Synthesis and photoluminescence properties of Sm^{3+} doped $KMgPO_4$ Phosphors for White Light emitting diodes

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Submitted by:

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CANDIDATE'S DECLARATION

I, Sarvjeet Singh, Roll No. 2K15/NST/08 student of M. Tech. (NanoScience and Technology), hereby declare that the project Dissertation titled "**Synthesis and photoluminescence properties of Sm^{3+} doped $KMgPO_4$ Phosphors for White Light emitting diodes**" which is submitted by me to the Department of Applied Physics, Delhi Technological University, Delhi in partial fulfillment of the requirement for the award of the degree of Master of Technology has not previously formed the basis for the award of any Degree, Diploma Associateship, Fellowship or other similar title or recognition.

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CERTIFICATE

I hereby certify that the Project Dissertation titled "**Synthesis and photoluminescence properties of Sm^{3+} doped $KMgPO_4$ Phosphors for White Light emitting diodes**" which is submitted by Sarvjeet Singh, Roll No. 2K15/NST/08, Department of Applied Physics, Delhi Technological University, Delhi in partial fulfillment of the requirement for the award of the degree of Master of Technology is an original contribution with existing knowledge and faithful record of research carried out by him under my guidance and supervision.

To the best of my knowledge this work has not been submitted in part or full for any Degree or Diploma to this University or elsewhere.

Place: Delhi

Date:

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Abstract

Sm^{3+}- doped $KMgPO_4$ was prepared by high-temperature solid-state reaction having exceptionally bright and stable photoluminescence in the orange (602 nm) region of the electromagnetic spectrum. The X-ray powder diffraction, photoluminescence (PL) emission, and excitation spectra were thoroughly measured. The PL spectra of prepared $KMgPO_4$ phosphor showed characteristic Orange emission when excited by 402 nm under UV excitation. The highest emission intensity was found for $KMgPO_4$:xSm^{3+} with a composition of x=0.0075 Sm^{3+} ions and this phosphor used for remaining studies. The photoluminescence at room temperature shows broad orange 5d-4f emission bands are peaked at 602 nm and only two weak Sm^{3+} emission band is observed at 565 nm and 652 nm respectively. The phosphor was found to be superior in terms of integrated PL intensity, degradation resistant and markedly superior properties as compared to its counterparts.

The objective of this dissertation is to synthesize the $KMgPO_4$ phosphor and study the photoluminescence properties of the $KMgPO_4$ phosphor doped with Sm^{3+} ions. These results can be used in the white LED for improved performance and stability. Further different characterization techniques used in the study of $KMgPO_4$ such as photoluminescence, SEM, XRD and FTIR.

The thesis has been divided into the various chapters. In chapter 1, Introduction for the research have been explained in brief. In chapter 2, different instrumentation used in the experimental work and synthesis of $KMgPO_4$ phosphor have been discussed. In chapter 3, the characterization of the prepared samples have been explained. The conclusion and future

work have been explained in chapter 4. Finally, all the references used in the research have been mentioned in the last.

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Abbreviations

SEM	**S**canning **E**lectron **M**icroscopy
FWHM	**F**ull **W**idth at **H**alf **M**aximun
LED	**L**ight **E**mitting **D**iode
RGB	**R**ed **G**reen **B**lue
FED	**F**ield **E**mission **D**isplay
XRD	**X** **R**ay **D**iffractometer
PL	**P**hotoluminescence
UV	**U**ltra **V**iolet
FTIR	**F**ourier **T**transform **I**nfrared **S**pectroscopy
CIE	**C**ommission **I**nternationale **d'**Eclairage
NTSC	**N**ational **T**elevision **S**tandard **C**ommittee
CRT	**C**atode **R**ay **T**ube
LCD	**L**iquid **C**rystal **D**isplay

Chapter 1

Introduction

1.1 History

Recently rare earth doped materials play a significant role in the area of solid state lighting. There are numbers of luminescent materials found in the last few decades. Rare earth ions drastically increase the performance of the phosphors in the view of the host structure. The fundamental component of the solid state lighting are phosphor and light emitting diode (LED). In this way, it is essential to develop new phosphors with enhancing performance, high color rendering index, energy efficient, and longer life cycle.

The word phosphor was concocted in the right on time of seventeenth century and a chemist, Vincentinus Casciarolo of Bologna, Italy, found an overwhelming crystalline stone with a gleam at the foot of a spring of gushing lava, and let go it in a charcoal stove proposing to change it to a respectable metal. Yet, rather than metal, he found that the sintered stone discharged red light oblivious after introduction to daylight. This stone was known as the "Bolognian stone", which is appeared in Fig. 1.1. At the present time, this stone is known as barite ($BaSO_4$) and used as the host for phosphor materials.

Figure 1.1: Bolognian stone

1.2 Importance of Rare-earths

Rare-earth ions are placed in the lanthanide series of the periodic table. The lanthanides from a special group of elements, usually shown at the bottom of the periodic table. 4f block elements are also called as lanthanides, lanthanons or rare earth. The first two names are given because of their strong resemblance to lanthanum. The name rare earth was given to them since they were initially separated from oxides for which old name was earth and which were thought to be rare. In fact, the name lanthanides have been derived from lanthanum, which is the prototype of lanthanides. Lanthanides constitute the first inner transition series. Furthermore, the group of elements known as lanthanide comprises fifteen elements in which a progressive filling of the 4f shell occurs. The group starts with lanthanum (Z=57) and ends with lutetium (Z=71).

The history of the lanthanides started in 1788 when Captain Arrhenius found a black stone near Yetterby in Sweden. In lanthanide group, the 4f cell has a different number of electrons while the ground state electronic configuration is $4f^{N}$ and the first excited configuration is $4f^{N-1}5d$. They may be divalent or trivalent in the rare earth ions in the material. The electronic configuration of these rare earth ions is $4f^{N}\ 5s^{2}\ 5p^{6}$ or $4f^{N-1}5s^{2}\ 5p^{6}$ in divalent or divalent respectively. Most of the electrons of the rare earth ions to be

found in the trivalent structure. The 4f orbitals are surrounding by the filled $5s^2$ $5p^6$ orbitals, which demonstrate the "atomic" nature of their spectra. The spectra of Ln compounds are sharp and are similar to the spectra of atoms. The shielded character of the 4f orbitals is also responsible for the unique optical properties of rare earth ions[2].

Trivalent lanthanides have been the most extensively used as activator ions because of the following reasons:

1. They emanate narrow lines, practically monochromatic light and have long outflow lifetimes.

2. They have many fluorescing states and wavelengths to select among the 4f electronic configurations.

3. Trivalent lanthanides have intraconfigurational f-f transitions which show small homogeneous line widths[3].

1.3 Luminescence

When a material absorbs energy, a portion of it is re-emitted in the form of photons having an energy corresponding to the visible or near visible region. This phenomenon is called luminescence. Luminescence process in the atom is shown in fig. 1.2. It is observed that photon emitted has a smaller energy than the absorbed photon. The atom jumps to an excited state by absorption of a photon by spontaneous emission. In this process, the blackbody radiation is not included. Luminescent materials are usually referred to the phosphors. The phosphors exhibit luminescence because of the presence of a few impurities called activator[4].

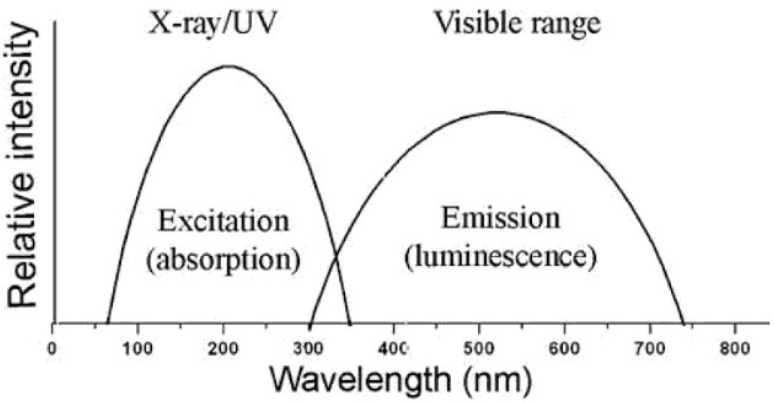

Figure 1.2: Diagram shows the energy absorbed by a phosphor material and this energy transferred to emitted light which has lower energy.

1.4 Fluorescence and phosphorescence

The forms of the luminescence that are used most often for analysis are fluorescence and phosphorescence. In both cases, ultraviolet-visible radiation is used to excite the molecules or ions.

1.4.1 Fluorescence

Fluorescence occurs when an electron in an excited level falls to a lower energy level with the simultaneous emission of radiation. During the transition, the electron maintains the same spin. Normally the transition is from an excited singlet state to the ground singlet state. Fluorescence occurs nearly instantaneously after the initial excitation and ceases when absorption ceases. Typically the electron falls to a lower electron level between 10^{-6} and 10^{-10} second alter the excitation.

1.4.2 Phosphorescence

Phosphorescence occurs when an electron in an excited level fall to a lower energy level with the emission of radiation. During the transition, the elec-

tron changes its spin state. In most cases, phosphorescence occurs during a transition from an excited triplet state to the ground state. Because the transition from a triplet level to a singlet level is 'forbidden' the average time required for the emission of radiation is of considerably greater than that during fluorescence. Phosphorescence begins immediately after excitation but typically continues for 10^{-6} to 100 seconds after the absorption ceases[5]. Dissimilar to fluorescence, a luminous material does not promptly re-transmit the radiation it retains.

1.5 Types of luminescence

The luminescence is divided into the different category based on the excitation mechanism. The examples of the luminescence are electroluminescence, chemo-luminescence, electro-chemoluminescence, bio-luminescence, photoluminescence, cathode-luminescence, radioluminescence, thermoluminescence which are described below.

1. **Electroluminescence:** Electroluminescence is an optical and electrical phenomenon in which materials emits the light in the influence of the light or storage magnetic field is called the electroluminescence. This type of luminescence is different from the black body radiation, from a chemical reaction, sound or any type of mechanical luminescence.

