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. The chapter contains the review of the history of phosphates and different types of phosphates including pyrophosphates. The detail information of the different type of phosphates and pyrophosphates materials is pointed out how pyrophosphates materials are useful for the luminescence application.

1.2. Basic of Luminescence

The word luminescence includes both fluorescence and phosphorescence. It was first introduced by the German physicist Eilhardt Wiedemann in 1888 [1-5]. The word luminescence originates from the Latin word ‘*lumen*’ means ‘*light*’ [6]. At present, the word luminescence is defined as a phenomenon in which the electronic state of a luminescent substance is excited by some kind of external energy given to the substance [7]. The excitation energy is released in the form of visible light, the near-UV or near-IR regions of electromagnetic wave spectrum [2, 8-10]. The definition of the luminescence phenomenon given is mainly applicable to the inorganic materials. But the terminology used for organic materials is the fluorescence and phosphorescence. In the fluorescence process, the emission of light occurs due to the excited singlet state, while the emission occurs from the excited triplet state is termed as phosphorescence [2, 11-13].

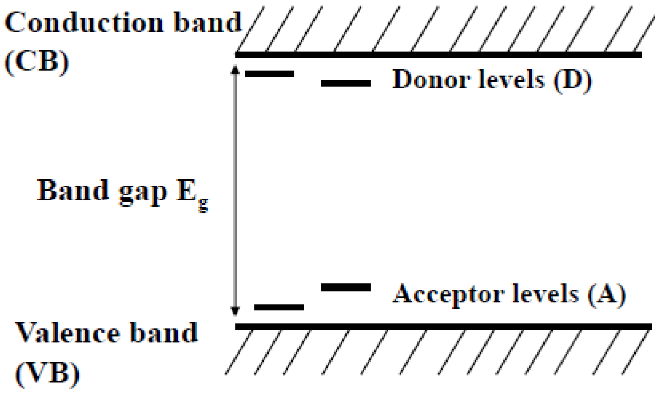
A luminescent phosphor is a solid, which converts certain types of energy into electromagnetic radiation over and above thermal radiation [7, 14]. *The word phosphor means “light bearer” in Greek and appears in Greek myths as the personification of the morning star Venus* [2, 8]. The luminescence from the phosphors can acquire by exciting the phosphor in different excitation radiations such as UV and visible radiation (photoluminescence), a beam of energetic electrons (cathodoluminescence), x-rays (x-ray excited luminescence), etc [14-18]. Thermoluminescence is one of the distinct ways to get luminescence, which is stimulation by the heating of luminescence, preliminary excited in a different way [19, 20]. Luminescence measures the energy levels of the luminescence centers formed inside the phosphors. 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 [21, 22]. The ground state is defined as the state with the lowest energy while the states with higher energy are called excited states. A center possesses several distinct reservoirs of energy levels, including electronic, vibrational, rotational, transitional, and those associated with nuclear and electron spin [21]. In luminescence phosphors, the energy levels of interest are those that are associated with electronic and vibrational transitions [23].

Rare earth doped inorganic luminescent materials are well known for emission in distinct wavelengths in the electromagnetic spectrum [24, 25]. The phosphors have a wide range of applications in the lighting devices such as cathode ray tubes (CRT), tri-phosphor fluorescent lamps, x-ray intensifying screens and newly developed vacuum mercury-free lamps [18, 26, 27]. 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" [28, 29]. LEDs are significantly energy-efficient lighting device with a long lifetime.

The basic theoretical concept of the physical phenomenon of luminescence mechanism was established from the configurational coordinate model. [2, 8, 30-32]. The spectral shapes of luminescence characteristic bands of the host or activator atom were explained on the basis of the configurational coordinate model [33, 34]. The theory for the phenomenon of luminescence due to the sensitization process interprets the excitation energy transfer to occur in the phosphor [6, 35]. In the case of RE^{3+} ions doped crystalline material gives prominent luminescence emission assigned due to the various characteristic electron allowed transitions of RE^{3+} ions [36-38]. The band structure formation in atoms, excitons present in semiconductors, and the crystal field of ionic crystal contributed can understand from the luminescence properties of the organic-inorganic phosphors [39, 40]. There are two different types of the mechanism involved in the principle of luminescence mechanism, one is a direct transition and the other is the indirect transition [41]. The indirect transition rout is much efficient than that of the direct transition rout for obtaining efficient luminescence. The indirect transition rout type semiconductors are suitable for developing the efficient luminescent phosphors for LEDs and semiconductors lasers [2, 31, 42]. The luminescence due to donor-acceptor pair production in extrinsic semiconductors was a conventional process to produce efficient luminescence phosphors [8].

