaMgWO_6{:}Dy^{3+}$ phosphor was reported by Bing Han et al. [36] in order to investigate the multifunctional behaviour of dysprosium. A similar host matrix was studied by Qian Yang et al. [37] by doping Sm^{3+} and Eu^{3+}. In order to achieve orange emission, Sm^{3+} is the suitable dopant to be incorporated. Yongbin Hua et al. [38] introduced novel orange-emitting $Ca_2GdNbO_6{:}Sm^{3+}$ with good thermal stability of 65.32 % at 150 °C. With its good orange-red emission, $Ca_2GdNbO_6{:}Sm^{3+}$ can be used in flexible display.

Apart from ordinary photoluminescence excitation and emission phenomenon, many more phenomenon of light emission were observed from the phosphors, namely energy transfer mechanisms, up-conversion luminescence, and persistent luminescence. Based on different phenomenon, applications of phosphor can be multiplied. Renping Cao et al. [39] reported an energy transfer mechanism in Ca_2MgWO_6 double perovskite by doping Sm^{3+} and Bi^{3+}. The effect of co-dopant directly reflects on the luminescence intensity of the parent activator. The addition of foreign dopant ions with good absorption ability can be a good choice to co-dope in order to improve the luminescence intensity. The phosphors with persistent luminescence get huge interest nowadays because of their diverse applications in bio-imaging, emergency light indicators, and memory devices. Puxian Xiong et al. [40] report persistent luminescence in the NIR region from a 2D layered perovskite Sr_2SnO_4 by doping Tm^{3+}. Another layered perovskite $Lu_2Sn_2O_7$ nanoparticles doped with europium was reported by Santosh K. Gupta et al. [41] for bioimaging and in color-tunable optoelectronics devices. As the fresh plants have more sensitivity towards far-red color light, phosphor with far-red emission capability can be beneficial for plant growth purposes. Several rare earth free double perovskites were reported previously for the plant cultivation application. Qi Sun et al. [42] proposed a far-red emitting $Ba_2GdTaO_6:Mn^{4+}$ double perovskite with excellent internal quantum efficiency of the order of 62%. Having a good CIE point, they proposed the same for indoor plant cultivation. Another tantalate double perovskite Ca_2LaTaO_6 doped with Mn^{4+} with far-red emission was reported by Renping Cao et al. [43] for plant growth purposes. They also built an LED device and conducted extensive research.

Recently, temperature sensors based on optical properties have been the subject of interest due to their medical and military applications. The study of temperature sensors is defined as optical thermometry. During the literature survey, several studies on the temperature sensor made of perovskites were reported. D. Stefanska et al. [44] studied the effect of Eu^{3+} concentration on the temperature sensing properties of Ba_2MgWO_6. They found that the studied phosphor maintains its temperature sensitivity within 77-200 K, and can be a good candidate for low-temperature sensing application. B.P. Singh et al. [45] reported upconverting layered perovskite $Y_2Ti_2O_7$ doped with Er^{3+} and co-doped with Yb^{3+} for temperature sensing. By adding Li^+ as a charge compensator, they found improved up-conversion luminescence intensity. Recently, in 2021, D. V. M. Paiva et al. [46] reported the Eu^{3+}-Tb^{3+} doped Sr_3MoO_6 double perovskite phosphor for its temperature sensing properties towards low temperatures.

Up-conversion luminescence is a phenomenon where a material absorbs multiple low-energy photons and subsequently emits a higher-energy photon. Unlike conventional luminescence, such as fluorescence or phosphorescence, where a material absorbs a higher-energy photon and emits a lower-energy photon, up-conversion luminescence utilizes a nonlinear optical process to convert two or more lower-energy photons, often in the infrared (IR) range, into a single higher-energy photon, typically in the visible or ultraviolet range. This process has diverse applications, including bioimaging, photovoltaics, optical data storage, and telecommunications, due to its ability to access wavelengths that are typically challenging to reach using conventional methods. During literature survey, some rare earth activated up-converting perovskites were found. Xiumei Yin et al. [47] reported layered perovskite $Y_2Ti_2O_7$ by doping well known up-converting rare earth dopant Er^{3+}. They found red up-conversion luminescence under the excitation wavelengths of 980 nm and 1550 nm. In addition, they found light shifting towards green spectral region upon Tm^{3+} co-doping. Shi Ye et al. [48] observed anomalous up-conversion from Eu^{3+}-Yb^{3+} co-doped $Sr_2Ca(Mo,W)O_6$ double perovskite under the excitation of 976 nm laser beam. They observed far-red emission of Eu^{3+} activator upon 976 nm excitation. Another investigation of up-conversion luminescence was done by K. Naveen Kumar et al. [49] by considering $NaLaMgWO_6$ double perovskite as a host matrix and

Er^{3+}/Yb^{3+} dopants. They optimized the up-conversion luminescence and proposed a new material for photonic applications.

From the literature survey, it is observed that the perovskites, especially the double perovskite got less attention for their thermoluminescence characterization. The double perovskite oxides were quite less investigated for their thermoluminescence properties. TL is the most popular characterization technique used for various types of dosimetry, such as personal dosimetry, medicinal dosimetry, and environmental dosimetry. In the mid-literature survey, a fluorite double perovskite Cs_2NaYF_6 doped with Tm^{3+} was reported for its dosimetry characteristic and was prepared by hydrothermal synthesis [50]. The authors reported a potential dosimeter for high-energy ionizing radiation. Junping Yuan et al. [51] reported a rare earth free Ca_2MNbO_6 (M=Ga, Al) double perovskite by doping Cr^{3+} for their TL characterization. They also give information regarding the trapping parameters.