2. **Chemiluminescence:** Chemiluminescence is the type of luminescence in which the radiation emits from the chemical reaction (mainly oxidation) as a light at a low temperature. The energy is released by the decay of excited state to the lower energy state. Chemo-luminescence is different from the fluorescence and the luminescence because, in the chemo-luminescence, excitation is the product of chemical reaction rather than absorption of a photon.

3. **Electrochemiluminescence:** In Electro-chemiluminescence the lu-

minescence is produced because of the electrochemical reaction in solution. Electrochemically created intermediates experience a very exergonic response to deliver an electronically energized state that at that point emanates light because of electron exchange (redox) responses. In semiconductors, electroluminescence happens because of a radiative mix of electrons and gaps. The energized electrons discharge their energy as photons.

4. **Bio-luminescence:** The light discharged by a bioluminescent organism is delivered by energy discharged from concoction responses happening inside (or ejected by) the living organism. It is a luminescence delivered by living organism and is believed to be a kind of normally happening chemo-luminescence. Example: fireflies

5. **Photo-luminescence:** Photoluminescence (known as PL) is light emission from any type of matter after the ingestion of photons (electromagnetic radiation). It is one of many types of luminescence (light emission) and is started by photoexcitation (excitation by photons), henceforth the prefix photo-.[1] according to quantum mechanics, photoluminescence is the phenomenon in which the excitation goes to the excited state and then return back to the ground state by accompanied by a photon. Different relaxation forms occur in which different photons are re-transmitted. In the general lighting, the energy absorbed by the mercury discharge lamp and absorbed by the one of the activator impurities and some energy s transferred to the second impurities by resonance. To obtain the desired color of the light, it is necessary to modify the relative concentration of these impurities.

6. **Cathode-luminescence:** Cathode-luminescence is the type of the luminescence in which the luminescence is generated through the electron beam at electrical cathode arc in the cathode ray tube. This principle is used in the cathode ray tube by this type of emission.

7. **Radio-luminescence:** Radio-luminescence occur in a material by providing energy through ionizing particles as alpha particles, beta particles, and x-ray radiation. This radiation causes the nuclear reaction resulting radio-luminescence.

8. **Thermos-luminescence:** This type of the luminescence is found in some type of crystalline materials in which the light is re-emitted by absorbing energy from electromagnetic radiation when the material is subjected to heat. The light emitted from the material is called thermos-luminescence. This phenomenon differs from the black body radiation.[6]

1.6 Phosphors and mechanisms of Luminescence

Phosphor materials are a luminescent materials which, produced subsequent light under the radiation by absorbing the energy and this process is generally called luminescence. In general, fluorescence means fast (Nano-second time) and phosphorescence means slow (Nano-second time). Phosphor material contains intentionally impurities in the host materials and the impurity concentration is generally low for maximum output luminescence while the efficiency of the luminescence is decreased when the quenching process starts as shown in the figure. Generally, phosphors are the polycrystalline materials which designed in such a way that it produces visible color emission[7]. After decades of research, thousands of the phosphor materials have discovered till now and they used in the different areas.

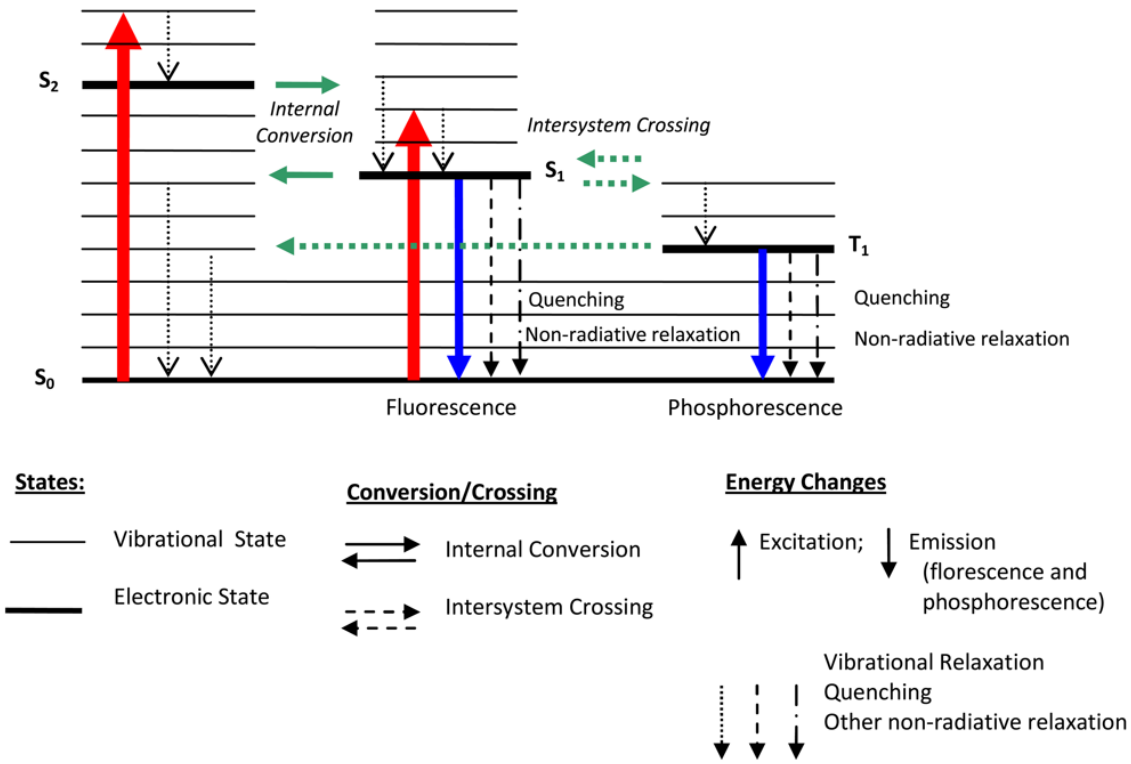

Figure 1.3: Mechanism of Luminescence

Mostly the emission is produced by the impurities added to the host materials and these impurities called the activator ions. Sometimes the luminescence is too slow that it is not visible under a normal condition so extra impurities are added to the host material which is called sensitizers which absorbs the adequate energy and transfers this energy to the activator. The color of the emission light is decided by the impurities added to the activator material. It is required that the structure of the host lattice not get change by incorporated the impurities added to it[8].

1.6.1 Excitation and Emission Spectra

Excitation and emission spectra are described in fig. 1.4. These spectra are recorded by the instrument which is called the spectrofluorometer. The spectrofluoromemeter contains two types of the spectrometer one is il-

luminating spectrometer and another is analyzing spectrometer. First, the material which shows some illumination undergo the illuminating spectrometer and then analyzing spectrometer examined the sample with the fixed illumination color. After obtaining the optimum brightest color by the illumination spectrometer the analyzer is fixed at the brightest emission color and spectra of the emission are recorded at different emission intensity with a fixed wavelength.

The wavelength of the light decided the color spectra and common unit for the fluorescence spectra are nanometers (nm). Visible spectra of the color are divided into approximate range shown in the bellows.

Violet and indigo color range: 400-450 nm

Blue and aqua color range: 450-500 nm

Green color range: 500-570 nm

Yellow and orange color range: 570-610 nm

Red color range: 610-750 nm

Blue and aqua color range: 450-500 nm

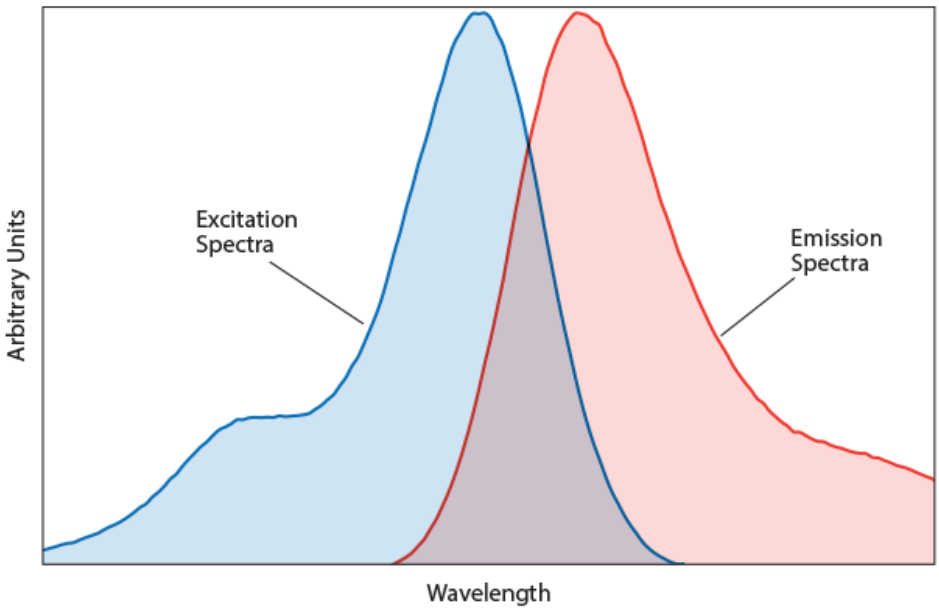

Figure 1.4: Emission and excitation spectra of a phosphor material

In the visible spectrum, the near UV-range is about 320 to 400 nm which is lying under the shorter wavelength and at a longer wavelength the near-infrared region in the rage of 750 to approximately 2500 nm. The fluorescence spectra used in the design of microscopy and filter design. There are broad spectra of the emission and excitation spectra for the certain substances. This substance is called fluorochromes and they have well-defined spectra of emission and excitation spectra. The typical spectra of the fluorochromes are showed in the figure and the difference between the peaks of these bands is called the Stokes shift[9].

1.6.2 Radiative Transition

There is a different mechanism of coming back to the ground state and the procedure of luminescent center to the ground state is observed as an emission radiation. The quantum efficiency of the luminescence is given by the photon emitted divided by the number of photons assimilated and sometimes in particular levels, the ratio of the measured lifetime to the mean lifetime is equal. There are two types of the transition one is a radiative transition and another is nonradiative transition the process follow. The radiative transition is competed by the transfer to another ion and the non-radiative transition is transfer to the different ions of similar nature also known as multiphonon relaxation. The configurational coordinate diagram is shown in below fig. 1.8. When the excitation phenomenon occurs then the electron is excited in the broadband area and transfer to the higher vibrational level of the excited state. After this, the center of relaxation is transferred to the lowest vibrational energy of the excited state and this causes excess energy which is transfer to the surroundings. The photon emission is competed by the lowest level of the vibrational level to the ground level and it is also concluded that the offset between the ground state to excited state is presumed[10].

