SYNTHESIS, MORPHOLOGY AND LUMINESCENT PROPERTIES OF RARE EARTH IONS DOPED TUNGSTATE PHOSPHORS FOR PHOTONIC APPLICATIONS

A Thesis Submitted

In Partial Fulfilment of the Requirements for the

Degree of

MASTER OF SCIENCE

In

PHYSICS

by

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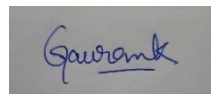(Formerly Delhi College of Engineering)
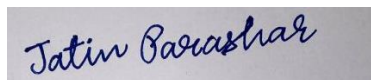Bawana Road, Delhi – 110042, India
June, 2024

CANDIDATE'S DECLARATION

I hereby certify that the work, which is presented in the Dissertation-II entitled **"Synthesis, Morphology and Luminescent Properties of Rare Earth ions doped Tungstate Phosphors for Photonic applications"** in partial fulfillment of the requirements for the award of the Degree of Master of Science in Physics, submitted to the Department of Applied Physics, Delhi Technological University is an authentic record of our own work carried out during a period from June 2023 to May 2024, under the supervision of **Prof. A.S Rao.**

The matter presented in the thesis has not been submitted for the award for any other course/degree of this or any other Institute/University.

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This is to certify that the student has incorporated all the corrections suggested by the examiners in the thesis and the statement made by the candidate is correct to the best of our knowledge.
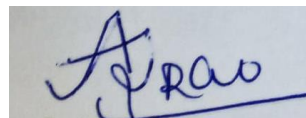
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<u>CERTIFICATE</u>

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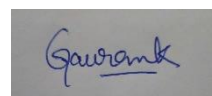
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ABSTRACT

In the realm of phosphor materials, the quest for highly efficient luminescent materials continues to drive research efforts. This work report gives a comparative analysis of the influence of different rare earth ions (Dy^{3+}, Sm^{3+}, and Eu^{3+}) on the luminescence properties of tungstate ($CaGdSbWO_8$:CGSW) phosphor material. The rare earth ion-doped tungstate phosphors were synthesized by a high-temperature solid-state reaction method and were systematically investigated and compared to understand their crystal structure, band gap, photoluminescence (PL) properties, and Commission International del'Eclairage (CIE).The X-ray diffraction (XRD) data well matched with the JCPDS (PDF#00-064-0231), and confirms the pure phase and crystallinity of the prepared phosphors. The band gap was calculated for the tungstate host doped with Dy^{3+}, Eu^{3+}, and Sm^{3+} ions using diffuse reflectance spectra (DRS).The PL result shows that Dy^{3+} can be excited over a broad range from 240to 480nm. Whereas, Eu^{3+} has an excitation range of 230to 545nm and Sm^{3+} has a range of 240 to 500nm. Under the 277nm excitation, Dy^{3+} shows the emission characteristic in the nearly pure white region whereas, Sm^{3+} shows the emission in the orange-red region when excited by using 273nm wavelength and finally Eu^{3+} shows the emission in deep-red region after exciting by 275nm wavelength. The CIE chromaticity coordinates of Dy^{3+}, Sm^{3+}, and Eu^{3+} ions confirm their emission in individual colour regions. The results obtained from the present study indicate the suitability of tungstate phosphors doped with Dy^{3+}, Sm^{3+}, and $Eu^{3+}$for various visible photonic applications.
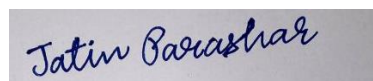
ACKNOWLEDGEMENTS

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LIST OF RESEARCH WORK AND PUBLICATIONS

(1) Title of the Paper (I): "Comparative luminescence studies of phosphors based on tungstate host doped with Dy^{3+}, Sm^{3+} and Eu^{3+} ions."

Author(s): Gaurank Yadav, Jatin Parashar and A S Rao.

Name of Conference: International Conference on Atomic, Molecular, Material, Nano and Optical Physics with Applications (ICAMNOP-2023)

Date and venue: December 20th-22nd (2023), Delhi Technological University.

Have you registered for the conference? Yes

Status of paper (Accepted/Published/Communicated): Accepted

Publish in: Springer Conference Proceedings (Scopus Indexed)

Date of paper communication: 20th March, 2024

Date of paper acceptance: 6th June, 2024

(2) Title of the Paper (II): "Synthesis, Structural and photoluminescence characteristics of Dy^{3+}/Eu^{3+} co-doped $CaGdSbWO_8$ phosphor for colour tunable white LEDs."

Author(s): Gaurank Yadav, Jatin Parashar, Anu Mor and A S Rao.

Journal: Crystal research and technology, Willey

Status of paper (Accepted/Published/Communicated): Communicated

Date of paper communication: 19th March, 2024

Date of paper acceptance: -----

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LIST OF ABBREVIATIONS

LED   -   Light-emitting diode

w-LED   -   White Light Emitting Diode

SSL   -   Solid State lighting

RE   -   Rare Earth (Metals)

CCT   -   Correlated Colour Temperature

CRI   -   Colour rendering index

JCPDS   -   Joint Committee on Powder Diffraction Standards

XRD   -   X-ray Diffraction

SEM   -   Scanning Electron Microscope

FWHM   -   Full Width at Half Maximum

CIE   -   Commission International De L' Eclairage

UV   -   Ultraviolet

PL   -   Photoluminescence

PLE   -   Photoluminescence Excitation

CHAPTER 1
INTRODUCTION

CHAPTER 1: INTRODUCTION

1.1 Phosphor

Solid materials called phosphors release light when they come into contact with radiations like electron beams, infrared or ultraviolet light. There are many phosphors and each phosphor has its own characteristic like emission of colours and the duration of glow. The word phosphors have been utilized since the 17th century, when an alchemist name Vincentinus Casciarolo in Bologna, Italy discovered a crystalline stone near a volcano. After exposure to sunlight, the stone emitted light in the red colour region in the dark, the name given to the stone was "Bolognian stone". The stone that was discovered was later found out to be barite ($BaSO_4$), and the outcome of the firing was BaS which is now recognised as a host for phosphor compounds. After this, there were many similar light emitting stones were found all across the Europe, the term phosphor were given to them derived from Greek word meaning "light bearer".

Phosphors are composed of composites such as oxide, oxynitride, sulfide, selenide, halide, borates, and oxyhalide, which are doped with minute amounts of activator ions. These activator ions may be rare-earth or transition element ions. The activator ions function as radiation or light centres, with various energy levels that can be activated or transferred [1, 2].

The energy absorption and emission phenomena have distinction which can be classified into two mechanisms [3]:

Up conversion: In this mechanism the photons of lower frequencies like IR are converted into photons of higher frequencies usually in visible regions. This phenomenon is also known as anti-Stokes emission [4, 5].

Down conversion: In this mechanism the photons of higher frequencies like UV or n-UV are converted into photons of lower frequencies usually in visible and IR region. This phenomenon is also known as Stokes emission [6].

A phosphor's efficiency is determined by its capacity to use excitation energy and emit light. To reduce afterglow, it is critical to reduce the duration between excitation and emission. The absorption of energy can occur at the activator ion or elsewhere in the lattice, but it must eventually be delivered to the radiating core before emission can occur[7]. The absorbed energy can also be dispersed using radiation-free mechanisms, resulting in a loss in quantum efficiency. Effective phosphors retain their ions, reducing energy loss from non-radiative transitions. Contaminant ions can absorb or redirect energy, reducing the material's luminous qualities [8].