Luminescent phosphors are mainly consisted of solid inorganic materials of a host lattice and purposely doped with impurities ions [25, 33]. The doping concentrations of the impurity ions should be low enough for the good luminescence phosphors, because of the luminescence efficiency usually decreases at certainly high concentration of doping due to the effect of concentration quenching [43-45]. Generally body color of the luminescence phosphors should be white. In most of the cases, the photoluminescence emission takes place on the intentionally doped impurity ions, which produce the desired emission according to its characteristic band transitions, are called activator ions [30, 31, 46]. In another case where the activator ions are not able to absorb the incident energy, other impurities ions can be added to the phosphor called as sensitizers [18, 47]. The sensitizer ion absorbs the incident radiation energy according to its energy states and consequently transfer the absorbed energy to the activators ions, which release the energy in the form of photons [31, 48]. The energy transfer process involves between sensitizer and the activator ions through the luminescent host. The PL emission color can be tuned by choosing the suitable impurity ions devoid of altering the host materials [44]. Some rare earth ions used as activator ions that shows characteristic emission due to their characteristic transition at specific spectral positions, which is hardly altered by the chemical environment of the host lattice [24, 49]. The characteristic emissions of RE^{3+} give comparatively sharp emission peaks of the spectral width of the order of few nm, while the broad emission bands with spectral width more than 50 nm in the visible part of the spectrum [31, 44, 45]. Broad PL emission occurred when the conjugation of the chemical bonds of the atoms in the ground state with the excited state differs significantly [25]. Broad band photoluminescence (PL) emission is observed in transition metal ions where the optical transitions occur in partly filled d-shell due to d→d transitions [14, 18]. It is also observed for the transitions between the 5d to 4f shell of rare-earth ions due to d→f transitions and for emission on ‘s^2’ ions that possess a lone pair of ‘s’ electrons [31, 44]. Sharp PL emission band are the characteristic of the material in which optical transitions takes place between the electronic states of atoms having the same chemical bonding character for the ground state and the excited state [49]. For the same phenomenon also occur in the optical transitions between electronic states that rarely participate in the chemical bonding due to f→f transitions in rare-earth ions [17, 36, 50, 51]. The optical processes involving electronic states, which participate in the chemical bond formation, the nature of the bonding (covalent, ionic) and the symmetry of the site, where the emitting ion is incorporated play a very significant role for emission. Majority rare earth ions show sharp emission bands due to optical transitions within the f-manifold, e.g., Tb^{3+} ($4f^8$-configuration) and Eu^{3+} ($4f^6$-configuration) [43]. In few rare-earth ions, broad emission bands are observed due to d→f emission, e.g., Eu^{2+} ($4f^7$-configuration) or Ce^{3+} ($4f^1$-configuration) [30, 44].