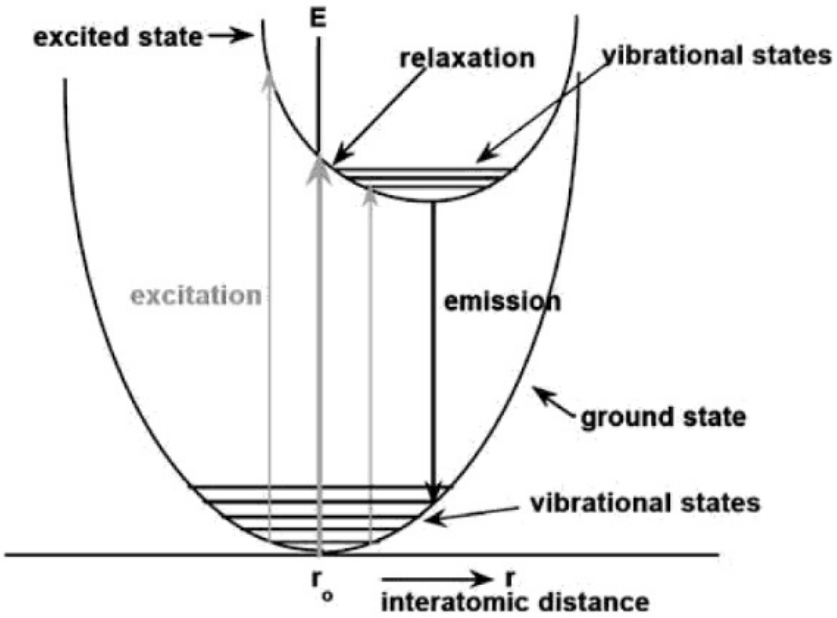

Figure 1.5: Configurational coordinate diagram representing radiative transitions

There are a few conceivable possibilities of coming back to the ground level. The observed emission from a luminescent center is a procedure of coming back to the ground state radiatively. The luminescence quantum productivity is characterized as photons discharged separated by photons assimilated, and much of the time is equivalent to the proportion of the measured lifetime to the radiative lifetime of a given level. The procedures contending with luminescence are radiative exchange to another ion and nonradiative exchanges, for example, multiphonon relaxation and energy exchange between various ions or, then again particles of a comparative nature. The last transfer is likewise named cross-relaxation. Fig. 1.5 demonstrates the configurational facilitate graph in a wide band emission. The presumption is made on an offset between the parabolas of the ground state and the excited state. It is cleared from the graph that the energy difference between the highest emission band to the band found and this distance is known as the stokes shift. The radiative transition is occurred due to the light absorbed

by the acceptor ions from the donor ion or molecules. The performance of the radiative transfer can be improved by designing a proper geometry.

1.6.3 Non-radiative Transition

The energy absorbed by the luminescent materials which are not transmitted as radiation is scattered to the unit crystal lattice. This energy shape the radiation spectrum which is less from this and associated with the radiation procedure. In order to study the non-radiative transition, the configurational arrange graphs are introduced in Fig. 2.4. In Fig. 2.4, there is a Stokes shift between the excited state and ground state. The relaxed excited state may achieve the intersection of the parabolas if the temperature is sufficiently high. Through the intersection, it is feasible for electrons to come back to the ground state in a non-radiative way. The energy is given up as heat to the lattice between the processes. The parabolas of ground state and energized state are parallel. If the energy distinction is equivalent or less than four to five times the higher vibrational recurrence of the encompassing, it can simultaneously energize a couple of high-energy vibrations, and subsequently, is lost for the radiation of phonons. This process is called non-radiative transition.

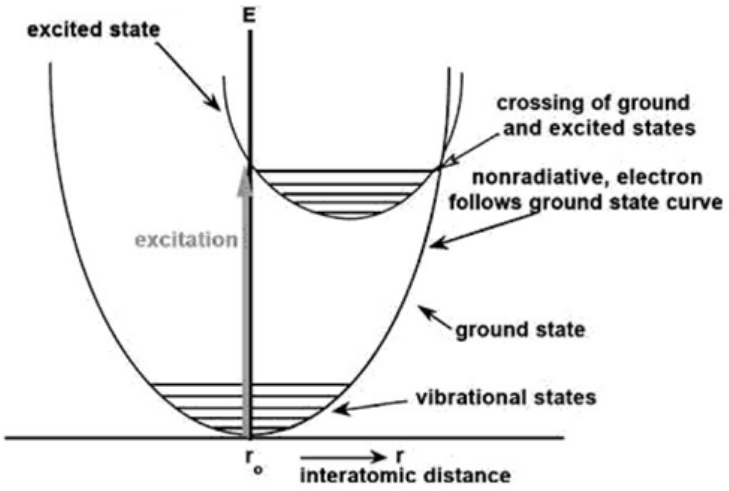

Figure 1.6: Configurational coordinate diagram representing non-radiative transitions

In a graph as appeared in Fig. 1.6, both radiative and non-radiative forms are conceivable. The parallel parabolas (strong lines) from a similar configuration are crossed by a third parabola began from an alternate configuration. The progress starting from the ground state to the lower excited state is optically prohibited, yet it is permitted to travel to the upper excited state. Excitation to the transition permitted parabola at that point relaxes to the relaxed excited condition of the second energized parabola. From there on, emission happens from it.

1.6.4 Multiphonon Relaxation

Multiphoton relaxation in lanthanide particles is a surely known process, opposite to other transition metal ions, which still require extra understanding. Energized electronic levels of rare earth in solids decay non-radiatively by energizing cross section vibrations (phonons). At the point when the energy gap between the energized level and the next lower electronic level is bigger than the phonon energy, a few cross-section phonons are produced in order to connect the energy gap. It was perceived that the most energetic vibrations are responsible for the non-radiative decay since such a procedure

can monitor energy in the lowest order.

1.6.5 Cross-Relaxation

There is a special case of the energy transfer in the luminescent materials which is known as the cross-relaxation and the original system loses energy by obtaining the lower state this lower state also may be ground state. Another system acquired the energy by going to the higher state. There are possibilities that the cross relaxation happens in the same lanthanides or two different elements in which the two pair of the energy level is displaced by the same amount. The diagram shows the cross-relaxation of the same pair of element.

At high concentration, cross relaxation factor dominates in the nonradiative transition and cross relaxation is found in the variety of ions. The difference between the two energy levels can be compared by the two or more photons.

1.7 Applications of Phosphors

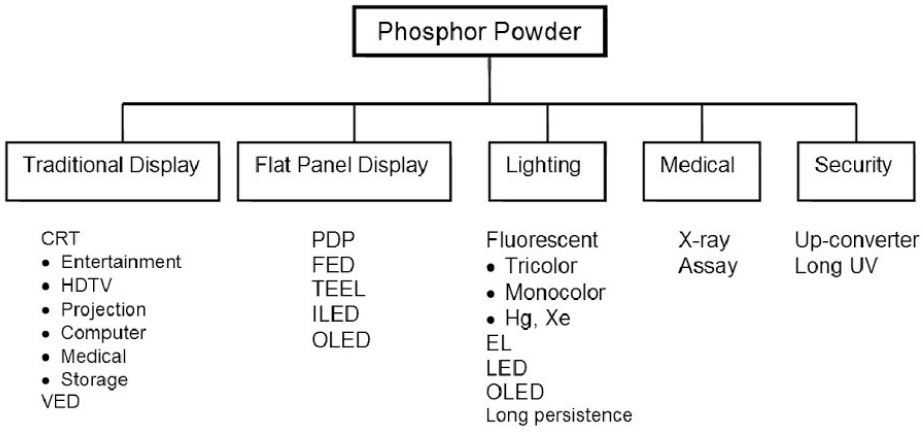

Figure 1.7: Phosphors applications

Lighting Phosphor layers give the greater part of the light created by fluorescent lights and are likewise used to enhance the light delivered by metal halide lights. Different neon signs utilize phosphor layers to create diverse shades of light. Electroluminescent display found, for example, in aircraft machine instrument boards, utilize a phosphor layer to produce glare-free illumination or as numeric and realistic display gadgets[11].

Phosphor Thermometry Phosphor thermometry is a temperature estimation approach that utilizations the temperature reliance of specific phosphors for this reason. For this, a phosphor coating is connected to a surface of intrigue and, normally, the decay time is the emission parameter that shows temperature. Since the light and recognition optics can be arranged remotely, the technique might be utilized for moving surfaces, for example, rapid engine surfaces. Additionally, phosphor might be connected to the end of an optical fiber as an optical simple of a thermocouple.

Cathode Ray Tubes Different phosphors are accessible relying on the requirements of the measurement instrumentation or display application. The brightness, shading, and constancy of the illumination rely on the sort of phosphor utilized on the CRT screen. Phosphors are accessible with constancy running from short of what one microsecond to a few seconds. For visual perception of brief transient occasions, long constancy phosphor may be desirable. For occasions which are quick and tedious, or, on the other hand, high recurrence, a short-constancy phosphor is generally preferable.

A CRT has a vacuum tube containing an electron gun cathode and a phosphor covered screen. The cathode is a source of the electron beam and electrons generated into the vacuum are attracted by an anode. The electrons are then focused and accelerated toward the screen by focusing and accelerating anode. Copper windings are wrapped around the tube and they act as steering coils. These coils make attractive fields inside the tube and these attractive fields direct the shaft toward the screen. By varying the voltages in these coils, the electron beam can be positioned at any point on the screen. When the electron beam strikes the phosphor coated screen, a

tiny bright visible spot is created on the screen. An image is formed when the beam is rastered across the screen. Color CRTs have three electron guns, one for each primary color. CRTs are used in oscilloscopes, television and computer monitors and radar targets. Typical values of the cathode to anode distance range between 25 to 100 cm. CRTs are very bulky and when bigger screens have required the length of the tube must increase.

