Chapter - 1

Introduction

And

Literature Review

1.1 Introduction

This chapter contains brief information of the luminescence phenomenon with its history and different type of luminescence. These chapter also contains the review of the history of pervoskite and different types of pervoskite. Detail information of the different type of pervoskites point out how these materials are useful for the luminescence application.

1.2 Introduction of Luminescence

Various kinds of luminescence emission are observed in nature such as lightening, aurora, fireflies, etc. The luminescence emission from the sea bacteria were observed by the ancient Chinese (1500-1000 B.C.). The information regarding to the knowledge of luminescence in India is found in holy writings of ancient India - the Vedas. Aristotle (384-382 B.C.) from Greece had observed light being emitted from decaying fish [1].

Perhaps the most important year in the history of luminescence is 1603, when the famous alchemist Bolognian Vincenzo Casearlolo, synthesized the first ever luminescent material by heating barium sulphate with coal. He found that during day time this new material apparently absorbed light from the Sun and then glowed for hours in the dark and for this reason, it was called lapis solaria meaning “Sun stone”. In the early 17th century the word *phosphor* was invented and its meaning remains unchanged [2]. Vincentinus Casciarolo from Bologna, Italy, discovered a massive crystalline rock with shine at the foundation of a volcano that lighted up it in a charcoal oven exacting to transform it to excellent metal. Casciarolo does not found any metal in place of that he revealed that the sintered rock shine red in the dark after exposure to sunlight. This rock is known as “Bolognian stone.” The rock unearthed resembles as barite ($BaSO_4$) after the fired product appears as Barium Sulphate (BaS), which is presently known to be a host for phosphor materials. *“Light-bearer” in Greek generally means as a phosphor that appears in Greek myths as the incarnation of the morning star Venus* [3]. Meanwhile, in 1740, using the Greek title Lltheosphorua, meaning stony phosphors, Fortunlo Licet wrote the first monograph on the Bolognian stone. Since then, there began a chain of experimental studies to confirm the luminescence phenomenon.

In 1888, the German physicist Eilhardt Wiedemann first introduced the word luminescence to include both phosphorescence and fluorescence [4-6]. In Latin, a word '*lumen*' means '*light*' from where the word luminescence originated. The definition of Luminescence is "an appearance in which the electronic state of a luminescent substance is excited by a different type of outer energy given to the material." [7]. The energy given to the luminescent substance to excite electrons from the ground state is emitted in the form of visible light, the near-UV or near-IR regions of the electromagnetic wave spectrum. The given definition of the luminescence phenomenon is mainly applicable to the inorganic materials, but for the organic materials the terminology used as fluorescence and phosphorescence [8].

A phosphor is a chemical material which emits light when exposed to electromagnetic radiation. Generally, a phosphor consists of a host lattice and a luminescent center which usually called an activator or a dopant. Activators are intentionally introduced impurities in a host lattice to serve as luminescent centers. In general, the host needs to be transparent to the radiation source through which it's excited. If more than one activator used additional activator are called co-activator or co-dopant or sensitizer [9, 10].

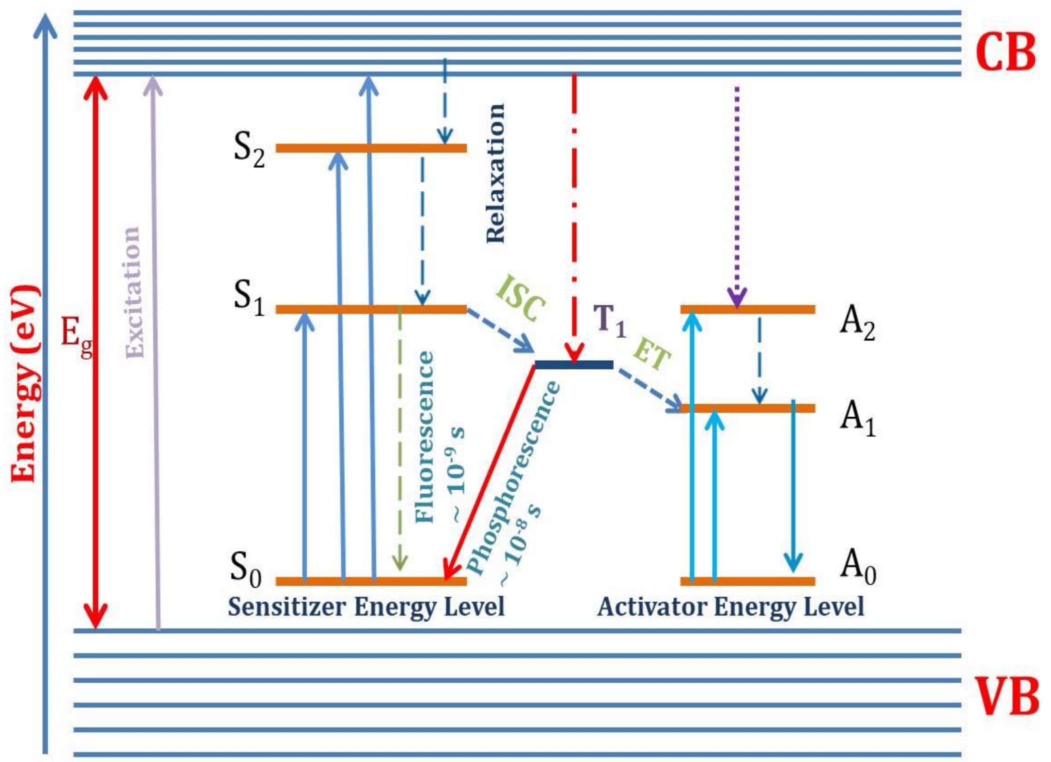
Phosphors can be classified according to the manner in which they emit light. Light emission can be a result of recombination in the bandgap or atomic transition where a dopant is responsible for the emission. Phosphors can be found in two forms, namely powders and thin films. In both powder and thin film forms, phosphors can be used in devices that emit light by the application of different excitation process [11-14].

The energy levels of the luminescent centers formed inside the phosphors were measures by luminescence. The energy level of a luminescence center is defined as its characteristic state, which is related to the physical nature of the center and to the energetic and dynamic processes that the center undergoes [9, 15]. The state with the lowest energy is defined as the ground state while the excited states have higher energy. A center possesses several distinct reservoirs of energy levels including electronic, vibrational, rotational, transitional and those associated with nuclear and electron spin [16]. In luminescent phosphors, the energy levels of interest are those that are associated with electronic and vibrational transitions [17].

1.2.1 Mechanism of Emission of Light in Phosphor

Phosphor materials are processed inorganic material having a host lattice and the rare-earth ions in the form of impurities. When the phosphors are excited by an external source of energy, an energy transfer process takes place in the material shown in Figure 1.1. The incident photon energy is absorbed either by the host or directly absorbed by the impurity ions; the absorbed energy by the host atom is transferred to the impurity atom (so-called activators). As a result of that, the activators emit energy in the form of visible light by relaxation of an excited electron to lower energy state. In most of the cases, the emissions of a photon from the phosphors are generated from impurities. The energy transfer mechanism in phosphor materials is described in Figure 1.1 [5]**.**

The luminescence process in phosphor materials explains in details [18], in Figure 1.1. When the excitation radiation incident on the phosphor material, it absorbed by the activator. The metastable state is a triplet state, while the ground state is a single state. The ground state of the activator energy level represents a singlet ground state (S_0). Against excitation by incident radiation, the activator energy level advanced to the singlet-excited state (higher than S_1) on absorbing energy from the host lattice. Following the energy absorption, the initial excited states of energy level relax to an energy level S_1 through the nonradiative (without emission of the photon) transition by emitting phonons or lattice vibrations [15, 19]. The intersystem crossing from a singlet state (S_1) to a triplet state (higher than T_1) takes place by spin-orbit coupling. In a triplet state, it decays downward comparatively quickly to the lowest energy level and once gets to the lowest triplet state it stuck there at least for a while. The excited triplet state (T_1) of the lowest energy level returns back to its ground state (S_0) by the photonic (radiative) emission, which emitted luminescent radiation. In the light emission (phosphorescence) process of the rare-earth doped phosphor materials, the color of the emitting light from phosphor material depends on the type of doping impurities in the host matrix [20]. For example, red phosphor could be produced by adding europium to Y_2O_3 cubic structure when UV or VUV used as the excitation source. The process of luminescence can be illustrated in Figure-1.2.