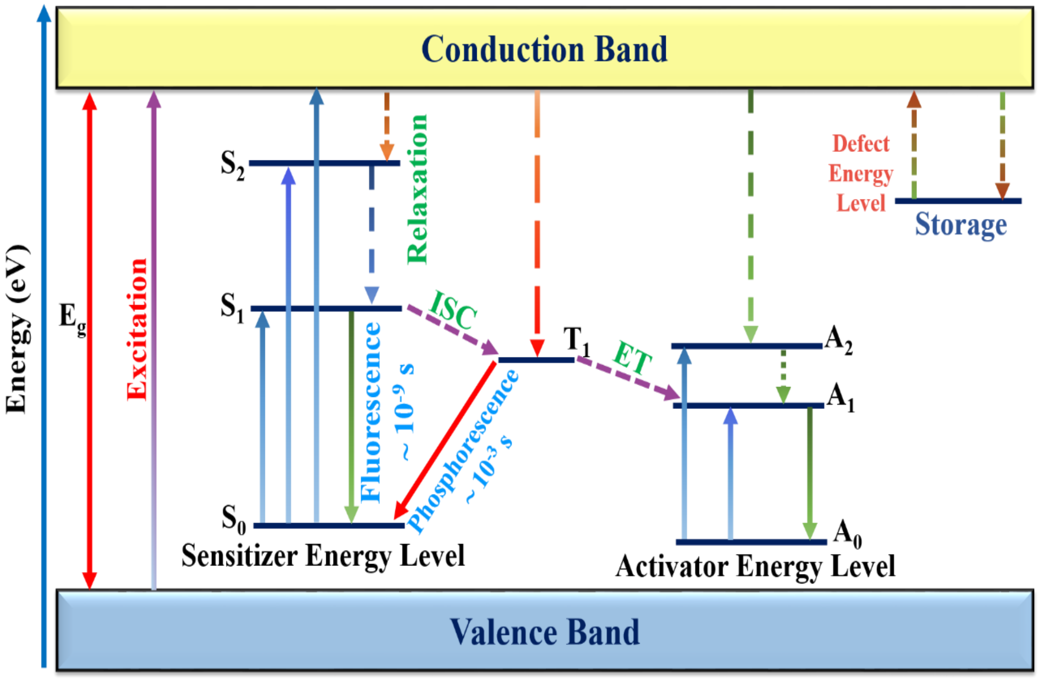
Thermoluminescence is the process in which the previously absorbed radiation energy released due to thermally stimulation energy supplied to the material [53-55]. There are three essential criterions required for the production of thermoluminescence. The first, the material must be an insulator or a semiconductor; metals do not exhibit luminescent properties due to overlapping of the conduction band and valence band [56]. Second, the material must be exposed to the ionization radiation which is absorbed and stored in material for a long time [54, 56]. Third, the TL emission of absorbed energy is prompted by simply heating the TL material [54, 56]. The characteristic of thermoluminescence occurs in some of the phosphors when the phosphor heated after the exposure, it emits the stored energy in the form of photons, the TL emission further cannot occur by simply cooling of phosphor and reheating again consecutively [57, 58]. In order to re-exhibit the thermoluminescence, the material has to be re-exposed to radiation. Thermoluminescence comes across favor uses in various scientific disciplines as archaeology, geology, medicine, solid-state physics, biology, and organic chemistry, etc. Thermoluminescence having a wide range of applications in radiation dosimetry to determine absorbed dose, age determination of rocks in geology, defect formed inside the solid materials, etc [54, 59]. Figure 1.1 shows the basic energy level diagram of the doped inorganic luminescent material. Figure 1.2 illustrates a different mechanism for absorption and emission processes takes place in luminescent material. In the most general case, the atom or molecules of the host reside in the lowermost vibrational energy level in the ground state, termed as valance band. After the absorption of incident radiation, these atoms or molecules can be elevated to the excited states. Classification of different types of luminescence occurs due to a different type of excitation energy and their respective examples are listed in Table 1.1.