Field emission displays A field emission display (FED) is a type of display that utilizes the electron emission source. This large area field emission strike to the colored phosphor which produces the visual display. In a general sense, a FED comprises a matrix of cathode beam tubes, each tube delivering a unit sub-pixel, assembled in threes to shape red-green-blue (RGB) pixels. FED display include the benefits of the CRT, particularly they have high contrast level and faster response time and also the packaging advantages of the liquid crystal display and flat panel technologies. These type of display required less power in compression of the LCD system[12].

X-ray and scintillators Intensifying screens are made of exceptionally delicate phosphors and utilized with photofluorography. When we are X-rayed, they lessen illumination to one hundredth of the ordinal light without intensifying screens.

- Intensifying screens have high sensitivity and high sharpness by innovation that influences a high-thickness phosphor to layer and gets ready ideal grain estimate dissemination.

- Sensitivity and sharpness are additionally enhanced by auxiliary outlining that guarantees successful light reflection and X-ray absorption characteristics.

- The surfaces of strengthening screens are ensured with an exceptional film to forestall darts and scars and to taking care of easy[13].

1.8 About the host ($KMgPO_4$)

The $KMgPO_4$ host comes under the $ABPO_4$ phosphate where A is the large monovalent cations and b is small bivalent cations. The structure of this host is tetrahedral built BO_4 matrix which hosts the large cation A. Among these compounds, $KMgPO_4$ phosphor is a special type of phosphor because of its coordination geometry[14]. The detailed inter-atomic structure of the $KMgPO_4$ phosphor is shown in the fig. 1.8.

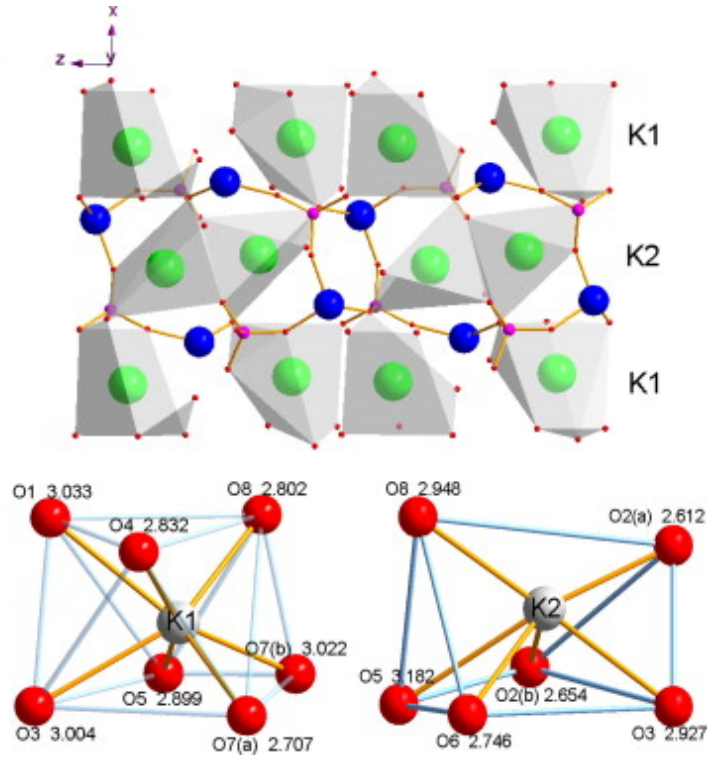

Figure 1.8: Crystal structure and coordination geometry of the $KMgPO_4$ with the inter-atomic distance of K (1) and K (2).

In this phosphor, there are two types of oxygen environment for the two magnesium atoms and this is the special outstanding feature of the $KMgPO_4$. The position of these two magnesium atoms shown in the fig. 1.8. in which the one Mg(2) located in the normal tetrahedron environment and other Mg(1) has five oxygen irregular environment in the crystal. Oxygen skeleton

is distorted by the irregularities of the Mg(1) in this phosphor. The diagram shows the seven and six folds coordination in which the two different sites K(1) O7 and K(2) O6 exists[15][16].

1.9 Aim of this research

1. To synthesize the single phase Sm^{3+} doped $KMgPO_4$ phosphor using conventional solid state method.

2. To study the structural, morphological properties by using X-Ray diffraction, FT-IR and SEM.

3. To study the photoluminescence properties of $KMgPO_4$:Sm^{3+} phosphor.

4. To calculate the chromaticity coordinates(x,y) using the photoluminescence spectra of the prepared phosphors.

5. To know the potential applications of this phosphor in solid state lighting applications and for white light LEDs.

Chapter 2

Synthesis and Characterization techniques

2.1 Sample Preparation

In this study, the Sm^{3+} doped $KMgPO_4$ phosphors were prepared by using conventional solid-state sintering. The starting materials potassium nitrate (K_2NO_3), magnesium carbonate ($MgNO_3.6H_2O$), ammonium dihydrogen phosphate ($NH_4H_2PO_4$) and samarium nitrate (Sm_2O_3 + HNO_3) powders were weighed in the stoichiometric ratio and ground in an agate mortar for 30 minutes. After drying, the mixed powders were placed in an alumina crucible and sintered in an muffle furnace. The samples first heated up to 100 °C for 2 h, 200 °C for 2h, 400 °C for 3h, 800 °C for 4h, and 1000 °C for 2 h. The products were quenched to room temperature. The Sm^{3+} doping concentration was fixed at the optimum value of 0.75 mol% in the $KMgPO_4$ host. The below figures shows the temperature profile and flow chart of sample preparation respectively.

2.1.1 Flow chart

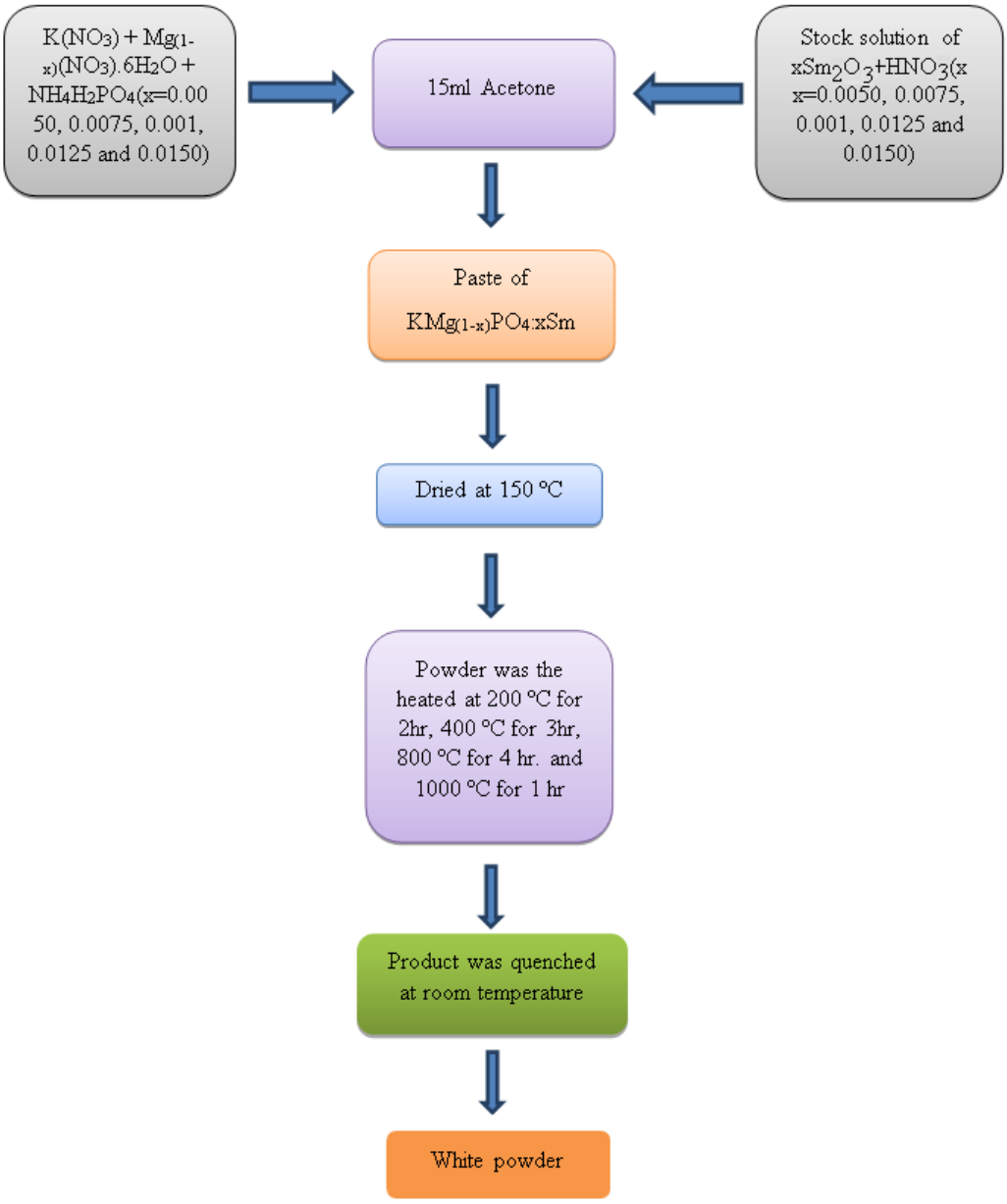

Figure 2.1: Flow chart of KMPT phoshor synthesized by solid state method.