VB = Valence Band
CB = Conduction Band
S_0, S_1, S_2 = Energy Levels of Sensitizers
A_0, A_1, A_2 = Energy Levels of Activators
T_1 = Metastable Triplet State
ISC = Inter System Crossing
ET = Energy Transfer

CHARACTERISTIC TIMES
Absorption 10^{-16} s
Vibrational relaxation $10^{-12} – 10^{-10}$ s
Lifetime of the excited state S_1 $10^{-10} – 10^{-7}$ s → fluorescence
Intersystem crossing $10^{-10} – 10^{-8}$ s
Lifetime of the excited state T_1 10^{-8} – 1 s → phosphorescence

Figure 1.1 Light emission mechanism in phosphor and characteristic times for each transition [5].

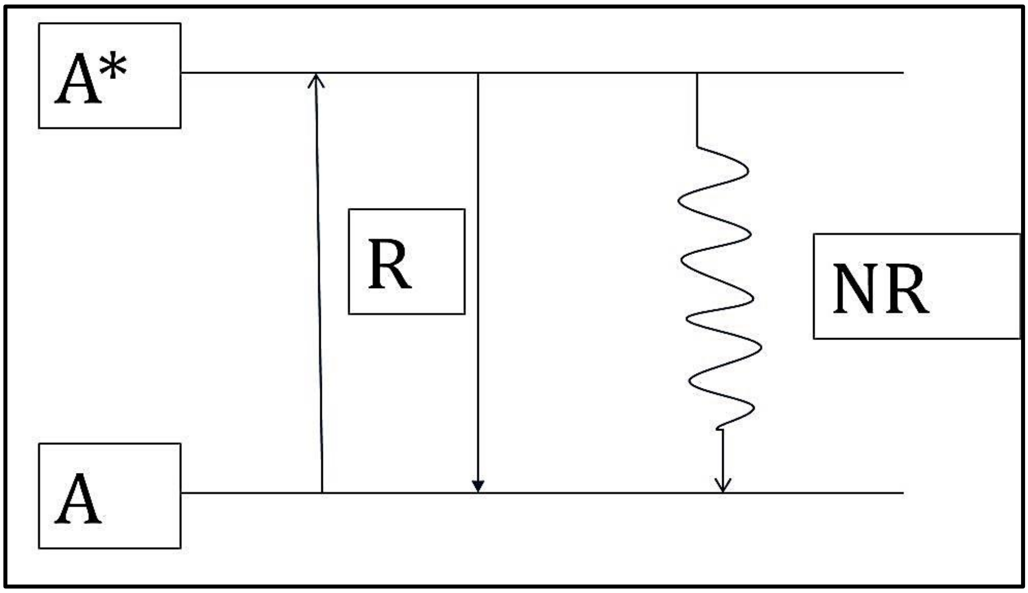


Figure 1.2 Energy level scheme of the luminescent ion A. The excited state of ion A is indicated by *, the radiative return by R, and the nonradiative return to the ground state indicated by NR [8].

Figure 1.2 illustrates that there are two types of transition process involved where an atom or molecule return to the ground state, one through radiative and another is non-radiative. The occurrence of the luminescence process is due to the radiative return. In non-radiative transition, the absorbed energy of incident photon is been emitted in the form of heat which could be quench the luminescence radiation of the phosphor. A proficient luminescent substantial is one in which non-radiative transitions following over the radiative ones [21]. Although realistically in the luminescent materials, the situation is highly complex than depicted in the above Figure 1.2.

The significant physical processes which play a vital role in a luminescent material are detailed as follows:

(a) Excitation

It is the method to change of state of an electron from the ground state to a higher energy state of luminescent material after getting energy from the energy source. After excitation by the ultraviolet or visible radiation, X-ray, γ-rays, etc., a luminescent material will release radiation. The host lattice is excited by the high-energy fast electrons/ X-rays/ gamma-rays, whereas activator can be directly excited by ultraviolet/ visible radiation [20–22]. The metal-ligand distance is the structural parameter, which varies during the vibration. The configurational coordinate diagram shown in Figure 1.3, where energy (E) plotted versus metal-ligand distance (R), with a minimum at R_0

the ground state is of parabolic shape, a vibrational mode is supposed to be harmonic. The restoring force F is proportional to the displacement:

$$F = -k(R - R_0) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.1)$$

$$F = \frac{1}{2}k(R - R_0)^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.2)$$

The force analogous to a potential energy and depends on R, which is parabolic and the minimum at R_0 of the parabola is equal to the equilibrium distance in the ground state [20].

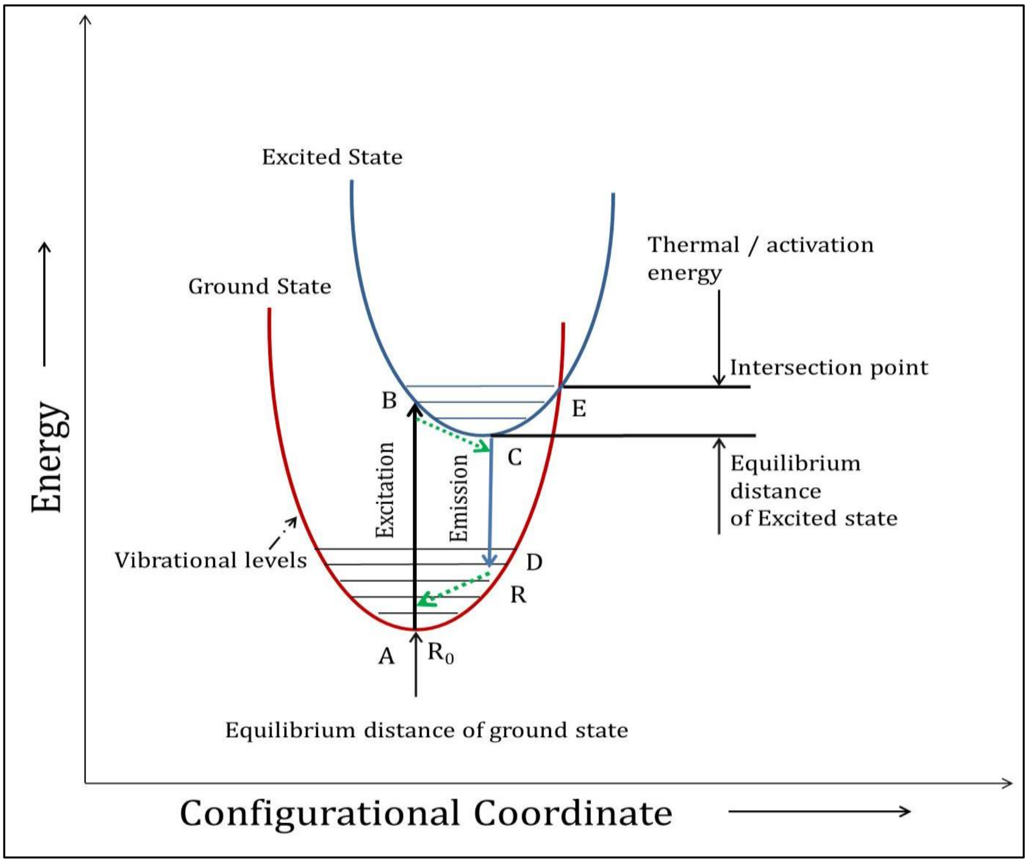


Figure 1.3 Configuration coordinate graph showing the excited state and vibrational states. The ground state (g) has the equilibrium distance [19].