Absorption via

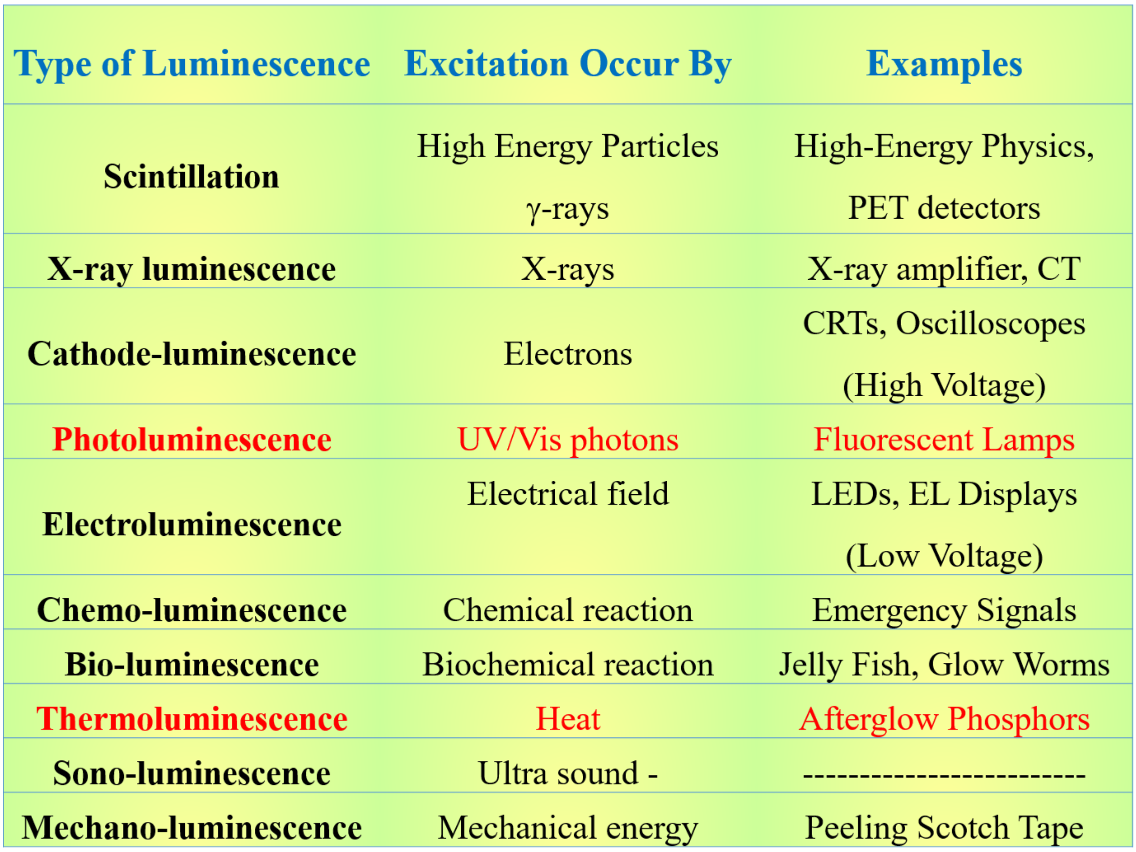
- Host lattice
  → Charge-Transfer or VB to CB
- Defects (colour centers)
  → Donor and acceptor levels

Figure 1.1 Energy level diagram of the doped inorganic luminescent material.



S_0, S_1, S_2, T_1, A_0, A_1, A_2 = Energy levels of the activators and sensitizers
ISC = Intersystem Crossing “spin-forbidden singulett-triplett transition”
ET = Energy transfer

Figure 1.2 Different mechanism for absorption and emission processes takes place in luminescent material.



Type of Luminescence	Excitation Occur By	Examples
Scintillation	High Energy Particles γ-rays	High-Energy Physics, PET detectors
X-ray luminescence	X-rays	X-ray amplifier, CT
Cathode-luminescence	Electrons	CRTs, Oscilloscopes (High Voltage)
Photoluminescence	UV/Vis photons	Fluorescent Lamps
Electroluminescence	Electrical field	LEDs, EL Displays (Low Voltage)
Chemo-luminescence	Chemical reaction	Emergency Signals
Bio-luminescence	Biochemical reaction	Jelly Fish, Glow Worms
Thermoluminescence	Heat	Afterglow Phosphors
Sono-luminescence	Ultra sound -	------------------------
Mechano-luminescence	Mechanical energy	Peeling Scotch Tape

Table 1.1 Types of luminescence, its causes, and applications.

1.3. Literature Review

1.3.1. Basic of Inorganic Phosphates

Phosphates and pyrophosphates are the different condensed and polymeric form of mono-phosphoric acid [60]. Pyrophosphate is one type of the phosphorus oxyanion with general formula $P_2O_7^{4-}$ also called as diphosphate or di-polyphosphate [61]. The oxyanion is generally termed as $M_XO_Y^{Z-}$ (M = C, S, P, F; O - Oxygen). Oxyanions are designed from a large number of the chemical elements which can be banded with one or more than one oxygen atoms. Phosphate materials are categorized into three types of phosphates; (i) monophosphates, (ii) condensed phosphates, (iii) oxyphosphates.