Objectives of the Thesis

After conducting an extensive review of the available literature, it becomes evident that perovskite hosts doped with rare earth ions have been the subject of numerous studies due to their remarkable luminescence properties and versatile applications in solid-state light sources, displays, temperature sensors, plasma display panels, radiation dosimetry, fluorescent lamps, optoelectronics, photonics, and more.

This thesis primarily focused on the synthesis and luminescence characterization of perovskite phosphors activated by different rare earth ions (Eu^{3+}, Tb^{3+}, and Ho^{3+}). While some of the perovskites have been thoroughly investigated as hosts in previous research, however the perovskites for thermoluminescence characterization get limited attention. Thus, this study, entitled "Luminescence Studies of Rare Earth Doped Perovskite Phosphors" attempts to explore the thermoluminescence and photoluminescence properties of the synthesized materials through experiments conducted on some rare earth-doped double perovskites.

- Synthesis of rare-earth doped perovskite phosphors using the combustion route of synthesis.
- Utilization of different characterization techniques, such as crystal structure identification using X-ray diffraction (XRD), examination of morphology using field emission scanning electron microscopy (FESEM), and functional group identification via Fourier transform infrared (FTIR) spectroscopy.
- Investigation of photoluminescence (PL) properties in several rare earth (Eu^{3+}/$Tb3^{+}$/Ho^{3+}) activated perovskite phosphors.

- Study of thermoluminescence (TL) properties in rare earth doped perovskite phosphors by irradiating them with high energy and low energy ionizing radiations, and calculation of TL parameters from the TL glow curves.

Thesis layout:

Chapter 2. Synthesis Method and Characterizations

In this study, we have used the combustion method for the preparation of perovskite materials. This method was chosen for its simplicity, high productivity, and cost-effectiveness. This chapter provides a comprehensive explanation of this method. Additionally, various characterization techniques used in this research are discussed along with the corresponding equipment. The characterization techniques include X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), Fourier-transform infrared spectroscopy (FTIR), thermoluminescence (TL), and photoluminescence (PL). Moreover, the determination of expected parameter using each characterization technique was discussed in brief.

Chapter 3. Niobate Based Double Perovskite Phosphors

This chapter of the thesis describes a study on the effects of Eu^{3+} dopants on the photoluminescence and thermoluminescence properties of Sr_2YNbO_6 double perovskite phosphor. The concentration of Eu^{3+} dopant was taken in the range of 1 mol% to 5 mol%. The synthesis of all the phosphor compositions was accomplished through the combustion process. The study employed various characterization techniques, including XRD, FESEM, FTIR, PL, temperature-dependent PL, and TL after irradiating the phosphor with the beta ionizing radiation. These techniques were used to confirm the compound, examine the surface morphology, analyse the internal structure, and assess the material's LED and radiation dosimetry features.

Chapter 4. Vanadate Based Double Perovskite Phosphors

This chapter presents an investigation on a vanadate double perovskite Sr_2YVO_6 phosphor doped with Eu^{3+}. The synthesis of this phosphor was carried out using the combustion synthesis method. To determine the phase and confirm the crystal structure, XRD was used. Additionally, structural analysis was performed using FESEM, EDAX, and FTIR spectroscopy. The phosphor Sr_2YVO_6 doped with Eu^{3+} underwent irradiation using two different ionizing radiations, namely beta and UV rays, with varying radiation doses. The PL properties were thoroughly examined to gain a comprehensive understanding of the phosphor's characteristics. In further analysis, the CIE study was utilized to calculate the chromaticity coordinates and color temperature, exploring the potential application of the phosphor displays. The overall obtained results give enough evidence for the phosphor under study to be incorporated into displays and TLD applications.

Chapter 5. Tungstate Based Double Perovskite Phosphors

Part-I

This section discusses the structural and luminescence optimization of terbium activated tungstate double perovskite Ca_3WO_6. A detailed structural study of the phosphor under study was carried out in terms of XRD, SEM-EDAX, and FTIR characterization techniques. The PL study's findings suggesting an efficient green emitting perovskite phosphor with excellent CIE color coordinates. Moreover, in TL, the phosphor is explored for its wide investigation aspects, such as the effect of doping concentration, the effect of radiation dose, and most important fading effect.

Part-II

In this section, a detailed discussion of the Ho^{3+} single-doped Ca_3WO_6 double perovskites' luminescence investigation is discussed. The phosphors were extensively studied for their structural characterization, including XRD, SEM-EDAX, and FTIR, which are prepared using combustion synthesis. An interesting phenomenon of up-conversion luminescence was observed in addition to down-conversion luminescence from single Ho^{3+} doped Ca_3WO_6 phosphor. A high thermal stability of the phosphor was obtained from temperature-dependent PL. Moreover, the TL display is also found to be quite interesting between undoped and doped Ca_3WO_6. In TL, the effect of doping, the effect of ionizing dose, and the effect of different heating rates on TL intensity were discussed in detail.

Chapter 6. Conclusion and Future Studies

Chapter 6 contains the conclusions drawn from the phosphors under study (25 samples) from chapters 3, 4, and 5. It also contains suggestions for future studies.

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