2.1.2 Temperature Profile

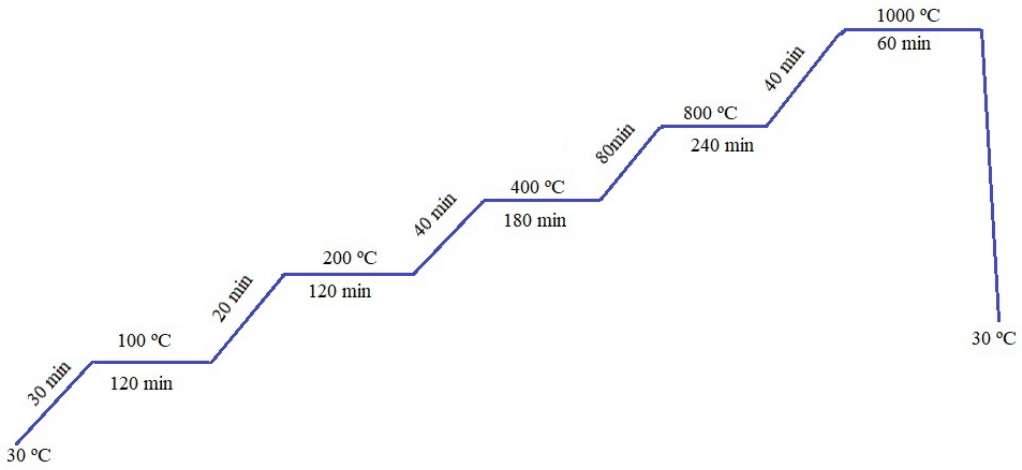

Figure 2.2: Temperature profile

2.2 Characterization techniques

The phosphors prepared by the solid state method were characterized by X-ray diffractometer, Scannig electron microscope(SEM), Spectrofluorophotometer and FTIR. The theory of these techniques with the experimental layout is discussed in this chapter. In this chapter different instruments used to study the properties of $KMgPO_4$ phosphor are described.

1. **X-Ray Diffractometer (XRD)):** X-Ray diffractometer is used to determine the phase of the phosphor and position of atoms in the crystal.

2. **Scanning Electron Microscope (SEM):** Scanning electron microscopy (SEM) is used to determine the morphology of surface and by using this determination of particle size is also calculated.

3. **Photoluminescence (PL):** photoluminescence-spectrofluorophotometer

is used to study the spectra of the phosphor which includes the emission, absorption, and excitation.

4. **Fourier-transform infrared spectroscopy (FTIR):** FTIR is utilized to determine the functional group in the given phosphor material along with infrared spectrum is also obtained.

2.2.1 X-Ray Diffractometer

Figure 2.3: XRD Machine

X-Ray diffractometer is extensively used to study the defects, crystal structure of solids and stresses. The diffraction is the type of Laue diffraction witch giving the coherent and incoherent scattering from the lattice. In XRD a

beam of the x-ray is diffracted by the crystal lattice and the wavelength of the beam is ranging from 0.07 to 0.2 nm.

The diffraction of the beam is given by the Braggs's law which states:

λ=2dsinθ

Here the d is the interplanar distance, λ is the wavelength of the x-ray beam and 2θ is the scattering angle from the specimens orientation. The obtained graph is used to analyze the crystalline and structural properties of the sample. The XRD does not require any detailed sample preparation because of non-destructive behavior.

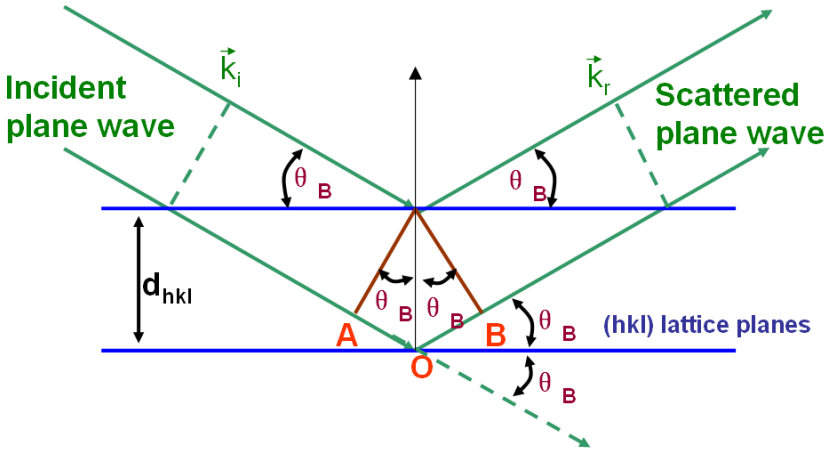

Figure 2.4: Bragg's law

Homogeneous and inhomogeneous strains in materials can be measured as X-ray intensity and are dependent on the Bragg angle. Uniform imperfection in the crystal solid diffracted the beam without changing the peak profile. A shift in the X-ray peak positions indicates a change in d-spacing caused by a change in crystal lattice constants. Irregular strains differ from crystallite to crystallite or even inside a solitary crystallite. Since XRD gives averaged information from all such crystallite volumes, it leads to broadening of the diffraction peaks, which increases with increase in sin θ. Peak broadening can also be due to the fine crystallite size, which is independent of sin θ. The contribution of crystallite size and lattice strain to peak broadening can be independently determined by peak profile analysis. In the absence of

inhomogeneous strains, the crystallite measure D can be evaluated from the peak width using Scherrer's formula.

$D = k\lambda / B\cos\theta_B$

Where,

λ = X-ray wavelength,

B = full width at half maximum (FWHM) height of a diffraction peak,

θ_B = diffraction angle also known as Bragg angle (in degree), and

K = Scherrer's constant (shape factor), which is of the order of unity for a spherical crystal and typical varies with the size of the crystalline.

In most cases, nanoparticles formed twin type structure and hence Scherrer's formula may not always give true particle sizes. It is also important to note that X-ray diffraction provides only an average crystallite size. The thickness of epitaxial and highly textured thin films can also be determined using XRD.

Due to lower energy of X-ray beam used, the X-ray diffraction intensities are low, particularly in case of low atomic number materials and hence, examine of phases with volume fractions is much difficult with XRD. Electron diffraction intensities are usually ∼108 times larger than that for XRD.[17]

2.2.2 Scanning electron microscopy

Scanning electron microscopy (SEM) is one of the most popular and widely used techniques for the characterization of nanomaterials and nanostructures. SEM can be effectively used to characterize specimens down to a resolution of few nanometers, with image magnification achievable in the range of 10 to over 300,000.

In addition to information on surface topography, SEM can also provide useful information on chemistry, crystal orientation, and internal stress distribution. SEM consists of an electron gun to emit electrons that are focused into a beam, with a very fine spot size of 5nm. Electrons are accelerated to energy values in the range of a few hundred eV to 50 KeV and rastered over the surface of the specimen by deflection coils. The working principle of the

Figure 2.5: ZEISS EVO-18 Scanning Electron Microscope

scanning electron microscope is shown in fig. 2.6.

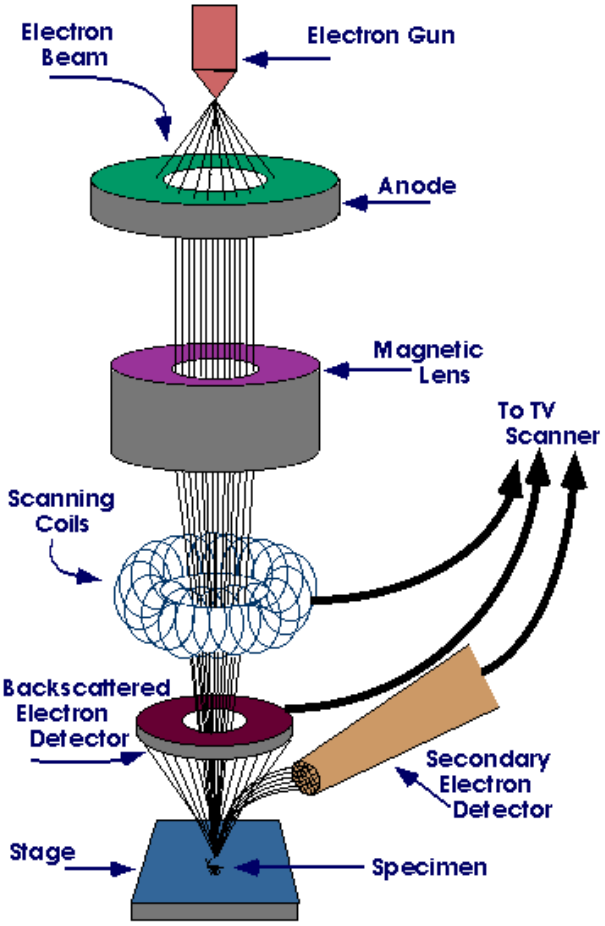

Figure 2.6: Working of Scanning electron microscope(SEM)

When an electron strikes to the sample then the emitted electrons and photons are emitted from the sample. The SEM image is formed by collecting these electrons and photon on a cathode tube ray (CRT). There are different techniques used in the SEM imaging depending upon what is detected and imaged. The principle image of the SEM image is produced by three types of electrons: secondary electron image, backscattered electron image, and elemental X-ray electron image[18].

2.2.3 Photoluminescence (PL)

Photoluminescence spectrofluorophotometer measure the energy conveyance of electrons produced by iotas and particles in different charge and energy expresses a compound irradiates with the xenon lamp source (150w) can transmit electrons called photoelectrons from atomic energy levels with a dynamic energy equivalent to the distinction between the photon energy hvph and the ionization energy Eion which is the energy required to totally expel an electron from a atomic energy level[19].

2.2.4 Instrument details

In the present study, RF-5301pc Spectrofluorophotometer instrument was used for the optical characterization of the samples. The setup of RF-5301pc spectrofluorophotometer which is used in this experiment to determine the emission and excitation spectra is shown in fig. 2.7.

Figure 2.7: Setup of the RF-5301pc Spectrofluorophotometer

The ray diagram of the working spectrofluorometer is drawn in the below

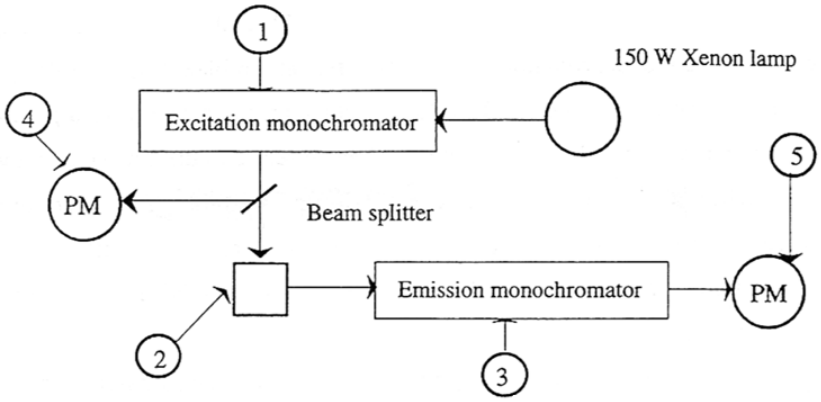

Figure 2.8: Ray diagram of RF-5301pc Luminescence Spectrofluorophotometer

figure. The excitation source used in this instrument is a xenon (150w) lamp. To start with testing a sample first switched on the xenon light and energy released by the source is focused onto the excitation monochromator with the help of a spherical mirror. Most of the part of the excitation beam is transmitted to the sample and this cause excitation of the sample and energy emitted from it once again focused onto the emission monochromator by the spherical mirror.