***Monophosphates*:** Monophosphates are the simplest tetrahedron anionic phosphates (PO_4^{3-}) unit having O/P ratio of 4:1. Monophosphates are the largest family of phosphates. All naturally abounded phosphates based minerals are monophosphates. Phosphate family also contain some substituted phosphates in which one or more oxygen of the tetrahedron PO_4^{3-} has been substituted by another atom, such phosphates are termed as PO_3H (phosphonate), PO_3S (thiophosphate) and PO_3F (fluorophosphate), etc. [62].

Oxyphosphates**:** The basic phosphates that can contain discrete oxygen atoms within the structure of phosphate-based materials are called as Oxyphosphates [63]. An additional oxygen atom in the structure does not associate with the anionic unit of phosphate. They have a high O/P ratio i.e., greater than 4:1 of monophosphates. Oxyphosphates are very similar to the oxide material and having a wide band-gap like an insulator. Due to the insulating property, oxyphosphates have been widely investigated for their structural properties, linear/non-linear optical, and electro-optical properties [64].

Condensed phosphates**:** The phosphates contain P-O-P bonds within the anionic unit and built from corner-sharing PO_4 tetrahedra called as Condensed phosphates or oligophosphates [65]. There are several ways to form the P-O-P bonds but the simplest way is a condensation reaction process in which water is eliminated and basic condensed phosphate is formed [66]. Condensed phosphates are the phosphates which have an O/P ratio between 7/2, 5/2, 5/4 [67]. There are three different category of the condensed phosphates due to three discrete geometries i.e., polyphosphates, cyclic phosphates and ultra-phosphates [68, 69].

The condensation reaction of a linear chain of phosphate tetrahedra which share one or two of their oxygen atoms to form a polyphosphate [70]. They are the polymer of phosphates that can form a chain of phosphates called as polyphosphates. The geometry of the polyphosphates can identify from the general formula $[P_nO_{(3n+1)}]^{(n+2)-}$, where ‘n’ is the number of phosphates tetrahedral [65, 71]. There are very few polyphosphates were synthesized where ‘n’ is greater than 4. In recent chemistry research, a large number of different inorganic triphosphates have been synthesized and characterized. Triphosphates structures contain the mono- and di-hydrogen tri-phosphate anions [72]. The layered inorganic triphosphates $MH_2P_3O_{10}\cdot 2H_2O$ (M= Al, Cr, Mn, Fe) are intercalation hosts similar to the lamellar orthophosphates [65, 73]. Tetraphosphates are less commonly studied than triphosphates. The best-defined examples of tetraphosphate are acid tetraphosphate, $(NH_4)_4H_2P_4O_{13}$, anhydrous materials [65]. Several high ordered polyphosphate anions with the longer chain up to at least $P_8O_{25}^{10-}$ have been investigated but few have been prepared and very few solid derivatives have been characterized.

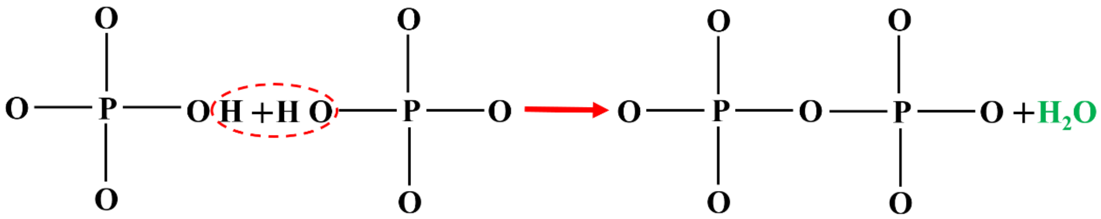


Figure 1.3 Formation of basic pyrophosphate "the basic condensed phosphates".

Figure 1.3 shows the formation of fundamental condensed phosphate. Pyrophosphates or 'diphosphates" are the basic polyphosphates in which the number of phosphate tetrahedral 'n' is 2 as noted in general formula [60, 68]. The diphosphate or pyrophosphate anion, $P_2O_7^{4-}$ is found in many inorganic and organic solids and minerals. The composition and structural formation of pyrophosphates are very similar to that of monophosphates [74]. The bonding geometry of O_B–PO_3 (O_B = bridging oxygen) group of pyrophosphates is similar to that of the bonding geometry of (H)O–PO_3 group of monophosphate. Size of the P–O_B bonds are near about the range 1.58–1.64 Å, however, the reported mean distance for seventeen diphosphates is 1.512 Å [65, 75]. There are several pyrophosphates were developed for a various application that has the general formula of $A^{4+}P_2O_7$, $A^{2+}{}_2P_2O_7$, $A^{1+}B^{3+}P_2O_7$, $A^{1+}{}_2B^{1+}{}_2$ P_2O_7, $A^{1+}{}_2B^{2+}P_2O_7$ and $A^{1+}{}_4P_2O_7$, where A and B are an inorganic atom.