The center is promoted from its ground state to an excited state in optical absorption. In the configurational coordinate diagram, the electronic transition shown as a vertical transition [14]. The horizontal lines in this diagram (Figure 1.3) are representing nuclear and the internuclear distance. Due to the lighter weight of the electrons compared to nuclei, the electrons move much faster than the nuclei. The electronic transition has seen highly appropriate and in the good estimation, place in static surroundings [5]. The nuclei reach their appropriate locations only later. The optical excitation of absorption initiates from lower vibrational level. Consequently, the vibrational wave function has its highest value while the most probable transition occurs at R_0 which represents in Figure 1.3 [24, 25].

(b) Emission

The radiative return to the ground state from an excited state is known as photon emission. By the conversion process, the dopant center attains a high vibrational level of the excited state. After reaching a higher energy level, the excited electron reverts to the weaker vibrational level of the excited state by emitting excess energy to the enclosing environment in the form of a photon. Alternately, the nuclei adjust their positions according to the excited state so that the interatomic distances equal the equilibrium distances relating to the excited state. This process is called the relaxation process [3]. During the relaxation process emission of high intensity will be not there. A very fast emission has a rate of 10^8 s^{-1} while the vibrational rate is about 10^{-13} s^{-1}. The excited electron can return to the ground state by naturally emitting radiation from the lowest vibrational level of the excited state. Rules for the emission and absorption are the same with a difference that emission occurs spontaneously while the absorption occurs non-spontaneously. Absorption occurs only in the presence of the radiation field and the reverse process of absorption called stimulated emission [26].

(c) Nonradiative Transitions

The manner of returning of an electron to the ground state after excitation without radiative emission is known as nonradiative transition. This radiationless process always competes with the emission process; hence such processes must be suppressed to achieve a high quantum yield of luminescent materials. For technological interest, a luminescent material should have a high quantum yield. Phosphors used in fluorescent lamps usually have a quantum efficiency of at least 0.75. All the quanta absorbed would be remitted if there are no nonradiative losses [4, 19, 20].

(d) Energy Transfer

Energy transfer between two ions with the assistance of a multi-phonon process also can be considered as a radiationless process relating to the sensitizer. Many examples of luminescent materials are available in which an excited defect center possibly transfer its energy to another center either emitting a photon or decaying nonradiatively to its ground state. This ion is called a sensitizer which takes in the exciting radiation and consequently transfers it to the dopant ions. This method explained by an example of $Ca_{10}K(PO_4)_7$: Eu^{2+}, Mn^{2+} where Eu^{2+} ion act as a sensitizer and Mn^{2+} as a dopant for CKP phosphor [27].

1.2.2 Classification of various types of Luminescence

Figure 1.4 shows various type of luminescence like photoluminescence, chemiluminescence, electroluminescence, radioluminescenc, mechnoluminescence, thermoluminescence, etc. Some of them are explained below like photoluminescence, chemiluminescence, bioluminescence, and thermoluminescence.

(a) Photoluminescence

When an insulator or semiconductor occupies electromagnetic radiation (photon), an electron may stimulate a higher energy quantum state. As the excited electron reverts to a lower energy state by transmitting energy in the form of a photon, the process is called photoluminescence (PL). Photoluminescence is a contactless non-destructive technique for investigating the electronic arrangement of material. PL is used extensively for the material state, level of contamination, detections of a defect, mechanism of recombination as well as it uses for resolution of the band gap [8].

PL may classify into two classes depend on their emission.

(i) Fluorescence and (ii) Phosphorescence

(i) Fluorescence: On releasing of excitation, an exponential afterglow is examined self-governing of the excitation intensity and temperature, with the existence of fewer than 10^{-8} seconds.

(ii) Phosphorescence: On removal of excitation, their lives another phenomenon of afterglow where decay is slower with multiple kinetics, usually dependent on the intensity of excitation and strongly dependent on temperature, with a life time of more than 10^{-8} seconds.

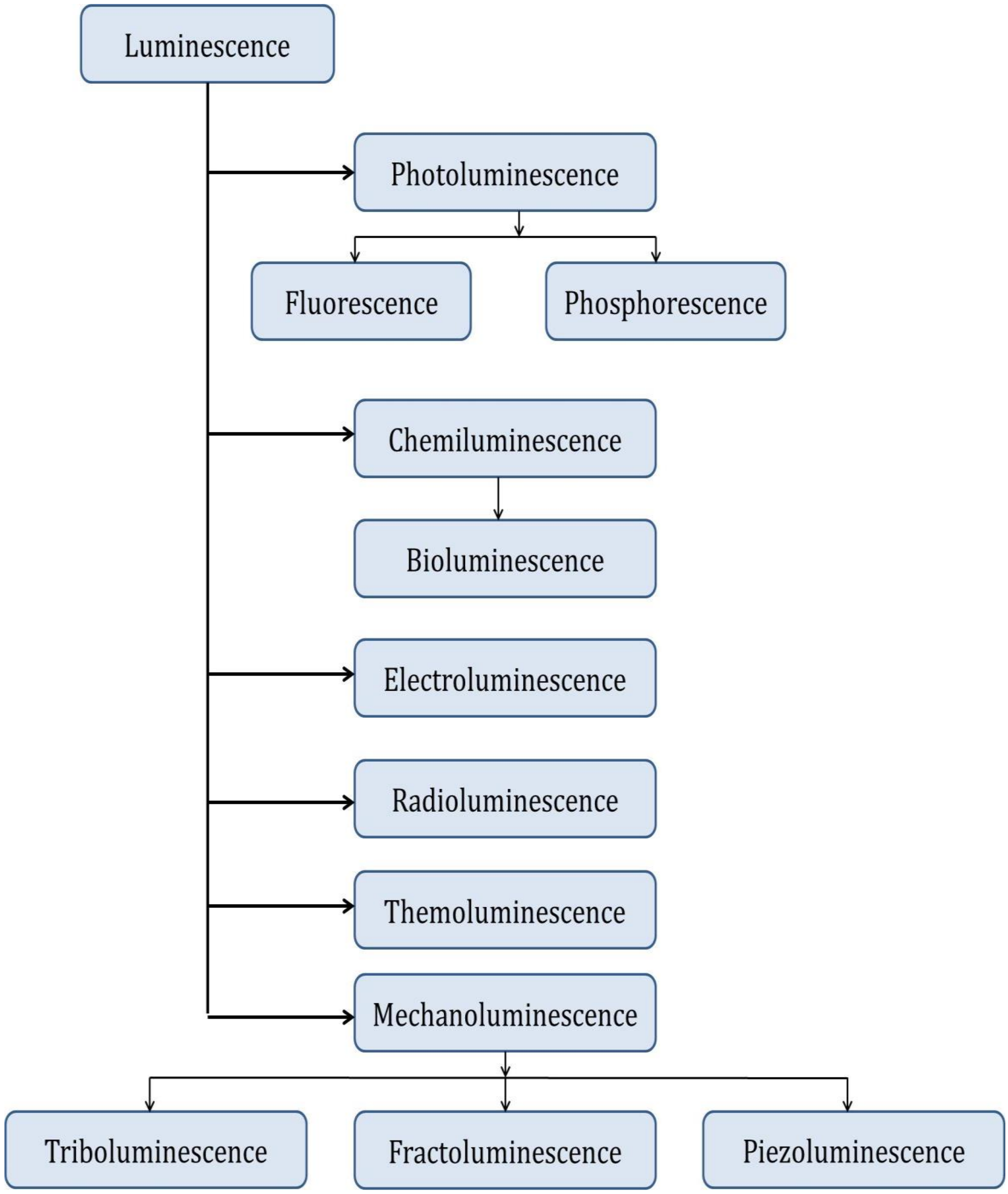


Figure 1.4 Classification of types of luminescence.