Phosphor materials are assessed according to key parameters, such as the variety of emitting colours (e.g., red, green, and blue), lumen equivalence, PL spectrum, quantum yield, and emission longevity. The colour points are determined by dividing the energy of the emission spectrum using the graphical rule of the Commission Internationale de l'Eclairage (CIE). A greater luminosity count signifies a more intense light, therefore phosphors ought to possess a higher lumen equivalence. A PL spectrum of electromagnetic radiation is produced when an atom or molecule experiences a transition from a state of greater energy to a state of lower energy. To be economically viable, phosphors must possess a prolonged emission lifespan. Decay time, sometimes referred to as afterglow or persistence, is the duration for the emission intensity to reduce to 10% of its original intensity after stimulation stops. The decay time is dictated by the inherent characteristics of the phosphor substance [9]. Phosphor materials has a huge number of applications like light emitting diode (LEDs), bio imagining, thermal sensors and other optical devices.

1.2 Host matrix

Phosphors convert energy from sources of excitation, like X-rays and UV radiation, into visible light. Phosphorus can be categorized into three types [10]:

(a) Host luminophore: This type phosphors contain active centres itself which absorbs the incoming radiation and also emits the radiation. Inorganic hosts exhibit favourable characteristics such as being physically, thermally, and chemically inert, which makes them highly suitable choices. Nevertheless, self-activated hosts are more desirable than inorganic hosts due to their ability to generate powerful and wide-ranging visible radiation when exposed to UV light [11, 12, 13].

(b) Host + activator: In this type of phosphors they have a host matrix and an activator, which functions as the emitting centre. In this category the host are inactive but having luminescent active centres. The activator utilizes the intrinsic radiation to amplify the emission intensity [14, 15].

(c) Host + sensitizer + activator: Phosphors of this category has a sensitizer which absorbs the incoming radiation, then the transfer of energy happens from sensitizer to activator in the host. Due to sensitizer there is an enhancement in the luminescent properties of the materials [16, 17].

1.3 Luminescence and its type

After the discovery of phosphors in 17th century every researcher were starting to do research to find various methods for luminescence and the reason behind them. Luminescence is a phenomenon of emission of radiation from a material not from heat. The material absorbs the incident radiation and re-emit the radiation in different wavelength resulting in luminescence. Excitation process in phosphor can occur due

to various methods like electricity, heat, mechanical force, chemical reaction etc. Luminescence can be seen on are day to day life like in lamps, television or smart phone screens etc.

From the different sources of excitation the luminescence phenomena can be divided into various categories [18, 19]:

(a) Photoluminescence: In photoluminescence the excitation of electrons happens when electromagnetic radiations incident the surface of the phosphor. It can be classified into two different types depending upon the process – Phosphorescence and Fluorescence. (Explained in sec 1.3.1)

(b) Chemoluminescence: In chemolminescence the emission of light occurs due to chemical reaction. There is no involvement of heat in this process and it does not requires any external light, it is self-contained within the chemical system. The emission of light is basically due to electronic transition within the molecules which are involved in the chemical reaction. Fireflies are a widely recognized instance of living organisms that demonstrate chemiluminescence. Luciferase, an enzyme, facilitates a chemical interaction between luciferin and oxygen, resulting in the release of light. Luminol, a chemiluminescent chemical, is utilized in forensic investigations to identify the existence of blood at crime scenes [20].

(c) Bioluminescence: It is a type of luminescence which arises from living organisms through chemical reactions. It can be seen in various organisms like in bacteria, fungi, insects and deep see fishes [21].

(d) Thermoluminescence: Thermoluminescence is the process by which certain materials, after being exposed to ionizing radiation, emit light when heated. This procedure is frequently employed in the fields of archaeology and geology for dating purposes, as well as in dosimetry to quantify radiation exposure. The fundamental concept is that some minerals and substances gather energy from ionizing radiation gradually, and this stored energy is released as light when the material is heated [22].

(e) Electroluminescence: In this method the luminescence occurs by the action of electric field on the phosphor. Like in LEDs the electron hole pair recombination results in the luminescence. When the luminescence occurs due to free electrons then it is called cathodoluminescence [23].

(f) Radioluminescence: Radioluminescence is the emission of visible light by some materials when they are exposed to ionizing radiation. This process is not the same as thermoluminescence, which is the process of a material emitting light upon heating after being subjected to ionizing radiation. Radioluminescence is the direct emission of light resulting from the interaction with ionizing radiation [24].

(g) Mechanoluminescence: Luminescence happens due to any type of mechanical action happens on the phosphor [25].

(h) Piezo-luminescence: When pressure is exerted on the substance, the luminescence happens, this method is called piezo-luminescence [26].

1.3.1 Understanding Photoluminescence through Jablonski diagram

Photoluminescence is the process by which a substance absorbs photons, or packets of light energy, and subsequently emits light. This phenomenon occurs when the material is subjected to light of a specific wavelength, resulting in the emission of light at a longer wavelength. Fundamentally, the substance assimilates energy from photons and emits it as light. Photoluminescence can be categorized into two primary forms: phosphorescence and fluorescence. These can be explained very simply through jablonski diagram.

Phosphorescence: Phosphorescence is the process by which substances continue to produce energy and glow even after the radiation source has been shut off. This glow gradually diminishes in brightness over a period of milliseconds to days. This phenomenon can arise when two excited states with different total spin exhibit similar energy levels. The ground state and one of the excited states are shown in the graphic as singlets (S=0), while the following excited state is shown as a triplet (S=1). Although spectroscopic transitions between singlet and triplet levels are forbidden by the rule $\Delta S=0$, there is no constraint if the excited states are transferred kinetically, that is, through radiationless transitions produced by collisions. Transfer between the two potential curves can only happen around the cross-over point. The molecule cannot return to the excited singlet state once it enters the triplet state and begins to lose vibrational energy. As a result, it will eventually arrive at the triplet state's level of zero velocity (υ'=0). Despite being technically forbidden by spectroscopic constraints, a transition from the present state to the ground state can nonetheless happen, albeit much more slowly than an electronic transition that is permitted. Phosphorescent materials have the ability to emit radiation for a prolonged period of time, ranging from seconds to minutes or even hours, after they have absorbed energy. The phosphorescence spectrum typically comprises of frequencies that are lower than those absorbed.