Cyclic phosphates or cyclopolyphosphates formed in a ring structure that contain maximum 12 tetrahedra, out of those three, four and six tetrahedra structures are widely studied. The general formula of cyclopolyphosphates is given by $[P_nO_{3n}]^n$, where n $\leq$ 3. In the structural geometry of cyclopolyphosphates each phosphate tetrahedron shares 2 oxygen atoms with its neighbor, giving an O/P ratio of 3:1 [68].

The anionic unit of ultraphosphates contains phosphate tetrahedra that can share 3 of their oxygen atoms due to which it can form several different structural geometries [76]. Inorganic ultraphosphates are anhydrous because it can easily endure hydrolysis due to the triply linked tetrahedra so that inorganic ultraphosphates are mostly unstable. The general formula for ultraphosphates is given by $[P_{(n+2)}O_{(3n+5)}]^{n-}$ [68].

1.3.2. Luminescence of Inorganic Pyrophosphates

Pure and doped inorganic pyrophosphates gathered scientific and technological important because of their luminescent, dielectric, semiconductor, catalytic, magnetic, fluorescent, and ion-exchange properties [77-80]. A large variety of properties and corresponding applications is the reason, why the synthesis of inorganic pyrophosphates is a more attractive field of research for researchers. Out of many properties, luminescent properties are significantly investigated by many researchers. Wide-bandgap rare-earth doped inorganic pyrophosphate materials have gained much more attention, for their potential applications in diverse areas such as X- and gamma-radiation detectors, lighting, display phosphors, light-emitting diodes, scintillators, and solid state lasers, and because they are highly transparent, easily shaped, and cost-effective [81, 82].

There are many research articles published based on various inorganic pyrophosphates groups, where the synthesis and luminescence properties were investigated for a different application. All possible phase formation and effect of Eu doping on photoluminescence properties of CaP_2O_7 is investigated by Doat et al. [83]. UV spectral emission of HfP_2O_7 and blue emission of Ti^{4+} doped HfP_2O_7 is investigated for their x-ray storage application by Schipper et al. [84]. The crystal structure and spectroscopic analysis as well as luminescence studies of $KErP_2O_7{\cdot}2H_2O$ were reported by Assaaoudi et al. [85]. Luminescence properties of Ce^{3+}-doped the first lutetium diphosphate $NH_4LuP_2O_7$ was shown by Li et al [81]. The investigation of the energy gap of ABP_2O_7 ($A = Na^+, Li^+$; $B = Al^{3+}, In^{3+}$) double phosphates from the electronic structure and the optical properties were reported by Hizhnyi et al [86]. UV-visible spectroscopic properties based on energy transfer occur in Ce^{3+} and Pr^{3+} doped $A^+RE^{3+}P_2O_7$ ($A^+ = Na, K, Rb, Cs$; $RE^{3+} = Y, Lu$) alkali rare earth diphosphates were investigated by Yuan et al [87]. The structural study of $LiFeP_2O_7$, $LiScP_2O_7$, and $NaScP_2O_7$ for conductivity measurement were reported by Kaepe et al [88]. The synthesis of single crystals of chromium doped potassium–(aluminum, indium) diphosphates $KA^{3+}P_2O_7$ ($A^{3+} = Al, In$) and its spectral luminescence properties were investigated by Nedelko et al [89]. Synthesis of a single crystal of Eu^{3+} doped $Na_2ZnP_2O_7$, its structural, spectroscopic studies, and investigation of luminescent properties was reported by Guerbous et al [90]. Orange-red luminescent properties of $Rb_2CaP_2O_7$: Eu^{2+} was investigated for its application as phosphor-converted LED-excited at near UV by Song et al [91]. Synthesis and investigation of the luminescent properties of $A^{2+}MgP_2O_7$: Eu^{3+} ($A^{2+} = Ca, Sr, Ba$) phosphor was reported by Rongfang et al [92]. Synthesis of Ce^{3+} Doped $SrCaP_2O_7$ by solid state diffusion technique and study of luminescent properties was reported by Kohale et al [93]. Synthesis of cerium doped calcium pyrophosphate ($Ca_2P_2O_7$: Ce^{3+}) through wet precipitation method and study effect of annealing temperature on its thermoluminescence (TL) and photoluminescence (PL) properties was reported by Lozano et al [94]. Thermoluminescence properties of copper and rare earth doped $Sr_2P_2O_7$ were investigated by Yazici et al [77]. UV and x-ray excited luminescence properties of Ce^{3+} doped $Sr_2P_2O_7$ under vacuum were investigated by Hou et al [95].