(b) Chemiluminescence

The emission of light resulted either by some chemical reaction or electrochemically redox reaction is known as Chemiluminescence. The chemical reaction creates few innovative molecules that can occupy its electrons in an excited state just after creation, and after that decay to the ground state offering visible light or liberate the energy in some other mode.

(c) Bioluminescence

The luminescence produced by living organisms is called bioluminescence. The bioluminescence is associated with chemiluminescence because the light-producing molecules are excited through a chemical reaction. Some living organisms like fireflies generate luciferin and luciferase chemicals. The light produced in fireflies through the catalytic oxidative reaction of luciferin pigment in the appearance of air and luciferase acts as a catalyst to increase the rate of reaction [28].

(d) Thermoluminescence

Thermally Stimulated Luminescence (TSL) or Thermoluminescence (TL) is stimulated thermally after primary irradiation given to a phosphor by some other means like α-rays, β-rays, γ- rays, UV rays or X-rays. [29]. Thermally stimulated luminescence (TSL) is the appearance of emission of light from a material that has earlier uncovered to ionizing emission under surroundings of raising the temperature. For thermally stimulated luminescence (TSL) heat act as a stimulator and for some other luminescence processes such as Electroluminescence, Chemiluminescence it acts as an exciting agent. Hence it's better known as thermally stimulated luminescence (TSL) [30–32].

Rare earth doped inorganic luminescent materials are well known for emission in distinct wavelengths in the electromagnetic spectrum [33], [34]. The phosphors used in the lighting things such as cathode ray tubes (CRT), tri-phosphor fluorescent lamps, intensifying screens of X-ray, and recently emerged vacuum mercury-free lamps [35]. It has other applications in a display such as plasma display panels and field emission displays. The momentous application of phosphors for light emitting diodes (LEDs) technology changes the history of the solid state lighting and has completely changed the “world of luminance” LEDs are significantly energy-efficient lighting device with a long lifetime [36].

1.3 Literature Review

1.3.1 Basic of Pervoskite

The pervoskite mineral was discovered in the Ural Mountains of Russia by Gustav Rose in 1839 and is named after Russian mineralogist Lev Perovski (1792–1856). In pervoskite, a divalent cation is consolidated with a quadrivalent cation. Within certain limits of cation size, different combinations of a divalent and a quadrivalent cation have the pervoskite structure with differing degrees of distortion from the ideal cubic form

[36–39]. Moreover, within certain cation-size limitations, other cation combinations with a total charge of six can proxy for the A^{2+}: B^{4+} combination. For example, lanthanum aluminate oxide ($LaAlO_3$) both are trivalent while in $KNbO_3$ (potassium niobate) have a monovalent and a pentavalent cation has the pervoskite structure [40], [41].

The initial work is performed by V. M. Goldschmidt and his scholars who developed a large number of ABO_3 compounds and determined their usual structure type. Goldschmidt (1927-36) also studied the factors determining structure type and clearly showed the influence of ionic radius and ionic polarizability as the predominant variables. A considerable number of researchers since have prepared a few more compounds to clarify or more closely define the relationship between the ionic radius and the structure type [41].

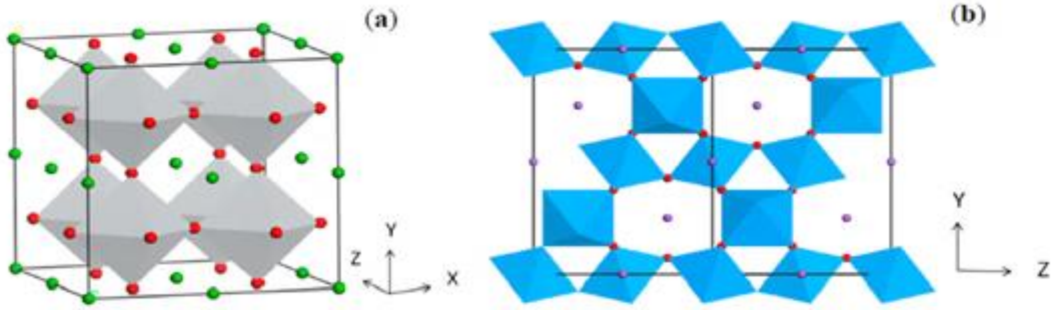


Figure 1.5 (a) Crystal structure of simple Pervoskite and (b) double pervoskite (red: oxygen, green and purple: A site cation, grey and blue: BO_6 octahedra).

Among the photo-functional materials, more consideration has been given to metal oxides with the band gap energy corresponding to near UV or visible light. For example, pervoskite type compounds because of a broad spectrum of potential applications [42–44]. The interest and the richness of this field occupy in its interdisciplinary nature and in the diversity of questions it raises on both fundamental and applied levels. As was quoted by Stolen et al. [45] these structures has been termed an inorganic chameleon due to their enormous flexibility. Various compounds take this or a related structure since the mother structure easily distorts or accommodates to the relative sizes of the ions producing the compound. The source of enchantment is the diversity of the characteristics and their high sensitivity to chemical tuning. In other words, a tiny change in chemical composition or/and crystal structure may effect huge changes in chemical and physical properties [46, 47].

Usually, in the pervoskite crystal structure, the A site is filled by the higher cation while the B site is occupied by the smaller cation. Pervoskites are one of the most valuable families of materials displaying characteristics suitable for various technological purposes [48]. Pervoskite compounds such as $PbZrO_3$, $BaTiO_3$, and $PbTiO_3$ are generally used as piezoelectric compounds [49]. $BiFeO_3$ thin films show multiferroic response [50] while compound such as $SrTiO_3$ has displayed excellent photocatalytic properties [51, 52]. The origin of such characteristics occupies in the crystal structure of pervoskites. The crystal structure of pervoskite has corner connected BO_6 octahedra and 12 oxygen coordinated A cations which placed in between the eight BO_6 octahedra. The complete structure of the octahedral connection results in a cubic lattice [53, 54]. However, depending on the ionic radii and electronegativity of the A and B site cations, tilting of the octahedra takes place, which gives rise to lower symmetry structures. As seen from Figure 1.5 the crystal structure B site cations are strongly bonded with the oxygen (or any other anion) while A site cations have comparatively limited interactions with oxygen. Depending on the type of cations occupying the lattice sites, these interactions could be modified to yield the different pervoskite crystal geometries [55–58].