Fluorescence: Fluorescence is the process in which substances generate energy promptly and cease glowing when the stimulating radiation is deactivated. The phenomenon can be elucidated by a diagram, where the molecule, following electronic excitation, is in a highly vibrational state. In this state, any surplus vibrational energy can be dissipated through intermolecular collisions. The conversion of vibrational energy into kinetic energy in the sample results in the generation of heat. This movement of energy across different levels without the emission of radiation is known as "radiationless". Once the excited molecule transitions to a lower vibrational state, it releases radiation and returns to its ground state. This emitted radiation, known as the fluorescence spectrum, typically has a lower frequency than the absorbed radiation. However, in certain circumstances, it can have a higher frequency. The duration from

when the substance is first absorbed to when it returns to its original state is extremely brief, approximately on a scale of 10-8 seconds.
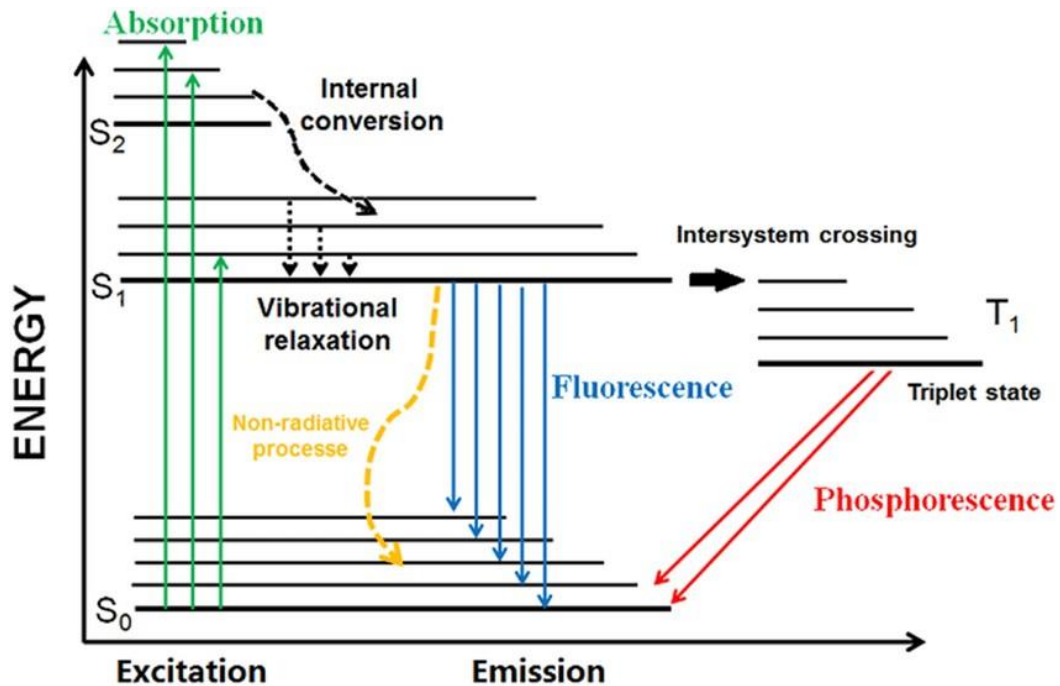

Fig 1.1: Jablonski diagram

1.4 White light emitting diodes (w-LEDs)

LEDs are a notable technological advancement of the twentieth century, offering environmentally friendly and energy-efficient artificial lighting. White LEDs, also known as w-LEDs, are the latest advancement in solid-state lighting (SSL) technology. They provide several advantages such as energy efficiency, dependability, increased output, long lifespan, high luminous efficiency, and eco-friendliness. Typically, w-LEDs are produced by utilizing optical excitation sources that have phosphor coatings. Nevertheless, in phosphor converted (pc) white light emitting diodes (w-LEDs), the epoxy-resin sealant deteriorates under elevated temperatures, resulting in a negative impact on both luminous efficiency and colour rendering index (CRI).

Significant study has been conducted on luminous materials doped with rare earth (RE) due to recent improvements in SSL technologies. A significant proportion of industrial energy is allocated to lighting, underscoring the importance of energy-efficient and eco-friendly solutions. SSL, which utilizes LEDs with p-n junctions, fulfils these requirements by offering advantages such as high luminous efficacy, low power dissipation, durability, and extended operational lifespan [27]. Presently, w-LEDs predominantly utilize blue-emitting diodes with a wavelength range of 450-470 nm to stimulate YAG:Ce phosphors, resulting in the emission of yellow light. However, this

approach does not include the red component, resulting in a low Colour Rendering Index (CRI) and a high Correlated Colour Temperature (CCT) [28]. Another option is to utilize an n-UV LED chip combined with RGB phosphors, although ensuring the accurate colour ratio can be difficult and expensive [10].

In order to tackle these problems, it is more economically efficient to introduce doping with a solitary rare earth ion, such as Dysprosium (Dy^{3+}), which exhibits emission bands in the blue and yellow areas. Dysprosium-doped phosphors generate white light with exceptional quantum efficiency, thermal stability, affordability, and favourable CIE and CCT values [29]. In order to achieve efficient white light emitting diodes (w-LEDs), it is necessary to take into account several factors such as semiconductor components, energy conversion, luminescence, and packaging technologies. The main difficulties in creating solid-state lighting (SSL) with fluorescent materials are attaining a high colour rendering index (CRI) and a good correlated colour temperature (CCT), all while preserving luminous efficiency and thermal stability. There are three primary methods for producing white light with LEDs: employing blue LEDs with YAG:Ce phosphor, utilizing n-UV LEDs with RGB phosphors, and employing single-phase component phosphor used with UV or n-UV LEDs [30]. The latter is attracting attention because of its reliability, efficiency, low energy usage, and environmentally friendly production. The advancement of w-LED applications relies heavily on the development of co-doped RE on single-phase phosphors. Ongoing research is focused on enhancing luminescence performance by employing charge compensation and ion replacement techniques [31, 32].
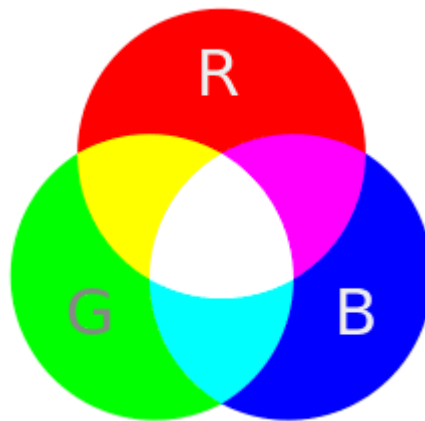

Fig 1.2: White Colour generation through Red, Green and Blue.

1.4.1 Properties to consider for w-LEDs

(i) CCT: A light source's colour appearance can be measured using the Correlated Colour Temperature (CCT). It compares the colour of the light to that of a reference source when heated to a specified temperature, which is measured in degrees Kelvin

(K). The CCT rating of a light is a broad indicator of its visual appearance, specifically referring to its perceived warmth or coolness. Contrary to the temperature scale, light source with a CCT value below 3200 K are generally seen as "warm" light sources, while those with a CCT exceeding 4000K are typically seen as having a "cool" appearance [33, 34].

(ii) CRI: Color rendering index (CRI) refers to the capacity of a light source to accurately replicate the colors of different objects when compared to an ideal or natural light source. A reference source, such as daylight, is characterized by a Color Rendering Index (CRI) value of 100. A CRI (Color Rendering Index) of 100 indicates the highest level of faithfulness to a reference, while a CRI below 0 indicates the lowest level of faithfulness.

(iii) Luminous efficacy: The term "luminous efficaciousness" describes a light source's ability to transform a certain kind of energy into light. It is measured in lumens per watt (lm/W), which is the ratio of the total luminous flux emitted by the light source to the electricity consumed [35].

- **Luminous efficiency:** Luminous efficacy can be standardized by dividing it by the highest achievable luminous efficacy, resulting in a dimensionless measure known as luminous efficiency. The definition states that the highest achievable luminous efficacy is equivalent to a luminous efficiency of 100%.