The angles of the gratings used in the excitation and emission monochromators are controlled by stepper motors. The emitted light is detected by a sensitive Photomultiplier tube (PMT) with high signal to noise ratio. The operation is software controlled. The excitation and emission wavelength (or range of excitation wavelengths in case of PL Excitation spectra or emission wavelength in case of PL emission spectra), the excitation and emission slit width and wavelength scan speed can all be controlled through software. The resultant PL spectra are shown on a computer screen which can be saved and printed.

1. Cell holder unit

2. Excitation monochromator unit

3. Emission monochromator unit

4. Photomultiplier tube of monitor side

5. Photomultiplier tube of fluorescence side

The range of the excitation and the emission monochromators can be selected independently according to the desired points of scan range. The monochromators have the following spectral range

1. Emission monochromator, which has ranged from 220 nm to 900 nm

2. Excitation monochromator, which has ranged from 220 nm to 900 nm

In this experimental work, the emission and excitation spectra are obtained by keeping the excitation source (Xe lamp) on at room temperature.

2.2.5 Furnace

Figure 2.9: High temperature furnace

The furnace used in this experimental work is muffle type furnace. The furnace is microcontroller based to precisely control the temperature during the solid state reaction. The furnace is working on the principle of Joule heating in which the resistant wire is used to produce the heat in a controlled manner. The setting button of parameters is accessible on the front side of the furnace.

Chapter 3

Results and Discussion

3.1 XRD pattern Analysis

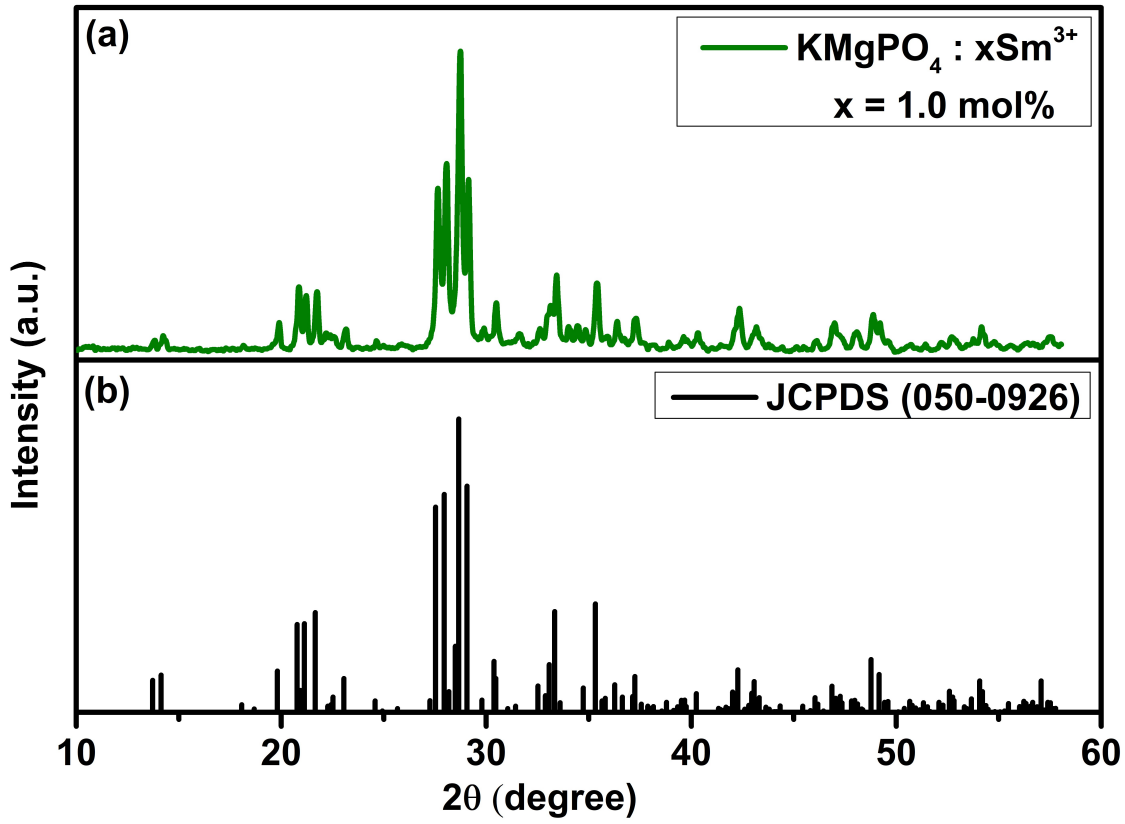

Figure 3.1: XRD spectra of (a) $KMgPO_4$:Sm^{3+} (0.75 mol%) Phosphor (b) $KMgPO_4$ JCPDS Card No.(050-0926).

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The synthesized $KMgPO_4$:0.75% Sm^{3+} sample was characterized by powder X-ray diffraction. The measurements were carried with CuKα radiation (1.5406Å). The XRD patterns shown in fig. 3.1 were analyzed and found to be in good agreement by comparing with the JCPDS card No. (050-0926). It is also observed that crystalline phase of the $KMgPO_4$ phosphor is approximately close (a=8.549, b=5.078 and c=18.996) and the prepared sample is structurally and chemically same to the $KMgPO_4$ phosphor. The average crystallite size calculated by using Scherrers relation: d=$0.9\lambda/\beta\cos\theta$, where λ is the wavelength of X-rays, β is the corrected full width at half maxima and θ is the scattering angle.

3.2 SEM image

Scanning electron microscopy has been used to study morphology and particle size of the phosphor powder for the $KMgPO_4$:0.75% Sm^{3+} phosphor. The particles in the SEM image appear to be highly crystalline with agglomeration nature as shown in fig. 3.2. The particle size for the phosphor powder falls in the range from sub-micrometers to micrometers.