For example, various degrees of tilting of the octahedra give rise to different crystal fields, which appear in different electronic and optical properties. The degrees of tilting may influence the band structure, electron-hole transport properties, photoluminescence, and dielectric behaviour [59, 60]. In the case of optical properties, pervoskite structures may offer significant advantages over the corresponding binary oxides for several reasons. Firstly, pervoskites could offer promising band edge potentials which allow several photoinduced reactions. For example, as compared to the binary oxides, several pervoskites have adequately cathodic conduction band (CB) energies for hydrogen evolution [60, 61]. Secondly, A and B site cations in the lattice give a broader reach to design and reconstruct the band structure as well as other photophysical properties.

Double Pervoskite

In the case of double pervoskites such as $A_2B_2O_6$, stoichiometric control of two cations at the B site is known to be advantageous for visible light photocatalysis.

Compounds with general formula $A_2B_2O_6$ belong to the double pervoskites and they have similar crystal structures as simple pervoskites. Double pervoskites have the basic structure of corner connected BO_6 octahedra and A cations enclosed inside. However, the connectivity of the octahedra may alter from structure to structure. Double pervoskites could contain different cations at the A or/and B sites, using a general form AA'BB'O_6 [62, 63]. Adaptation of distinct cations at the A and B sites modify the optical properties of the compound significantly. Complex compounds propose feasibility of combining the elements from a narrow gap and wide gap binary compounds to exploit the properties of both types of oxides and thus are potentially useful as a visible light phosphor [64].

Tolerance Factor

Goldschmidt had evolved the concept of a "tolerance factor" to reveal the limits in terms of ionic radii within which a specific structure may require from combinations of various elements. Formula for tolerance factor given by Goldschmidt [65] is as follow:

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1.3)}$$

Where, t = tolerance factor for the pervoskite structure.

R_A = ionic radius of the larger cation in double oxides.

R_B = ionic radius of the smaller cation in double oxides.

R_O = ionic radius of oxygen.

He concluded that the tolerance factor for pervoskite structures may be in the limit of t = 0. 99 to t = 0.77. The compounds with the formula of $A^{2+}B^{4+}O_3$, both A & B are small show the corundum - ilmenite structure [66]. In the way towards higher tolerance factor, the structures are progressively more distorted. In the opposite route, towards less tolerance factor, the structures are distorted apart from the simple cubic form, but in a different mode [67].

Another significant innovative research line is represented by several organic-inorganic materials that crystallize in the pervoskite structure, ABX_3. To create materials with the remarkable characteristics of these systems, researchers must rely on the construction of the three-dimensional structure. The common organic-inorganic pervoskites are based around B = Ge^{2+}, Sn^{2+}, Pb^{2+}, and X is usually a halide. These hybrid systems have a much wider range of applications in areas such as magnetism, photoluminescence, and nonlinear optics [68].

1.3.2 Luminescence of Pervoskite

Photoluminescence depends on electronic excitations. These are a significant addition to spectroscopies concerning lattice excitations. The composition of initial and photoexcited states is essential to understand. Due to their broad utilization and for importance in getting into the nature of luminescence processes. [69]. It permits one to improve theoretical principles for predicting the nature of the tools for photoinduced methods. Therefore, PL operation controlled by controlled filling the progression of the electronic arrangements is one of the fascinating issues of condensed matter physics. The analysis of problems opens a probability to explain the importance of the PL response and the optical properties of the materials. By the joint analysis of the results obtained by band structure calculations and UV-visible diffuse reflectance and PL spectroscopies Ye et al. [67] have been characterized the photoluminescence and photocatalytic properties of $SrSnO_3$ pervoskite.

A renewed study has been latterly paid to the luminescence properties of pervoskite materials containing titanium such $SrTiO_3$, $BaTiO_3$, (Ba, Sr)TiO_3, both in the form of crystalline and disorder microstructures, due to their exceptional potential in electro-optical applications [70–72]. Such a property is integral to the ABO_3 pervoskite crystal family, which reveals a broad band emission in the visible spectral region (so-called ‘green’ luminescence) peaking at around 2.4eV for $SrTiO_3$ [73] and 2.5eV in $BaTiO_3$ [74].

The synthesis, characterization, and investigation of luminescence characteristics of pervoskite phosphors have been the case of numerous modern types of research, and the similar electronic structures have been analyzed very broadly by experimental or/and theoretical practices. [67, 70, 75–77]. These attributes are open to various fields of research for such material applications inciting additional efforts in the study of their behavior under different circumstances. Among this class of materials, lead titanate ($PbTiO_3$) and strontium titanate ($SrTiO_3$) in their crystalline form are typical wide band gap semiconductors with about 3.0 eV for $PbTiO_3$ and 3.4 eV for $SrTiO_3$[78, 79]. The photoluminescence property of the titanate type compounds has been detected in crystalline samples by Grabner in 1969 [80]. Inappropriate, when a pure single crystal of $SrTiO_3$ is excited by UV radiation, a broad greenish luminescent band emerges whose intensity decreases quickly when the temperature is above 50 K [73, 81].

From the literature, different approaches to describe the radiative oxidation taking place in pervoskite type structures. But it is well confirmed that contaminations, surface states, and defects play a significant role in the PL properties of pervoskite-type oxides [71, 82–84]. PL analysed in undoped or doped nano-crystalline powders and amorphous thin films of pervoskite oxides [82, 85, 86]. Recently, pervoskite type red and green phosphors were found and optimized [87, 88] and blue light emission was also reported [89, 90].

1.4 Objectives of the Thesis

The objectives of the research presented for the thesis are as follows:

- Rare earth doped and co-doped pervoskite phosphors for the different concentration of doping was synthesized by the solid state reaction method and combustion method at heating temperature of 1200°C and $900^{O}C$ for 3 hours, respectively. Undoped pervoskite also synthesis by hydrothermal method.
- For this research, Sr_2CeNbO_6; Sr_2GdTaO_6: Eu^{3+}, Er^{3+}; Sr_2GdNbO_6: Eu^{3+} and Ba_2CeNbO_6: Eu^{3+} phosphors with different concentration of Eu^{3+} and/ or Er^{3+} were synthesized.
- To fulfill the objective of the study, synthesized phosphors were characterized for structural and morphological analysis by powder X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), and Scanning Electron Microscopy (SEM).
- Photoluminescence properties were examined by recording the excitation, and by recording PL emission spectra for the particular excitation wavelengths obtained from excitation spectra of rare earth doped and co-doped pervoskite phosphors. The PL properties of the phosphor were investigated for its applications in solid-state lighting.

1.5 Thesis Layout

Chapter 2: Experimental Methods and Characterization Techniques

In this chapter, the basic information of hydrothermal and combustion synthesis method is explained with its principle, useful parameters, theoretical background and recent scope of the synthesis method in material science and technology. The detailed procedure to prepare phosphors required materials, sample preparation has been explained in this chapter. In this chapter, different characterization techniques like X-ray diffraction, Fourier Transformation Infrared Spectroscopy (FTIR), Photoluminescence and Scanning Electron Microscopy (SEM) are explained in detail.

Chapter 3: Synthesis and Photoluminescence studies of Strontium Cerium Niobate Nanophosphor

In this chapter, synthesis method and characterization of Strontium Cerium Niobate oxide was explained in detail. The result of characterization was also discuss in detail with require graphs and images.

Chapter 4: Photoluminescence studies of Europium doped Strontium Gadolinium Niobate Oxide

In this chapter, synthesis method and characterization of undoped and doped Strontium Gadolinium Tantalum oxide was explained in detail. The result of characterization was also discuss in detail with require graphs and images.

Chapter 5: Synthesis and Photoluminescence studies of undoped and Europium doped Barium Cerium Niobate Oxide

In this chapter, synthesis method and characterization of Barium Cerium Niobate oxide was explained in detail. The result of characterization was also discuss in detail with require graphs and images.