(iv) Quantum efficiency: The quantum efficiency of a phosphor material is the precise measurement of the proportion of emitted photons to absorbed photons. The term "quantum yield" is another name for it.

1.5 Selection of host material

To select a host some of the properties are observed to have best host for respective applications. The properties are:

(a) For optical applications, it is crucial to have a host lattice with low phonon energy and excellent chemical and temperature stability.

(b) The host lattice must possess a wide energy bandgap and excellent optical transparency in both the visible and ultraviolet spectra.

(c) Within 4f energy levels the optical transitions of dopant ions are significantly influenced by the host lattice materials. For example, the crystal field produced by the host lattice can remove the requirement for selecting particles with the same parity and alter the likelihood of f-f transitions.

(d) Host materials with low lattice phonon energies are desirable because they exhibit little non-radiative loss and high radiative emission.

(e) Trivalent rare earth (RE) ions have identical ionic size and chemical characteristics, making their inorganic compounds excellent host materials for RE dopant ions. Furthermore, alkaline earth ions such as calcium (Ca^{2+}), strontium (Sr^{2+}), and barium (Ba^{2+}), as well as certain transition metal ions like zirconium (Zr^{4+}) and titanium (Ti^{4+}), also display a similar ionic size to rare earth (RE) ions. Consequently, host materials often utilize inorganic substances that contain these ions.

1.5.1 Different hosts for w-LEDs

Borate based inorganic host: Borates are minerals that occur naturally and consist of boron. They are classified as members of the 5th group of the periodic table. Borate compounds are crucial materials for the creation of phosphors due to their easy synthesis at temperatures less than others, exceptional physical and chemical properties, and high quantum efficiency [36, 37, 38].

Phosphate based inorganic host: Phosphorus is highly advantageous for luminescent materials due to its inexpensive cost, high luminous efficiency, ease of synthesis, low water solubility, excellent chemical and thermal stability, good charge stabilization, and effective absorption of near-UV light [39, 40].

Silicate based inorganic host: Silicate-based phosphor materials are widely used in solid-state lighting due to their exceptional temperature and chemical durability, impressive quantum efficiency, straightforward fabrication, and structural versatility. [16, 41].

Vandate based inorganic host: Vanadate-based phosphor materials demonstrate remarkable chemical and thermal stability, low phonon energy, high optical damage threshold, and may be readily produced. The vanadate phosphor displayed exceptional ultraviolet (UV) absorption and intense visible emission as a result of charge transfer occurring between V^{5+} and O^{2-} ions within the [VO_4] tetrahedron, which possesses Td symmetry [42, 43].

Aluminate based inorganic host: Aluminium phosphors have notable characteristics, such as the capacity to easily adjust the emission, exceptional chemical and thermal stability, affordability, lack of toxicity, and environmental friendliness. Consequently, they find extensive use in many industries [44].

Oxide based inorganic host: Metal oxide semiconductors have garnered significant interest in recent years because to their reduced power consumption, extended operating lifespans, elevated luminous efficiency, eco-friendliness, and robustness. These materials possess the inherent capability to naturally emit light within the blue-red range of the visible spectrum and can also be infused with rare-earth ions [45].

Fluoride based inorganic host: Fluorides exhibit significantly lower lattice vibrational energies in comparison to oxide-based systems, resulting in reduced suppression of excited states of RE ions [46].

Tungstate based inorganic host: Tungstate is the quintessential inorganic luminescent substance. CaWO4 is a naturally-occurring luminous material that possesses a Scheelite structure. Tungstate compounds have inherent phosphorescent properties due to the presence of W^{6+} ions coordinated by four Oxygen atoms in a tetrahedral arrangement. These complexes possess excellent chemical and thermal stability [47, 48].

1.6 Rare Earth (RE) Ions

The advancement of phosphors has resulted in the widespread usage of rare earth (RE) elements as luminous centres or activators in various host lattices. These elements are employed for their capacity to generate precise spectrum distributions, rendering them extremely efficient for commercial applications despite their expense. The market for luminous materials doped with rare earth elements (RE) has been consistently growing due to its exceptional quantum efficiency, stability, and wide range of applications.

Rare earth (RE) elements generally comprise a group of 17 elements, which include the 15 lanthanides (ranging from La with atomic number 57 to Lu with atomic number 71), as well as Sc with atomic number 21 and Y with atomic number 39. These elements are abundant in the Earth's crust, although they are seldom found in concentrated and economically feasible forms. The lanthanides, namely Ce^{3+} to Lu^{3+}, possess partially occupied 4f orbitals, leading to distinctive luminescent characteristics for each ion's energy level. Luminous ions are commonly employed as dopants in different host phosphor lattices.

RE ions are essential in display technology because of their remarkable luminescent capabilities, characterized by distinct peak emission bands. Additionally, they play a important role in the detection of radiation and the illumination of solid-state materials. In order to be suitable for industrial applications, phosphors need to possess high efficiency in luminescence, unparalleled chemical stability and temperature control, extended operational lifespan, and environmentally friendly properties [49]. These qualities are attained by appropriately doping with rare earth (RE) elements, which has been a major area of research.

Phosphors doped with rare earth elements can be categorized into two main groups according to their emission properties: broad band emission phosphors (such as Eu^{2+}, Tb^{3+}, Gd^{3+}, Yb^{3+}, Dy^{3+}, Ce^{3+}) and narrow band emitting phosphors (such as Sm^{3+}, Tm^{3+}, Er^{3+}, Nd^{3+}) [50]. The 5d-4f transitions in ions such as Eu^{2+} and Ce^{3+} exhibit high sensitivity to local structural changes, resulting in the production of broad band emissions. On the other hand, the majority of 4f levels are not affected by the nearby arrangement of atoms because of the shielding effect. As a result, they produce consistent and stable emission spectra with distinct characteristics [51].

By manipulating the concentration of doping and desired occupancy of rare earth (RE) ions at different crystallographic sites, it is feasible to accurately modify the optical properties of the host materials [10]. The crystal field interaction, particularly with the

5d orbital, has a substantial impact on the emission colour and excitation wavelength of 4f-5d transitions. As an illustration, the 5d excited state of the Ce^{3+} ion is greatly influenced by the arrangement of the crystal, leading to a notable shift towards longer wavelengths in the emission spectrum.

In summary, rare earth ions are essential for the advancement of high-performance luminescent materials, specifically for use in solid-state lighting (SSL) and display technologies. Their distinctive electronic configurations and transitions serve as a basis for developing effective, enduring, and adaptable lighting solutions.

Fig 1.3: Periodic table highlighting Rare earth elements.

CHAPTER 2
CHARACTERIZATIONS TECHNIQUES

CHAPTER 2: CHARACTERIZATIONS TECHNIQUES

2.1 X-Ray Diffraction

X-ray diffraction is a widely used technique for determining the crystal structure, phase purity, size of crystallites, and distance between crystal planes, lattice parameters, and stresses in materials. This method was developed by German Physicist Von Laue in 1912. English Physicists W.H. Bragg and W.L. Bragg were the first ones to successfully used XRD method to determine the crystal structures of different crystals.

The X-Rays are electromagnetic waves having wavelength of about few Angstroms (10^{-10} m). They were discovered by the German Physicist Roentgen in 1895.