From the literature survey, it is found that different inorganic pyrophosphates show good luminescent behavior. Out of different type of pyrophosphates, the majority were synthesized by solid-state method, a sol-gel method, wet precipitation method. There are very few research article in which the luminescent properties rare earth doped of strontium pyrophosphate were investigated. Therefore, strontium pyrophosphate is taken as a host material which is doped with different rare earth elements to enhance the luminescent properties of the host. The rare earth doped and co-doped strontium pyrophosphate was synthesized by combustion method which is the easiest method from the synthesis of efficient luminescent materials.

1.4. Objectives of the Thesis

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

- Rare earth doped and co-doped Strontium Pyrophosphate ($Sr_2P_2O_7$) phosphor for the different concentration of doping was synthesized by the combustion method at heating temperature 1200°C for 3 hr.
- For this research, $Sr_2P_2O_7$: x RE^{3+} (RE^{3+} = Ce, Eu, Tb, Dy, Er, Gd; x = 0.5, 1.0, 1.5, 2.0, 2.5, 5.0 mol%) and $Sr_2P_2O_7$: 1.0 mol% Ce^{3+}, 1.0 mol% RE^{3+} (RE^{3+} = Eu, Tb, Dy, Er, Gd, Sm) phosphors were synthesized.
- The 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 $Sr_2P_2O_7$ phosphors. The PL properties of the phosphor were investigated for its applications in solid-state lighting.

- Thermoluminescence properties were examined after irradiating the phosphors by β-radiation for different doses. The thermoluminescence behavior of the rare earth doped and co-doped $Sr_2P_2O_7$ phosphors were investigated for the effect of doping concentration, the effect of various doses, fading effect after exposure, and the sensitivity of the phosphor to proposed its application in radiation dosimetry.

1.5. Thesis Layout

Chapter 2. Experimental Method

In this chapter, the basic information of 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.

Chapter 3. Structural Characterization

This chapter contains the fundamental details of the characterization techniques used to characterize the synthesized phosphor. It contains basic information about X-ray diffraction, Fourier Transform Infra-Red spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). The chapter contains experimental results, discussion and its outcomes of above-mentioned characterization techniques of rare earth doped strontium pyrophosphate.

Chapter 4. Photoluminescence of Strontium Pyrophosphate

In this chapter, the basic information of photoluminescence (PL) is described in detail. The principle of photoluminescence, theoretical background, and PL mechanism, instrumentation of PL spectrometer, applications of phosphor, etc are explained briefly. The chapter contains some significant experimental results and discussion of photoluminescence property of rare earth doped strontium pyrophosphate. The outcome of PL results has been discussed on the basis of theory and its application in detail.

Chapter 5. Thermoluminescence Strontium Pyrophosphate

In this chapter, the basic information of thermoluminescence (TL) is described in detail. The principle of thermoluminescence, theoretical background, and TL mechanism, methods for TL parameters estimation, instrumentation of TL reader, etc are explained briefly. The chapter contains experimental results and discussion of thermoluminescence property of rare earth doped strontium pyrophosphate after beta irradiation. Characterization study of the TL glow curves has been done by evaluating the kinetic parameters, activation energy, and frequency factor using several standard analytical methods of TL analysis. The outcome of TL results has been discussed on the basis of theory and its application in detail.

Chapter 6. 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 prepare strontium pyrophosphate phosphor.

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