Chapter 6: Synthesis and Photoluminescence studies of undoped, single doped and double doped Strontium Gadolinium Tantalum Oxide

In this chapter, synthesis method and characterization of undoped and doped Strontium Gadolinium Tantalum oxide was explained in detail. The result of characterization was also discuss in detail with require graphs and images.

Chapter 7: Conclusion

In this chapter, the brief summary of the information on the outcome of the results are explained on the basis of the application of the prepared pervoskite phosphor.

References

[1] E. N. Harvey, “A History of Luminescence From the Earliest Times Until 1900,” *Am. Hist. Rev.*, vol. 44, p. 692, Jul. 1958.

[2] P. N. Yocom, “Future requirements of display phosphors from an historical perspective,” *J. Soc. Inf. Disp.*, vol. 4, no. 3, p. 149, 1996.

[3] E. M. J. Weber, A. A. Kaminskii, M. J. Weber, M. J. Weber, and M. J. Weber, *PHOSPHOR HANDBOOK*, 2nd ed. FL: CRC Press Taylor & Francis Group 6000 Broken Sound Parkway NW, Suite 300 Boca Raton, FL 33487-2742.

[4] K. V. R. Murthy and H. S. Virk, “Luminescence Phenomena: An Introduction,” *Defect Diffus. Forum*, vol. 347, pp. 1–34, Dec. 2013.

[5] B. Valeur and M. N. Berberan-Santos, *Molecular Fluorescence: Principles and Applications*, 2nd ed., vol. 8. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA, 2012.

[6] B. Valeur and M. N. Berberan-Santos, “A brief history of fluorescence and phosphorescence before the emergence of quantum theory,” *Journal of Chemical Education*, vol. 88, no. 6. pp. 731–738, 2011.

[7] A. Chmyrov, “Photo-induced dark states in fluorescence spectroscopy – investigations & applications,” KTH, Stockhom, 2010.

[8] D. L. Dexter, “A theory of sensitized luminescence in solids,” *J. Chem. Phys.*, vol. 21, no. 5, pp. 836–850, 1953.

[9] M. Gaft, R. Reisfeld, and G. Panczer, *Modern Luminescence Spectroscopy of Minerals and Materials*, vol. 1. Cham: Springer International Publishing, 2015.

[10] I. P. Sahu, D. P. Bisen, N. Brahme, and R. K. Tamrakar, “Enhanced luminescence performance of Sr2MgSi2O7:Eu2+ blue long persistence phosphor by co-doping with Ce3+ ions,” *J. Mater. Sci. Mater. Electron.*, vol. 27, no. 1, pp. 554–569, Jan. 2016.

[11] L. Tu, X. Liu, F. Wu, and H. Zhang, “Excitation energy migration dynamics in upconversion nanomaterials,” *Chem. Soc. Rev.*, vol. 44, no. 6, pp. 1331–1345, 2015.

[12] G. Blasse, “New compounds with pervoskite-like structures,” *J. Inorg. Nucl. Chem.*, vol. 27, no. 5, pp. 993–1003, May 1965.

[13] G. Blasse and A. F. Corsmit, “Electronic and vibrational spectra of ordered pervoskites,” *J. Solid State Chem.*, vol. 6, no. 4, pp. 513–518, Apr. 1973.

[14] G. Blasse and B. C. Grabmaier, *Luminescent Materials*. Berlin, Heidelberg: Springer Berlin Heidelberg, 1994.

[15] R. Boyn, “4f–4f Luminescence of Rare-Earth Centers in II–VI Compounds,” *Phys. Status Solidi*, vol. 148, no. 1, pp. 11–47, 1988.

[16] G. Blasse, “Chemistry and Physics of R-activated Phosphors,” in *Handbook on the Phystcs and Chemlstry of Rare Earths*, J. K.A. Gschneidner and E. L., Eds. North-Holland Publishing Company, 1979, pp. 237–274.

[17] S. S. Harilal, B. E. Brumfield, N. L. Lahaye, K. C. Hartig, and M. C. Phillips, “Optical spectroscopy of laser-produced plasmas for standoff isotopic analysis,” *Appl. Phys. Rev.*, vol. 5, no. 2, 2018.

[18] R. C. Ropp, *Luminescence and the Solid State*, 2nd ed., vol. 21. Elsevier B.V., 2004.

[19] D. Singh, V. Tanwar, S. Bhagwan, and I. Singh, “Recent Advancements in Luminescent Materials and Their Potential Applications,” in *Advanced Magnetic and Optical Materials*, Hoboken, NJ, USA: John Wiley & Sons, Inc., 2016, pp. 317–352.

[20] C. . Ronda, T. Jüstel, and H. Nikol, “Rare earth phosphors: fundamentals and applications,” *J. Alloys Compd.*, vol. 275–277, pp. 669–676, Jul. 1998.

[21] Ravina *et al.*, “Judd-Ofelt Itemization and Influence of Energy Transfer on Sm3+ ions Activated B2O3-ZnF2-SrO-SiO2 Glasses for Orange-Red Emitting Devices,” *J. Lumin.*, p. 117651, Sep. 2020.

[22] A. Zych, A. Leferink op Reinink, K. van der Eerden, C. de Mello Donegá, and A. Meijerink, “Luminescence properties of lanthanide doped alkaline earth chlorides under (V)UV and X-ray excitation,” *J. Alloys Compd.*, vol. 509, no. 13, pp. 4445–4451, Mar. 2011.

[23] L. Sudheendra *et al.*, “NaGdF 4 :Eu 3+ Nanoparticles for Enhanced X-ray Excited Optical Imaging,” *Chem. Mater.*, vol. 26, no. 5, pp. 1881–1888, Mar. 2014.

[24] T. YANAGIDA, “Inorganic scintillating materials and scintillation detectors,” *Proc. Japan Acad. Ser. B*, vol. 94, no. 2, pp. 75–97, 2018.

[25] C. Görller-Walrand and K. Binnemans, “Spectral intensities of f-f transitions,” in *Handbook on the Physics and Chemistry of Rare Earths*, Elsevier, 1998, pp. 101–264.

[26] M. Pollnau, “Are absorption and spontaneous or stimulated emission inverse

processes? The answer is subtle!," *Appl. Phys. B*, vol. 125, no. 2, p. 25, Feb. 2019.

[27] S. Ye, F. Xiao, Y. X. Pan, Y. Y. Ma, and Q. Y. Zhang, "Phosphors in phosphor-converted white light-emitting diodes: Recent advances in materials, techniques and properties," *Mater. Sci. Eng. R Reports*, vol. 71, no. 1, pp. 1–34, 2010.

[28] E. H. White, E. Rapaport, H. H. Seliger, and T. A. Hopkins, "The chemi- and bioluminescence of firefly luciferin: An efficient chemical production of electronically excited states," *Bioorg. Chem.*, vol. 1, no. 1–2, pp. 92–122, Sep. 1971.

[29] I. P. Sahu, D. P. Bisen, N. Brahme, R. K. Tamrakar, and R. Shrivastava, "Luminescence studies of dysprosium doped strontium aluminate white light emitting phosphor by combustion route," *J. Mater. Sci. Mater. Electron.*, vol. 26, no. 11, pp. 8824–8839, Nov. 2015.

[30] N. Kunkel, A. D. Sontakke, S. Kohaut, B. Viana, and P. Dorenbos, "Thermally Stimulated Luminescence and First-Principle Study of Defect Configurations in the Pervoskite-Type Hydrides LiMH 3 :Eu 2+ (M = Sr, Ba) and the Corresponding Deuterides," *J. Phys. Chem. C*, vol. 120, no. 51, pp. 29414–29422, Dec. 2016.