The diffraction of light is a well-known phenomenon in optics. The bending of light by the obstacle or an aperture is called diffraction. The diffraction occurs because the corners of the obstacle acts as secondary source of the light and there is a phase relation between each wave emitting from these secondary sources. The necessary condition for diffraction to occur is that width of the obstacle must be lesser or comparable to the wavelength of the wave. So, X – rays can be diffracted from the crystal lattice as the inter-planar distances (d) are comparable to the wavelength of the x rays. The phase difference generated due to the atomic planes are given by the relation

$$2d \sin \theta = n\lambda \tag{2.1}$$

This equation is known as Bragg's law

Here, d refers to inter planar distance, λ is the wavelength of the X-ray used and θ is called Bragg's angle.
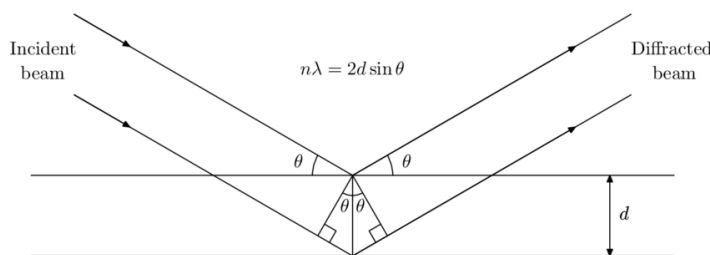

Fig. 2.1. Bragg's law

The X rays falling on the sample and gets diffracted in all direction, and detected by a detector that can be either movable or fixed. On the basis of geometry of the experiment there are three types of XRD methods:

1. Laue's method

2. Rotating crystal Method
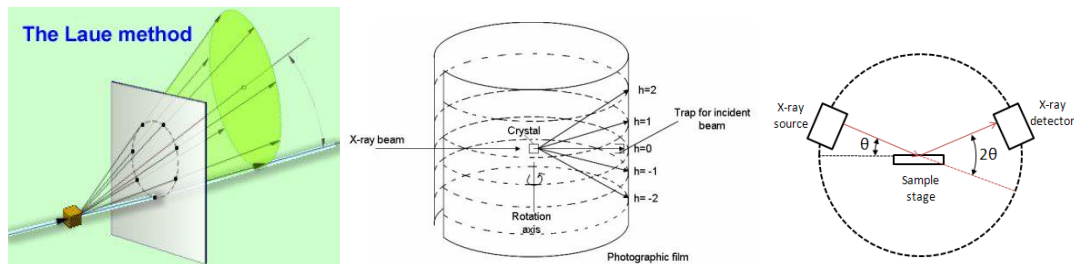
3. Debye-Scherrer method (Powder crystal method)

Fig. 2.2. Types of X-ray diffraction methods

Powder crystal method is generally used, in this sample is in fine powder form. The diffracted beams intensity at different diffraction angle (θ) is obtained by the detector. The intensity of diffracted beam at different θ position depends upon the crystal structure and atomic planes alignment. The obtained spectrum is then matched with the standard available databases that are provided by Joint Committee on Powder Diffraction Standards (JCPDS). This spectrum is used for determining the crystal structure and other parameters.

The structural properties and phase purity of the un-doped CGSW sample were analysed using XRD diffractometer at 40kV and 40mA, where Bragg's angle (2θ) data were recorded in the range of 20˚ to 80˚ using Bruker D-8 Model Advance diffractometer with Cu-Kα as radiation [52].
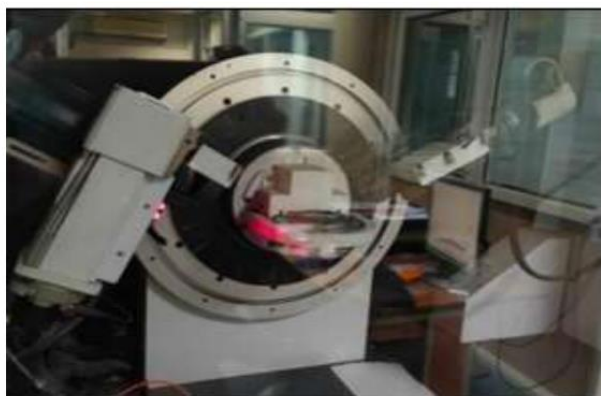

Fig. 2.3. X-Ray Diffractometer

2.2 Scanning Electron Microscopy

Electron microscopes use a beam of electrons which are at very high energy instead of light to observe the object at very small scales. It provides higher magnification with great resolution compared to that of optical microscopes. It consists of an electron

source, magnetic lenses to focus the electron beam, and detectors to detect the signals. Scanning electron microscopy is used to determine the morphology of the sample. The electron beam is focused on a small area of a sample which transfers energy in that area removing electrons from that area of sample called secondary electrons. The primary electrons that are reflected from the sample are called backscattered electrons. Sometimes, X-rays are also generated due to the electron and sample interaction. The different kind of signal provides different types of information about the sample. To get the complete SEM image of the sample, the electron beam is swept across the whole area of the specimen, and signals obtained are then converted into images revealing the morphology and composition of the surface.

The X-rays generated by the sample are used to analyze the elemental composition and concentration of elements in the sample, this analysis is done by energy dispersive spectrometer (EDS) [53].
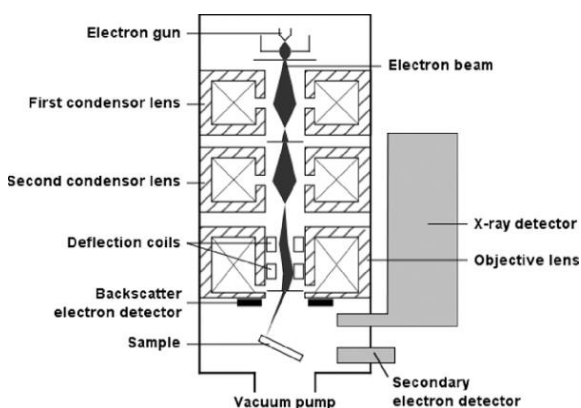

Fig. 2.4. Scanning Electron Microscope

2.3 Fourier infrared transform spectroscopy (FT-IR)

Infrared (IR) region of the electromagnetic spectrum can be used to excite the vibration levels of the molecules. The sample is irradiated with the IR in the range 400-4000 cm^{-1}, different molecular groups present in the sample absorbs the radiation of different energy range causing stretching and bending vibrations of bonds in molecules. In stretching vibrations the bond length changes between two atoms, whereas in bending vibrations the angle between the atoms with the bond length changes. The absorbance or transmittance data of sample is plotted with the energy range to obtain a FTIR spectrum and different energy bands on the spectrum can be used to identify the different functional groups present in the sample. FTIR can be used to find the OH content in the sample which should be low in case of phosphors as it absorbs the exciting energy and can lower the efficiency of the phosphor. The FTIR spectrometer works on the principle of Michelson interferometer where a beam splitter splits the beam into two parts and two mirrors are placed at right angles out of which one is fixed while other one is movable, resultant beam from these two mirrors forms an interferogram. Which passes through the sample and then to a detector which detects the photons of which wavelength is absorbed or transmitted. The detector signal