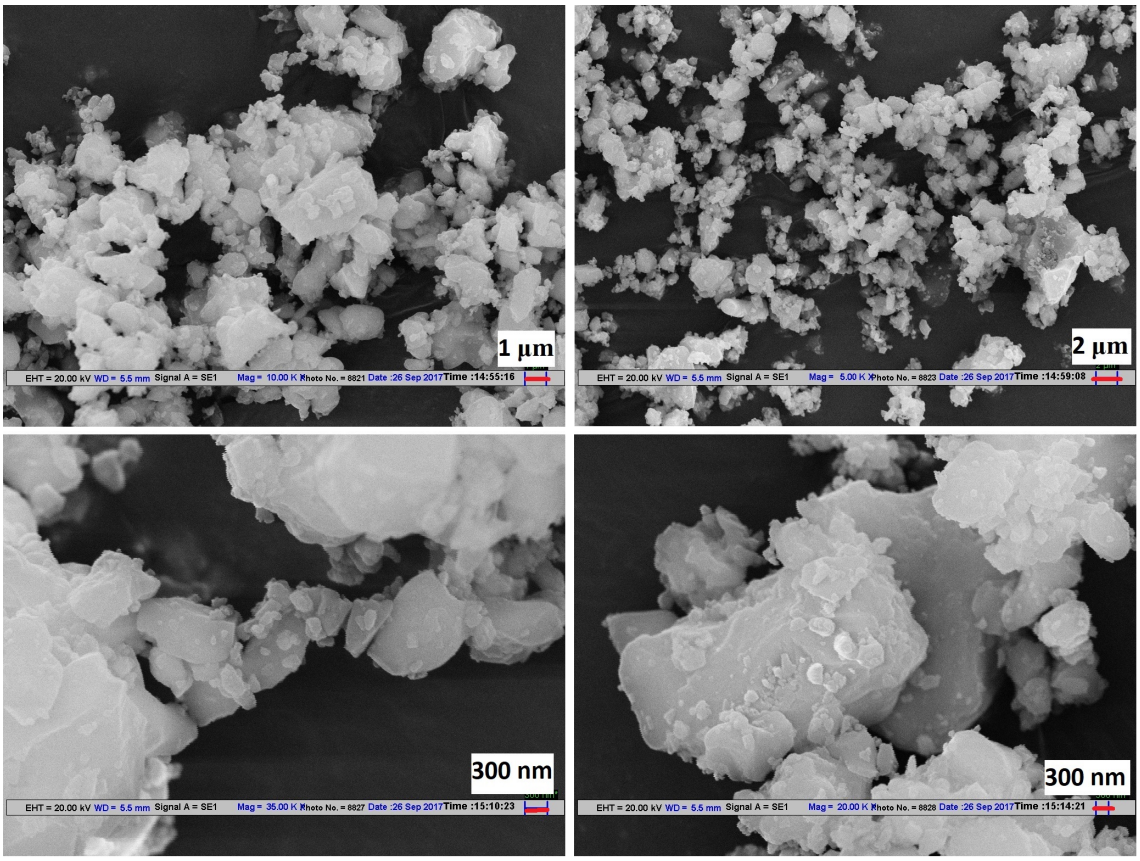

Figure 3.2: SEM Images of $KMgPO_4$ phosphor

3.3 Fourier-transform infrared spectroscopy (FTIR)

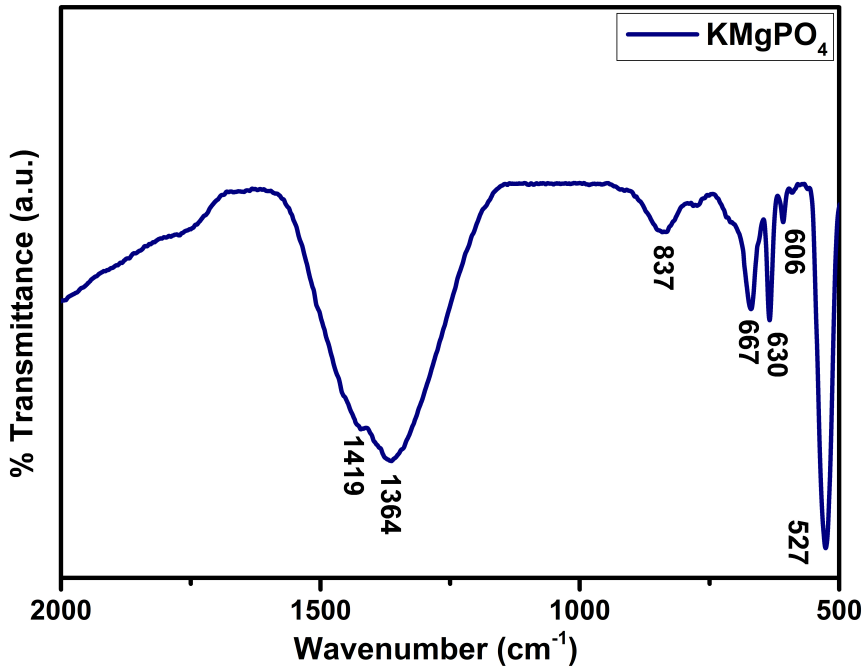

Figure 3.3: FT-IR Spectrum of $KMgPO_4$

From fig.3.3, it was observed that $KMgPO_4$ phosphor exhibit characteristic peaks in FT-IR spectra, since they have distinguishing positions of the absorption bands occurred due to vibrations of water of crystallization, tetrahedral PO_4^{3-} units and metal oxygen bonds. The medium intense bands appeared nearly at 1364 cm^{-1} and 1419 cm^{-1} in the spectrum indicate the H-O-H bending modes of vibrations suggesting the presence of water [40]. A medium absorption band at 606.68 cm^{-1} indicates the wagging modes of vibration of the coordinated water and the Metal-Oxygen bond in the complex.

Many common compounds exhibit the unique spectra which extend from 400 cm^{-1} to 4000 cm^{-1}.Fourier-transform infrared spectroscopy (FTIR) spec-

tra of this compound were interpreted on the basis of PO_4^{3-} vibrations. In the FT-IR spectrum, the v1 symmetric stretching vibration of tetrahedral PO_4^{3-} anions was found at medium band 606 cm^{-1}. The position of the symmetry vibration is dependent on the crystal, cations present, and type of material. While the asymmetric stretching vibration v3 of phosphate anions in the material were found between 667 cm^{-1} and 837 cm^{-1}. Similarly the asymmetric bending vibration v4 of PO_4^{3-} were observed at 527 cm^{-1}.so it is concluded that the v1 and v3 described the symmetric and asymmetric stretching of the P-O bonds, while the v2 and v4 contain only O-P-O symmetric and asymmetric with a small effect of P vibration[12]. Thus, the FT-IR spectra of $KMgPO_4$ phosphor prove the presence of water of hydration, P-O bond and PO_4^{3-} ion and metal-oxygen bond.

3.3.1 Excitation spectra

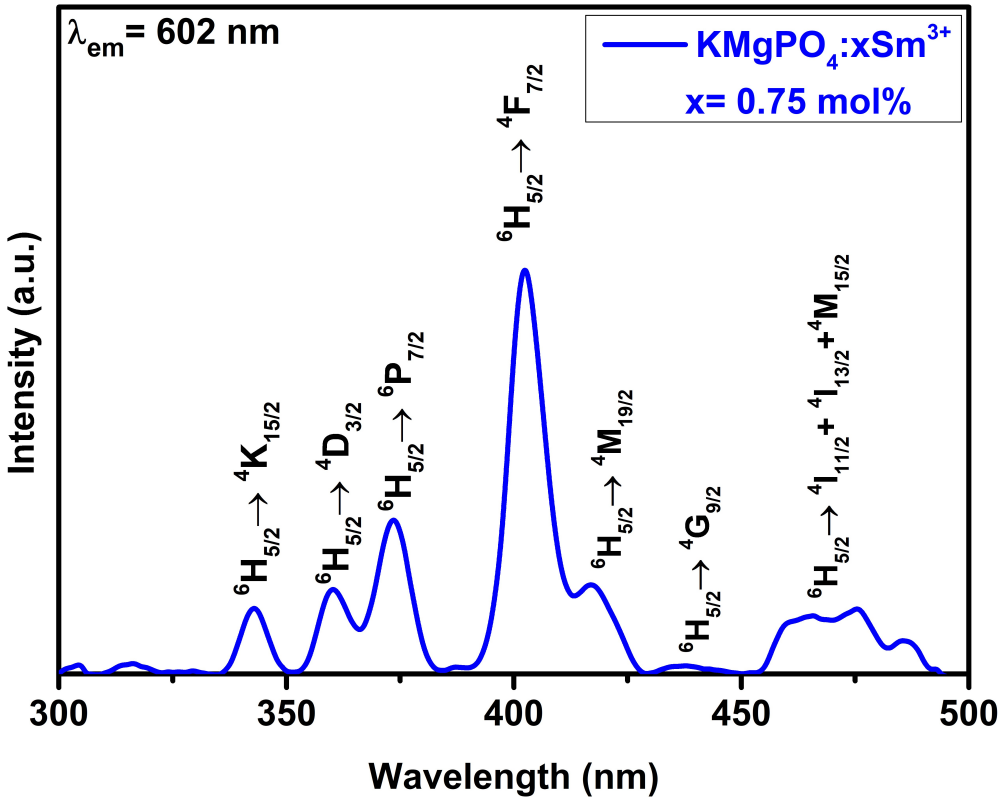

Figure 3.4: Excitation spectrum measured with the emission monitored at 602nm

3.3.2 Emission spectra

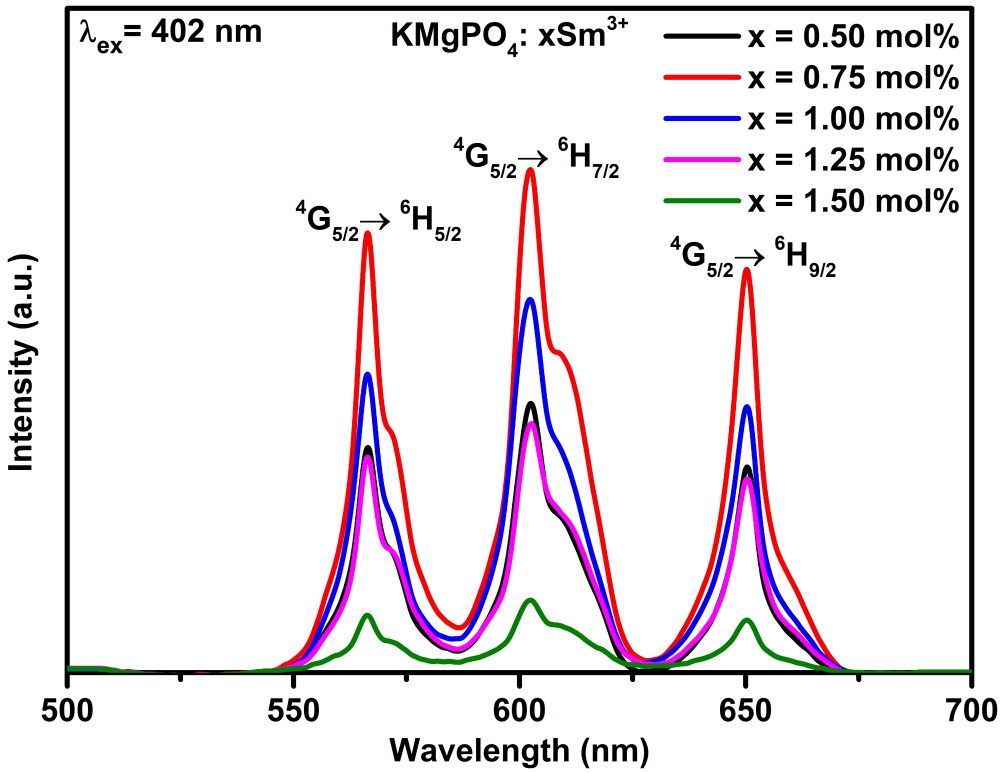

Figure 3.5: Emission spectra excited at 402 nm of $KMgPO_4$:xSm^{3+} phosphors with diffrent concentrations of Sm^{3+} ions (x=0.005, 0.0075, 0.001, 0.0125 and 0.0150)

Photoluminescence excitation and emission spectra are shown in figures 3.4 to 3.5 respectively. The emission spectra of the $KMgPO_4$ phosphor is recorded with the 402 nm excitation wavelength and the emission spectra are recorded by monitoring at 602 nm emission wavelength. It is observed from the emission spectra that there are three peaks which denote the de-excitation of $^4G_{5/2}$ level of Sm^{3+} ions to its lower multiples of ^6H_J; where J is 5/2, 7/2 and 9/2. For all emission spectrum, the emission bands are observed in the 550-700 nm spectral region.

Among the excitation wavelength, the 402 nm was the intense band compared to the other and this wavelength selected as the ideal wavelength

for the excitation. Fig. 3.5 shows the emission spectra at λ_{ex}=402 nm of $KMgPO_4$:xSm^{3+}(x=0.5, 0.75, 1.0, 1.25, and 1.50 mol %). Spectra show the emission peaks at the 565 nm, 602 nm, and 652 nm which corresponds to the $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$ and $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition respectively. These peaks are related to the different moment involved in the $KMgPO_4$:xSm^{3+} phosphor. These moments are the magnetic dipole moment, electric dipole moment and combine magnetic and electric dipole moment. The emission peak observed at the 565 nm($^4G_{5/2} \rightarrow {}^6H_{5/2}$) is due to the purely magnetic dipole moment. Similarly, second emission peak at the 602 nm($^4G_{5/2} \rightarrow {}^6H_{9/2}$) is due to the purely electric dipole moment and the third emission peak observed at the 652 nm ($^4G_{5/2} \rightarrow {}^6H_{7/2}$) due to the both electric and magnetic dipole moment[20]. To understand the symmetry of this phosphor it is required to find the ratio of magnetic dipole moment to the electric dipole moment. The maximum intense peak observed due to the magnetic dipole moment so there is no deviation from the inversion center and this suggests that symmetrical arrangement of atoms in the material. Cross-relaxation found in the material due to the closeness of the Sm^{3+} ions and this gave the optimal quenching at beyond 0.75mol%, when Sm^{3+} doping increasing then there are great possibilities that improvement in the energy exchange of Sm^{3+} ions inside the material.