[31] M. Martini and F. Meinardi, "Thermally stimulated luminescence: New perspectives in the study of defects in solids," *La Riv. del Nuovo Cim.*, vol. 20, no. 8, pp. 1–71, Aug. 1997.

[32] D. R. Rao, M. S. Ramachandra Rao, and S. A. K. Reddy, "Thermally stimulated luminescence of alkaline earth sulphide phosphors doped with cerium and samarium impurities," *Mater. Sci. Technol.*, vol. 3, no. 8, pp. 616–620, Aug. 1987.

[33] J. Andrés, V. Longo, L. Cavalcante, M. L. Moreira, J. Varela, and E. Longo, "A fresh look at the structural, ferroelectric and photoluminescent properties in pervoskites," *Photoluminescence Appl. Types Effic.*, no. JANUARY, pp. 119–161, 2012.

[34] K. V. Dabre, K. Park, and S. J. Dhoble, "Synthesis and photoluminescence properties of microcrystalline Sr 2 ZnWO 6 :RE 3+ (RE = Eu, Dy, Sm and Pr) phosphors," *J. Alloys Compd.*, vol. 617, pp. 129–134, Dec. 2014.

[35] T. H. Gfroerer, "Photoluminescence in Analysis of Surfaces and Interfaces," in *Encyclopedia of Analytical Chemistry*, Chichester, UK: John Wiley & Sons, Ltd,

2006.

[36] N. P. Patel, M. Srinivas, D. Modi, V. Vishwnath, and K. V. R. Murthy, “Luminescence study and dosimetry approach of Ce on an α-Sr2 P2 O7 phosphor synthesized by a high-temperature combustion method.,” *Luminescence*, no. August, Sep. 2014.

[37] A. T. Kozakov *et al.*, “Valence state of cations in manganites Pr1-Ca MnO3 (0.3 ≤ x ≤ 0.5) from X-ray diffraction and X-ray photoelectron spectroscopy,” *J. Alloys Compd.*, vol. 740, pp. 132–142, Apr. 2018.

[38] J. Mizusaki, “Oxygen nonstoichiometry and defect equilibrium in the pervoskite-type oxides La1−xSrxMnO3+d,” *Solid State Ionics*, vol. 129, no. 1–4, pp. 163–177, Apr. 2000.

[39] S. Hull, “Superionics: crystal structures and conduction processes,” *Reports Prog. Phys.*, vol. 67, no. 7, pp. 1233–1314, Jul. 2004.

[40] H. LIPSON, “Crystal Structures,” *Nature*, vol. 163, no. 4147, pp. 622–622, Apr. 1949.

[41] M. L. Keith and R. Roy, “Structural relations among double oxides of trivalent elements,” *Am. Miner.*, vol. 39, no. 1/2, pp. 1–23, 1954.

[42] S. Murugesan, M. N. Huda, Y. Yan, M. M. Al-Jassim, and V. (Ravi) Subramanian, “Band-Engineered Bismuth Titanate Pyrochlores for Visible Light Photocatalysis,” *J. Phys. Chem. C*, vol. 114, no. 23, pp. 10598–10605, Jun. 2010.

[43] D. S. Vavilapalli *et al.*, “Photoactive Brownmillerite Multiferroic KBiFe 2 O 5 and Its Potential Application in Sunlight-Driven Photocatalysis,” *ACS Omega*, vol. 3, no. 12, pp. 16643–16650, Dec. 2018.

[44] J. He, P. Zhang, X. Liu, S. Wu, L. Hu, and L. Xu, “Structural characteristics and spectral response of composite transition metal oxide photocatalytic materials,” *J. Mater. Sci.*, vol. 51, no. 15, pp. 7049–7072, Aug. 2016.

[45] S. Stølen, E. Bakken, and C. E. Mohn, “Oxygen-deficient pervoskites: Linking structure, energetics and ion transport,” *Phys. Chem. Chem. Phys.*, vol. 8, no. 4, pp. 429–447, 2006.

[46] S. K. Gupta, P. S. Ghosh, N. Pathak, A. Arya, and V. Natarajan, “Understanding the local environment of Sm 3+ in doped SrZrO 3 and energy transfer mechanism using time-resolved luminescence: a combined theoretical and experimental approach,” *RSC Adv.*, vol. 4, no. 55, pp. 29202–29215, 2014.

[47] C. Liu, Z. G. Neale, and G. Cao, “Understanding electrochemical potentials of

cathode materials in rechargeable batteries," *Mater. Today*, vol. 19, no. 2, pp. 109–123, Mar. 2016.

[48] A. S. Bhalla, R. Guo, and R. Roy, "The pervoskite structure—a review of its role in ceramic science and technology," *Mater. Res. Innov.*, vol. 4, no. 1, pp. 3–26, Nov. 2000.

[49] D. Damjanovic, "Piezoelectric properties of pervoskite ferroelectrics: unsolved problems and future research," *Ann. Chim. Sci. des MatÃ©riaux*, vol. 26, no. 1, pp. 99–106, Feb. 2001.

[50] N. Nuraje and K. Su, "Pervoskite ferroelectric nanomaterials," *Nanoscale*, vol. 5, no. 19, pp. 8752–8780, 2013.

[51] Q. Jia, A. Iwase, and A. Kudo, "BiVO4-Ru/SrTiO3:Rh composite Z-scheme photocatalyst for solar water splitting," *Chem. Sci.*, vol. 5, no. 4, pp. 1513–1519, 2014.

[52] Kazuhiro Sayama, Kazuaki Mukasa, Ryu Abe, Yoshimoto Abe, and Hironori Arakawa, "Stoichiometric water splitting into H2 and O2 using a mixture of two different photocatalysts and an IO3−/I− shuttle redox mediator under visible light irradiation," *Chem. Commun.*, no. 23, pp. 2416–2417, 2001.

[53] P. V. Balachandran and J. M. Rondinelli, "Interplay of octahedral rotations and breathing distortions in charge ordering pervoskite oxides," Mar. 2013.

[54] H.-C. zur Loye, Q. Zhao, D. E. Bugaris, and W. M. Chance, "2H-pervoskite related oxides: Synthesis, structures, and predictions," *CrystEngComm*, vol. 14, no. 1, pp. 23–39, 2012.

[55] N. Wagner, R. Seshadri, and J. M. Rondinelli, "Property control from polyhedral connectivity in ABO3 oxides," *Phys. Rev. B*, vol. 100, no. 6, p. 064101, Aug. 2019.

[56] X. Liu and K. Sohlberg, "Theoretical calculations on layered pervoskites: implications for photocatalysis," *Complex Met.*, vol. 1, no. 1, pp. 103–121, Dec. 2014.

[57] P. Kanhere and Z. Chen, "A Review on Visible Light Active Pervoskite-Based Photocatalysts," *Molecules*, vol. 19, no. 12, pp. 19995–20022, Dec. 2014.

[58] J. Cong *et al.*, "Spin-induced multiferroicity in the binary pervoskite manganite Mn2O3," *Nat. Commun.*, vol. 9, no. 1, p. 2996, Dec. 2018.

[59] W. F. Zhang, J. Tang, and J. Ye, "Photoluminescence and photocatalytic properties of SrSnO3 pervoskite," *Chem. Phys. Lett.*, vol. 418, no. 1–3, pp. 174–

178, 2006.

[60] W. H. Lin, C. Cheng, C. C. Hu, and H. Teng, “NaTaO3 photocatalysts of different crystalline structures for water splitting into H2 and O2,” *Appl. Phys. Lett.*, vol. 89, no. 21, pp. 1–4, 2006.