consists of interferogram in time domain by which final FTIR absorption is obtained by the Fourier transform of this signal (changing of time domain into frequency domain) .
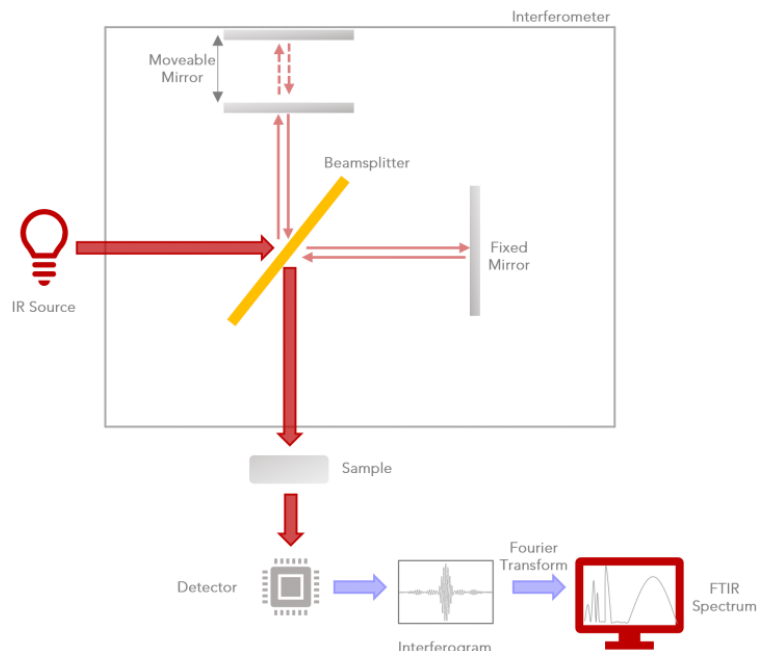

Fig. 2.5. FT-IR Spectroscopy

2.4 Diffused Reflectance Spectroscopy (DRS)

Diffused reflectance spectroscopy is form of absorption spectroscopy done by UV-Visible part of the electromagnetic spectrum it can be applied to determine electronic energy levels and the optical energy band gap. In this technique, the light reflected from the sample is recorded instead of light transmitted through the sample. Generally, the UV-Vis spectroscopy is done by dispersing the sample in a suitable liquid but if the particle size is not small enough it precipitates in the solution because of which absorption spectrum is difficult to interpret, to avoid these complexities diffused reflected spectrum of powdered sample is used. Kubelka and Munk proposed this theory to use the DRS.(ref For UV-VIS formula paper) The optical energy band gap is calculated from DRS curve using the formula

$$[F(R_\infty)h\nu]^n = C(h\nu - E_g) \tag{2.2}$$

Where, hν represents the energy of a photon of frequency ν, E_g the optical energy band gap, and $F(R_\infty)$ the Kubelka-Munk function ($R_\infty = R_{sample}/R_{standard}$).Here, C is proportionality constant and n = ½ or 2 for indirect or direct band gaps, respectively. The Kubelka-Munk (K-M) function can be obtained using the following equation

$$F(R) = \frac{(1-R)^2}{2R} = \frac{k}{s} \tag{2.3}$$

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In this equation, the sample's reflectance, molar absorption coefficient, and scattering coefficient are represented by the variables R, k, and s, respectively.

The Ultraviolet Visible (UV-Vis) spectroscopy study of prepared sample was done via Jasco V-770 spectrophotometer [54].

Fig. 2.6. Jasco V-770 Spectrophotometer

2.5 Photoluminescence (PL) Spectroscopy

When light hits the sample the photon of incident light is absorbed causing the electrons to move to higher energy (excited) states by the process named photo-excitation, from these higher energy states they come back to initial states resulting photo-luminescence. The emission energies can be higher or lower than the excitation energies. The phosphors are classified in two categories based on energy conversion either up converting where emitted energy is higher or down converting where emitted energy is lower than excitation energy. Two types of spectra are obtained in PL spectroscopy, a PL excitation spectrum revealing the details about the excitation wavelengths that can be used for photo-excitation and a PL emission spectrum showing the emission ranges of the sample. The rare earth ions doped phosphors materials generally have excitation in UV or near UV range, and their emission lies in the whole visible range. A PL spectrometer consist a light source which can emit light of multiple wavelengths, a monochromator to select a particular wavelength, sample holder and a detector to detect the spectrum of light transmitted from the sample. The monochromator uses a diffraction grating for wavelength selection. The sample holder has a cell made of material that is transparent to the wavelengths being used. The detector has a photomultiplier tube to amplify the signals and recording of spectra. The intensity of the light with the corresponding wavelengths is measured. The peaks in the spectra are caused by the transitions from different energy levels. The spectra of

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samples with different doping concentrations can be measured one by one. The intensity variation of a particular peak in different sample can give the information about the energy transfer processes that might be occurring. It may happen that there is sensitizer present in the sample absorbs the excitation energy and transfers its energy to the luminescent active centre in the sample.

The photoluminescence excitation and emission spectra of phosphor were analysed using a Xenon lamp based Jasco 8300 FP Spectro fluorophotometer [55].

Fig.2.7. Photoluminescence Spectro fluorophotometer

2.6 Time resolved fluorescence Spectroscopy

This is an important spectroscopy, which provides details about the lifetimes of the excited states, probabilities and efficiency of energy transfer process from a donor to acceptor ions. A short pulse is used for excitation of the sample pulse is kept as short as possible (shorter than the decay time). Intensity of the emission is measured with the time and fluorescent decay curves are obtained. The lifetime is then calculated by doing exponential fitting of the curves. The decay curve of co-doped phosphor fitted well with triple exponential function expressed by an empiric al equation as:

$$I(t) = B + A_1 e^{\frac{-t}{\tau_1}} + A_2 e^{\frac{-t}{\tau_2}} + A_3 e^{\frac{-t}{\tau_3}} \qquad (2.4)$$

Where, I(t) is used to denote the luminescence intensity at time t; B, A_1, A_2 and A_3 are taken as constants; time period is denoted by t and τ_1, τ_2 and τ_3 shows the lifetimes of exponential components. Using fitting function, the effective lifetime can be calculated using following formula [56]:

$$\tau_{eff} = \frac{A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2}{A_1\tau_1 + A_2\tau_2 + A_3\tau_3} \qquad (2.5)$$

Fig. 2.8. Time Resolved Fluorescence Spectroscopy

CHAPTER 3
EXPERIMENTAL PROCEDURE

CHAPTER 3: EXPERIMENTAL PROCEDURE

3.1 Synthesis of Samples

A tungstate host doped with Dy^{3+}, Eu^{3+} and Sm^{3+} ions were prepared through conventional high temperature solid state reaction method. The precursor chemicals used for sample preparation were calcium carbonate ($CaCO_3$), gadolinium oxide (Gd_2O_3), antimony trioxide (Sb_2O_3), tungsten trioxide (WO_3), dysprosium oxide (Dy_2O_3), europium oxide (Eu_2O_3), and samarium oxide (Sm_2O_3). All the chemicals used for sample preparation were high grade, and obtained from commercial sources. The chemicals were measured according to their stoichiometric ratio and after mixing properly, grinded in agate mortar for 30 min. The sample obtained then stored in alumina crucible and then sintered in programmable furnace at 1300˚C for 5h. Then the obtained sample were cooled naturally to room temperature and grinded uniformly to obtained final sample.