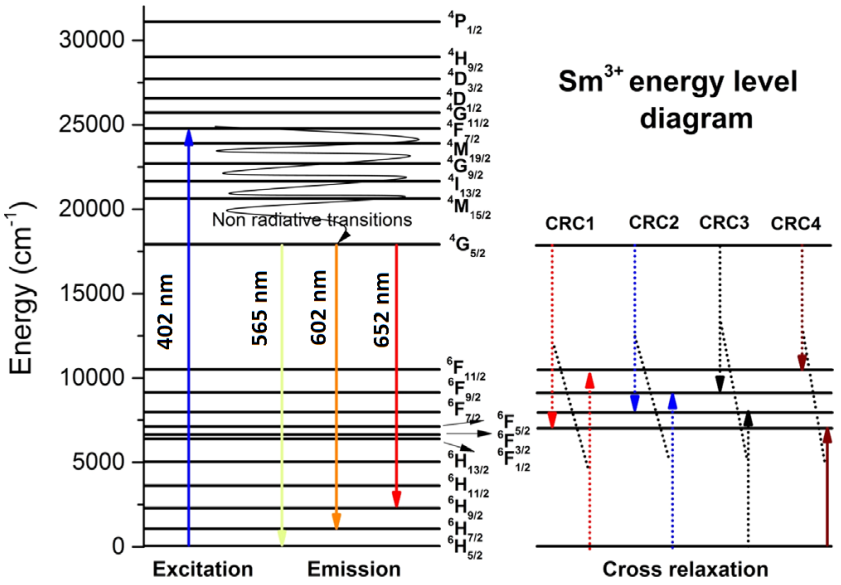

Figure 3.6: Partial energy level diagram and cross relaxation channels of Sm^{3+} ions.

Nonradiative radiation occurs in the material depends on the different factors namely exchange cooperation, radiation re-retention, and multipolar activity. These activities occur between the rare earth materials.The partial energy level diagram of the Sm^{3+} ions in $KMgPO_4$ phosphor is shown in the figure. When the populated is energized to the $^4F_{7/2}$ by the 402 nm wavelength then the underlying populace is relaxed to the $^4G_{5/2}$ level which is non-radiative relaxation of the Sm^{3+} ions in the $KMgPO_4$ phosphor. It is observed from the partial energy level diagram that there are small energy levels between the $^4F_{7/2}$ to $^4G_{5/2}$ which leads to the non-radiative transition. This non-radiative transition is isolated from the underlying energy level $^4F_{7/2}$. According to this, it is cleared that there is two principle relaxation (radiative transition and non-radiative transition by energy exchange) which could drain the $^4G_{5/2}$ state to lower level ground state. Sm^{3+} doped $KMgPO_4$ phosphor exhibit cross relaxation as shown in the above figure. The cross relaxation in this phosphor are as follow: CRC1:($^4G_{5/2}$+$^6H_{5/2}$) → ($^6F_{5/2}$+$^6F_{11/2}$), CRC2:($^4G_{5/2}$+6H5/2) → ($^6F_{7/2}$+^{6}F9/2), CRC3:($^4G_{5/2}$$^6H_{5/2}$) → ($^6F_{9/2}$+$^6F_{7/2}$) and CRC4:($^4G_{5/2}$+$^6H_{5/2}$) → ($^6F_{11/2}$+$^6F_{5/2}$)[21].

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3.4 Peak intensity at different Sm^{3+} concentration

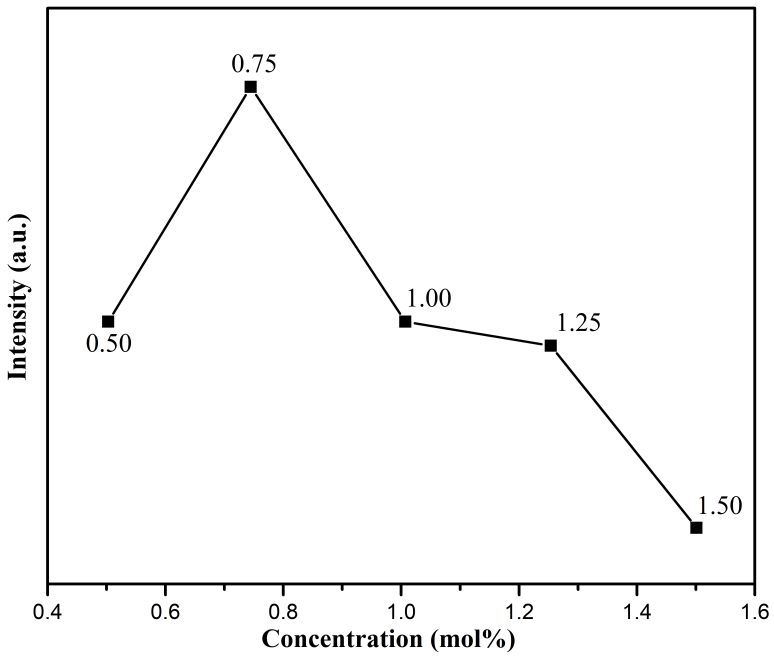

Figure 3.7: The relationships between the intensity of the emission peak and Sm^{3+} ion concentrations

It is observed from the graph that there is no shift in the band position of the excitation and emission spectra of the phosphor and the only change in the intensity of the peaks. The intensity of the peaks increase or decrease with a change in the concentration of the Sm^{3+} ion in the host material. The maximum intensity is achieved at the 0.75% concentration and beyond this limit, the quenching process starts and emission intensity begin to decrease.

3.5 CIE Diagram

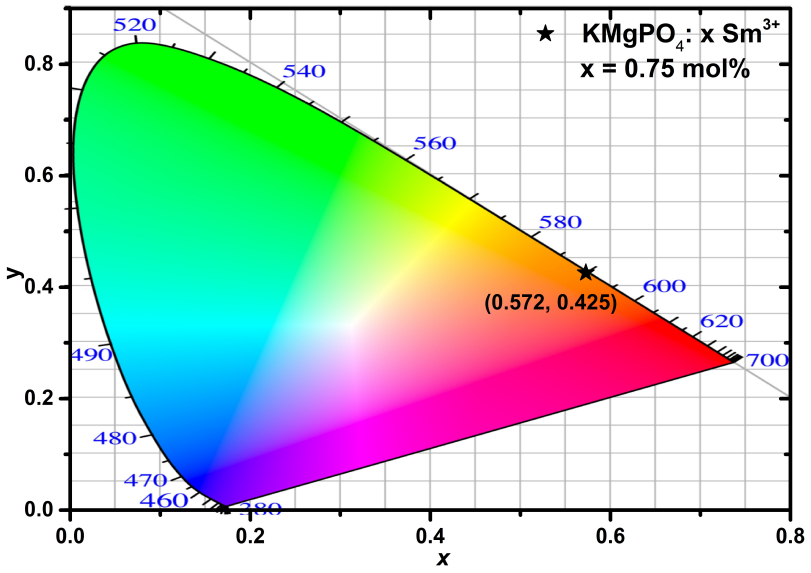

Figure 3.8: Chromaticity coordinates for Sm^{3+} doped $KMgPO_4$ phosphor in CIE chromaticity diagram.

The Commission Internationale de L'Eclairage(CIE) chromaticity coordinates calculated for $KMgPO_4$:0.75 Sm^{3+} phosphors are indicated in fig. 3.8. The emission color analyzed with the help of CIE Coordinates. The calculated CIE chromaticity are found to be (0.572, 0.425) under 402 nm excitation as indicated in fig. 3.8, which is close to the standard orange chromaticity for the national Television Standard Committee(NTSC) system. It is observed from fig. 3.8 that the (x,y) chromaticity coordinates located in pure orange region and the calculated color purity to be 99% which confirms the pure emission of orange light from $KMgPO_4$:0.75Sm^{3+} phosphor. The advantage of this phosphor is that this material can be used in Near-UV based blue-cyan-orange white LEDs.

Chapter 4

Conclusions

In conclusion, Sm^{3+} doped $KMgPO_4$ phosphors were successfully synthesized by using conventional solid state reaction method. SEM analysis indicates that these phosphor powder particles are agglomerated and vary from sub-micrometers to micrometers. The XRD pattern of the $KMgPO_4$ phosphor well matched with the JCPDS card no. (050-0926). It is also observed that this phosphor effectively excited by the 402 nm wavelength and the intense peak of the emission spectra is obtained at 602 nm. The luminescent properties were carried out for different Sm^{3+} concentrations to know the optimized doping concentration and found to be 0.75 mol% of Sm^{3+}. Excitation with 402 nm, the phosphor shows one broadband emission at 602 nm related to the 4f- 4f transitions of Sm^{3+}. The FT-IR spectra of $KMgPO_4$ phosphor prove the presence of P-O bond and PO_4^{3-} ion and metal-oxygen bond. The CIE chromaticity coordinates results show that these phosphor samples emit red-orange light color with chromaticity coordinates (0.64, 0.34) close to NTSC standards under the 402 nm excitation which will be useful for NUV-based white light emitting diodes. Hence, Sm^{3+} doped $KMgPO_4$ phosphor is a potential candidate for the solid-state lighting applications.

Chapter 5

Future Work

1. New various synthesis roots will bw explored to enhance the emission intensity of the phosphor.

2. Since the phosphor has excitation at 402 nm, it could be blended well with the commercial yellow emitting phosphor, covered onto a thin glass substrate, illuminated using blue-transmitting LED and ascertain the enhanced emission of color rendering index in WLEDS.

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