[61] E. Fabbri, A. Habereder, K. Waltar, R. Kötz, and T. J. Schmidt, “Developments and perspectives of oxide-based catalysts for the oxygen evolution reaction,” *Catal. Sci. Technol.*, vol. 4, no. 11, pp. 3800–3821, 2014.

[62] H. Mohammadian-Sarcheshmeh and M. Mazloum-Ardakani, “Recent advancements in compact layer development for pervoskite solar cells,” *Heliyon*, vol. 4, no. 11, p. e00912, Nov. 2018.

[63] T. Saha-Dasgupta, “Double pervoskites with 3d and 4d/5d transition metals: compounds with promises,” *Mater. Res. Express*, vol. 7, no. 1, p. 014003, Jan. 2020.

[64] P. Kanhere and Z. Chen, “A review on visible light active pervoskite-based photocatalysts,” *Molecules*, vol. 19, no. 12, pp. 19995–20022, 2014.

[65] V. M. Goldschmidt, “Die Gesetze der Krystallochemie,” *Naturwissenschaften*, vol. 14, no. 21, pp. 477–485, 1926.

[66] O. Fukunaga and T. Fujita, “The relation between ionic radii and cell volumes in the pervoskite compounds,” *J. Solid State Chem.*, vol. 8, no. 4, pp. 331–338, Dec. 1973.

[67] A. Ohtomo and H. Y. Hwang, “A high-mobility electron gas at the LaAlO3/SrTiO3 heterointerface,” *Nature*, vol. 427, no. 6973, pp. 423–426, Jan. 2004.

[68] C. N. R. Rao, A. K. Cheetham, and A. Thirumurugan, “Hybrid inorganic-organic materials: A new family in condensed matter physics,” *J. Phys. Condens. Matter*, vol. 20, no. 8, 2008.

[69] L. Tang, L. Zhu, Y. Wang, and C. Fang, “Uncovering the Hidden Excited State toward Fluorescence of an Intracellular pH Indicator,” *J. Phys. Chem. Lett.*, vol. 9, no. 17, pp. 4969–4975, Sep. 2018.

[70] E. Longo *et al.*, “Density functional theory calculation of the electronic structure of Ba0.5Sr0.5TiO3: Photoluminescent properties and structural disorder,” *Phys. Rev. B*, vol. 69, no. 12, p. 125115, Mar. 2004.

[71] E. Orhan *et al.*, “Room-temperature photoluminescence of BaTiO3: Joint experimental and theoretical study,” *Phys. Rev. B*, vol. 71, no. 8, p. 085113, Feb.

2005.

[72] T. L. Chen, X. M. Li, K. S. Wan, W. L. Zhu, and G. Pezzotti, "Spectral-resolved microprobe cathodoluminescence investigations of Al-doped single-crystalline Ba 0.6 Sr 0.4 TiO 3 thin films," *Appl. Phys. Lett.*, vol. 87, no. 18, pp. 1–3, 2005.

[73] T. Hasegawa, M. Shirai, and K. Tanaka, "Localizing nature of photo-excited states in SrTiO3," *J. Lumin.*, vol. 87, pp. 1217–1219, 2000.

[74] G. Godefroy and C. Gonzalo, "Intrinsic luminescence from BaTiO3 crystals," *Ferroelectrics*, vol. 25, no. 1, pp. 467–470, 1980.

[75] P. H. Borse, J. S. Lee, and H. G. Kim, "Theoretical band energetics of Ba(M0.5Sn0.5)O3 for solar photoactive applications," *J. Appl. Phys.*, vol. 100, no. 12, p. 124915, Dec. 2006.

[76] M. Duan, X. Kuang, J. Li, and Z. Jiao, "Theoretical study of local lattice structure of Mn2+ in pervoskite fluorides A2MF4 (A=K, Rb; M=Mg, Zn, Cd) series," *J. Phys. Chem. Solids*, vol. 68, no. 2, pp. 299–304, Feb. 2007.

[77] R. I. Eglitis, E. A. Kotomin, V. A. Trepakov, S. E. Kapphan, and G. Borstel, "Quantum chemical modelling of electron polarons and green luminescence in PbTiO 3 pervoskite crystals," *J. Phys. Condens. Matter*, vol. 14, no. 39, pp. L647–L653, Oct. 2002.

[78] J. Meng, Y. Huang, W. Zhang, Z. Du, Z. Zhu, and G. Zou, "Photoluminescence in nanocrystalline BaTiO3 and SrTiO3," *Phys. Lett. A*, vol. 205, no. 1, pp. 72–76, Sep. 1995.

[79] C. D. Pinheiro, E. Longo, E. R. Leite, and P. S. Pisani, "STRUCTURE EFFECTS ON THE OPTICAL PROPERTIES OF THIN (PbLa) TiO 3 FILMS," *Lat. Am. Appl. Res.*, vol. 176, no. 37, pp. 171–176, 2007.

[80] L. Grabner, "Photoluminescence in SrTi O3," *Phys. Rev.*, vol. 177, no. 3, pp. 1315–1323, Jan. 1969.

[81] R. Leonelli and J. L. Brebner, "Time-resolved spectroscopy of the visible emission band in strontium titanate," *Phys. Rev. B*, vol. 33, no. 12, pp. 8649–8656, Jun. 1986.

[82] M. L. Moreira, J. Andrés, V. M. Longo, M. S. Li, J. A. Varela, and E. Longo, "Photoluminescent behavior of SrZrO3/SrTiO3 multilayer thin films," *Chem. Phys. Lett.*, vol. 473, no. 4–6, pp. 293–298, May 2009.

[83] R. Pązik, D. Hreniak, W. Stręk, A. Speghini, and M. Bettinelli, "Structural and luminescence properties of Eu3+ doped BaxSr1−xTiO3 (BST) nanocrystalline

powders prepared by different methods," *Opt. Mater. (Amst).*, vol. 28, no. 11, pp. 1284–1288, Aug. 2006.

[84] M. Anicete-Santos *et al.*, "Contribution of structural order–disorder to the room-temperature photoluminescence of lead zirconate titanate powders," *J. Lumin.*, vol. 127, no. 2, pp. 689–695, Dec. 2007.

[85] J. Yu, J. Sun, J. Chu, and D. Tang, "Light-emission properties in nanocrystalline BaTio3," *Appl. Phys. Lett.*, vol. 77, no. 18, pp. 2807–2809, 2000.

[86] L. S. Cavalcante *et al.*, "Experimental and theoretical correlation of very intense visible green photoluminescence in BaZrO3 powders," *J. Appl. Phys.*, vol. 103, no. 6, p. 063527, Mar. 2008.

[87] A. T. De Figueiredo *et al.*, "Correlation among order-disorder, electronic levels, and photoluminescence in amorphous CT:Sm," *Chem. Mater.*, vol. 18, no. 12, pp. 2904–2911, 2006.

[88] H. Mizoguchi, P. M. Woodward, C. H. Park, and D. A. Keszler, "Strong near-infrared luminescence in BaSnO3," *J. Am. Chem. Soc.*, vol. 126, no. 31, pp. 9796–9800, 2004.

[89] V. M. Longo *et al.*, "Strong violet-blue light photoluminescence emission at room temperature in SrZrO3: Joint experimental and theoretical study," *Acta Mater.*, vol. 56, no. 10, pp. 2191–2202, 2008.

[90] D. Kan *et al.*, "Blue luminescence from electron-doped SrTiO3," *Appl. Phys. Lett.*, vol. 88, no. 19, p. 191916, May 2006.