Fig. 3.1 Programmable Furnace

3.2 Characterisation of Samples

The structural properties and phase purity of the CGSW phosphor were analysed using Bruker D-8 Model Advance diffractometer (XRD) at 40kV and 40mA, the Bragg's angle (θ) data were recorded in the range of 20˚ to 60˚ with Cu-Kα radiation. The UV-Vis spectra were measured from 200-1500 nm range of prepared sample using Jasco V-770 spectrophotometer, while the photoluminescence emission and excitation spectra were analysed via xenon lamp based Jasco 8300 FP Spectro fluorophotometer.

CHAPTER 4
RESULTS AND DISCUSSION

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Structural analysis

4.1.1 XRD analysis

The XRD pattern of un-doped CGSW phosphor is shown in Fig.1. The presence of sharp peaks suggests that prepared phosphor is crystalline in nature. The peaks are well matched with the JCPDS data (PDF#00-064-0231) which confirms purity of the synthesized phosphor. According to JCPDS, CGSW matrix has a tetragonal scheelite structure with I41/a (No. 88) space group and lattice parameters being a = b = 5.2408 Å, c = 11.2692 Å and $\alpha = \beta = \gamma = 90°$. In the crystal structure of CGSW, Sb and W atoms are connected with four O atoms to form SbO_4 and WO_4 tetrahedrons, while Ca^{2+} and Gd^{3+} ions occupy eight coordinated sites to form an irregular dodecahedron. The average size of the crystallites was determined using the conventional Debye-Scherrer formula [57]:

$$\beta \cos \theta = \frac{K\lambda}{D} \tag{4.1}$$

where β represents full width at half maxima of XRD peaks, θ represents the peak positions, λ is wavelength of the X ray used for the recording of XRD pattern (Cu K_α=1.54 Å), D here is the average crystallite size and K = 0.94 is the Scherrer constant. The average size of the crystallite was calculated to be 44.51 nm.
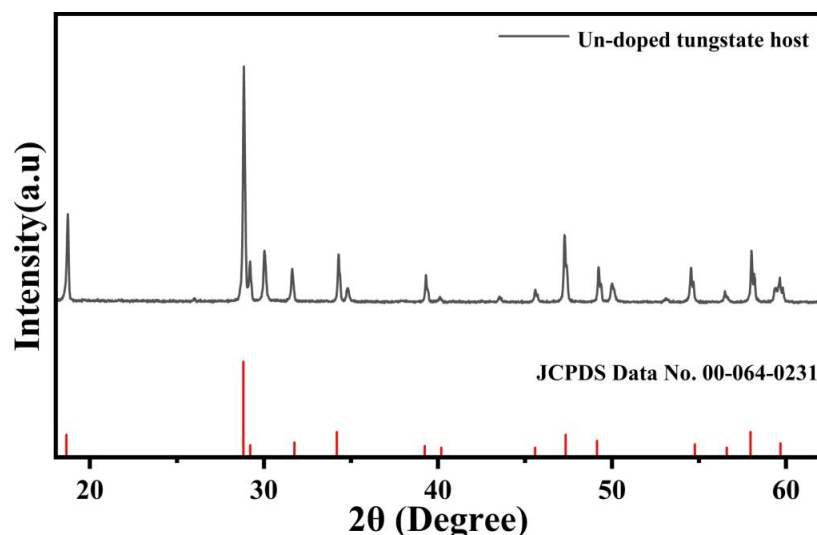
Fig.4.1. XRD pattern of un-doped tungstate host.

4.2 Optical property analysis

4.2.1 UV-Vis spectroscopy and bandgap analysis

Fig.2 shows the diffused reflectance spectra (DRS) of the Dy^{3+}, Eu^{3+}, and Sm^{3+} doped tungstate phosphor in the range of 200 to 1500 nm. The band between 200-350 nm is common in all spectra which correspond to the band to band transition of the tungstate host. The bands between 350-1500 nm correspond to the transitions of doped RE ions. The transitions of Dy^{3+} ions from ground state $^6H_{15/2}$ to excited states $^6F_{5/2}$, $^6F_{7/2}$, $^6F_{9/2}$, and $^6F_{11/2}$ are observed at wavelength 805, 911, 1099, and 1295nm, respectively[58]. The $^7F_0 \rightarrow ^5L_7$ transition of Eu^{3+} ions is seen at wavelength 372 nm[59]. The Sm^{3+} ions transition from $^6H_{5/2}$ to $^4F_{7/2}$, $^6F_{11/2}$, $^6F_{9/2}$, $^6F_{7/2}$ and $^6F_{5/2}$ are observed at 411, 956, 1094, 1251, and 1398nm, respectively [47].
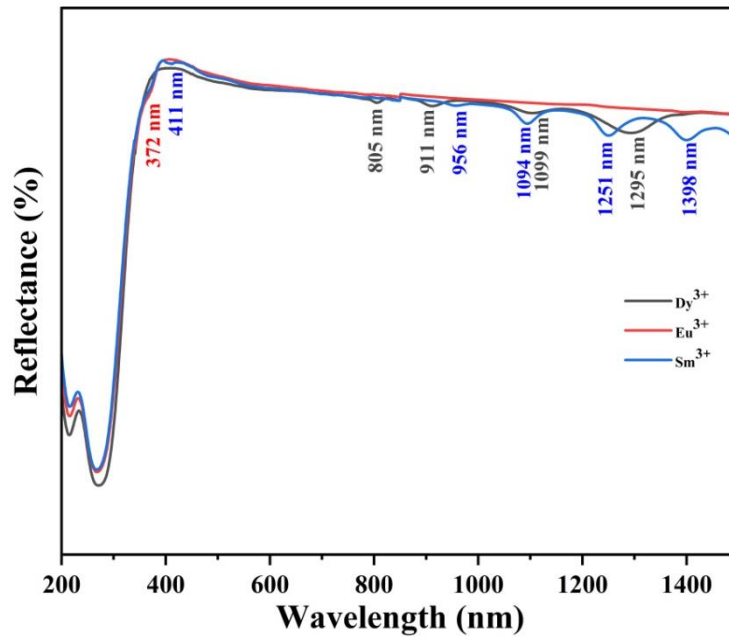
Fig.4.2. DRS of tungstate host doped with 1 mol % of Dy^{3+}, Eu^{3+} and Sm^{3+} ions.

The optical energy band gap was calculated using [60]

$$[F(R_\infty)h\nu]^n = C(h\nu - E_g) \tag{4.2}$$

In this equation $F(R_\infty)$ is Kubelka-Munk function ($R_\infty = R_{sample}/R_{standard}$), h is the Planck's constant, ν is the frequency of the light used, E_g is the band gap, C is constant of proportionality, and n takes value ½ and 2 for direct and indirect band gap.

The Kubelka-Munk function can be obtained by [61]

$$F(R) = \frac{(1-R)^2}{2R} = \frac{k}{s} \tag{4.3}$$

Where R, k, and s represent sample's reflectance, molar absorption coefficient, and scattering coefficient respectively.

Fig. 3 shows the plot between F(R) and energy (hv). The optical energy band gap was calculated by extrapolating the linear part of the plot. The calculated optical energy band gap for Dy^{3+}, Eu^{3+}, and Sm^{3+} doped tungstate phosphor was found to be equal to 4.03, 4.07 and 4.07eV respectively.
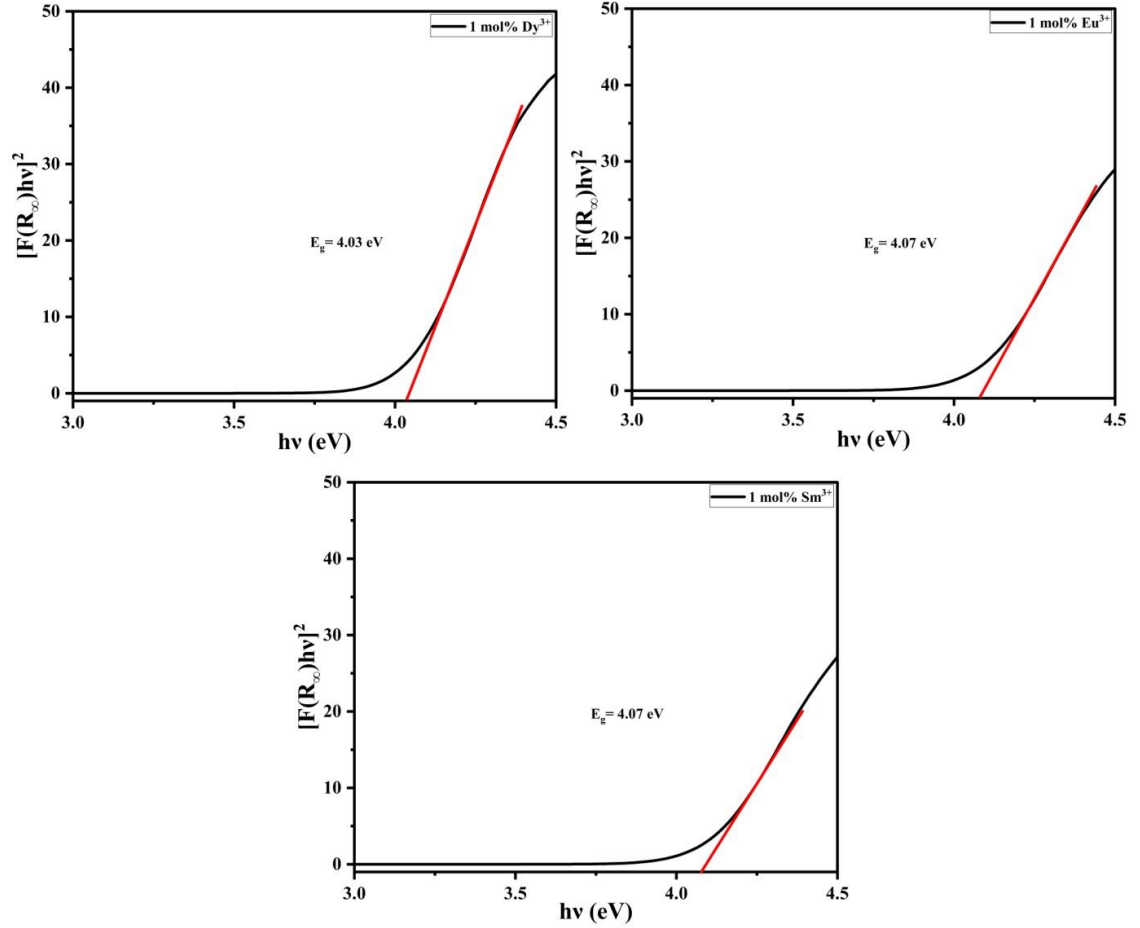

Fig.4.3. Optical band gap of tungstate host doped with 1 mol % of Dy^{3+}, Eu^{3+} and Sm^{3+} ions.

4.2.2 Analysis of photoluminescence properties

The PL excitation and emission spectrum of tungstate phosphor doped with Eu^{3+}, Dy^{3+} and Sm^{3+} ions are shown in Fig.4. All excitation spectra show broadband ranging from 225-325 nm this band is called charge transfer band (CTB) because of the charge transfer from $O^{2-} \rightarrow W^{6+}$ in the host, electrons from 2p states of O^{2-} are excited to 5d states of W^{6+} [62]. The spectra show several narrow peaks between 325-460 nm, these correspond to the characteristics of f-f transitions of doped rare earth ions.

For Dy^{3+} ions doped phosphor: The excitation spectrum was monitored at 576nm narrow peaks are observed at 325, 351, 365, 387, 426, and 451nm ascribed to

transitions of Dy^{3+} from $^6H_{15/2}$ level to $^4M_{17/2}$, $^6P_{7/2}$, $^6P_{5/2}$, $^4K_{17/2}$, $^4G_{11/2}$, and $^4I_{15/2}$ levels respectively[63].

For Eu^{3+} ions doped phosphor: The excitation spectrum was monitored at 614nm, sharp peaks are located at 364, 383, 397, 417, 464 and 536nm which are caused by transitions from $^7F_0$ level to $^5D_4$, $^5L_7$, $^5L_6$, $^5D_3$, $^5D_2$, and $^5D_1$ levels respectively of Eu^{3+} ions[64].

For Sm^{3+} ions doped phosphor: The excitation spectrum was monitored at 610nm, and several sharp peaks were observed at 345, 362, 376, 405, 420, 440, and 464nm due to f-f transitions of Sm^{3+} ions from $^6H_{5/2}$ to $^4H_{9/2}$, $^4D_{3/2}$, $^6P_{7/2}$, $^4F_{7/2}$, $^4M_{19/2}$, $^4I_{15/2}$, and $^4I_{11/2}$ respectively[65], [66].

As it is clear from the excitation spectra of all three cases that CTB is highly intense so, the host excitation wavelength was used to measure the emission spectra in Eu^{3+}, Dy^{3+}, and Sm^{3+} doped tungstate phosphor.

For Dy^{3+} ions doped phosphor: The emission spectrum was measured under the excitation wavelength of 277nm. Three peaks are observed at 485, 578, and 667 nm which corresponds to $^4F_{9/2} \rightarrow ^6H_{15/2}$, $^4F_{9/2} \rightarrow ^6H_{13/2}$, $^4F_{9/2} \rightarrow ^6H_{11/2}$ transitions of Dy^{3+} ions, respectively. The 485 nm wavelength results in blue colour emission, 578 nm wavelength is in the yellow region and the 667 nm whose intensity is minimum results in red colour emission.

For Eu^{3+} ions doped phosphor: The emission spectrum was monitored at an excitation wavelength of 275nm, peaks located at 578, 591, 612, 655, and 703nm are observed. These peaks are ascribed to $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$ and $^5D_0 \rightarrow ^7F_4$ transitions of Eu^{3+} ions, respectively.

For Sm^{3+} ions doped phosphor: The emission spectrum was measured at 273 nm excitation. The transitions correspond to $^4G_{5/2} \rightarrow ^6H_{5/2}$, $^4G_{5/2} \rightarrow ^6H_{7/2}$, $^4G_{5/2} \rightarrow ^6H_{9/2}$ and $^4G_{5/2} \rightarrow ^6H_{11/2}$ of Sm^{3+} ions are observed as peaks at 566, 605, 647, and 709nm respectively. The Eu^{3+} and Sm^{3+} ions have the emission in the red colour region.
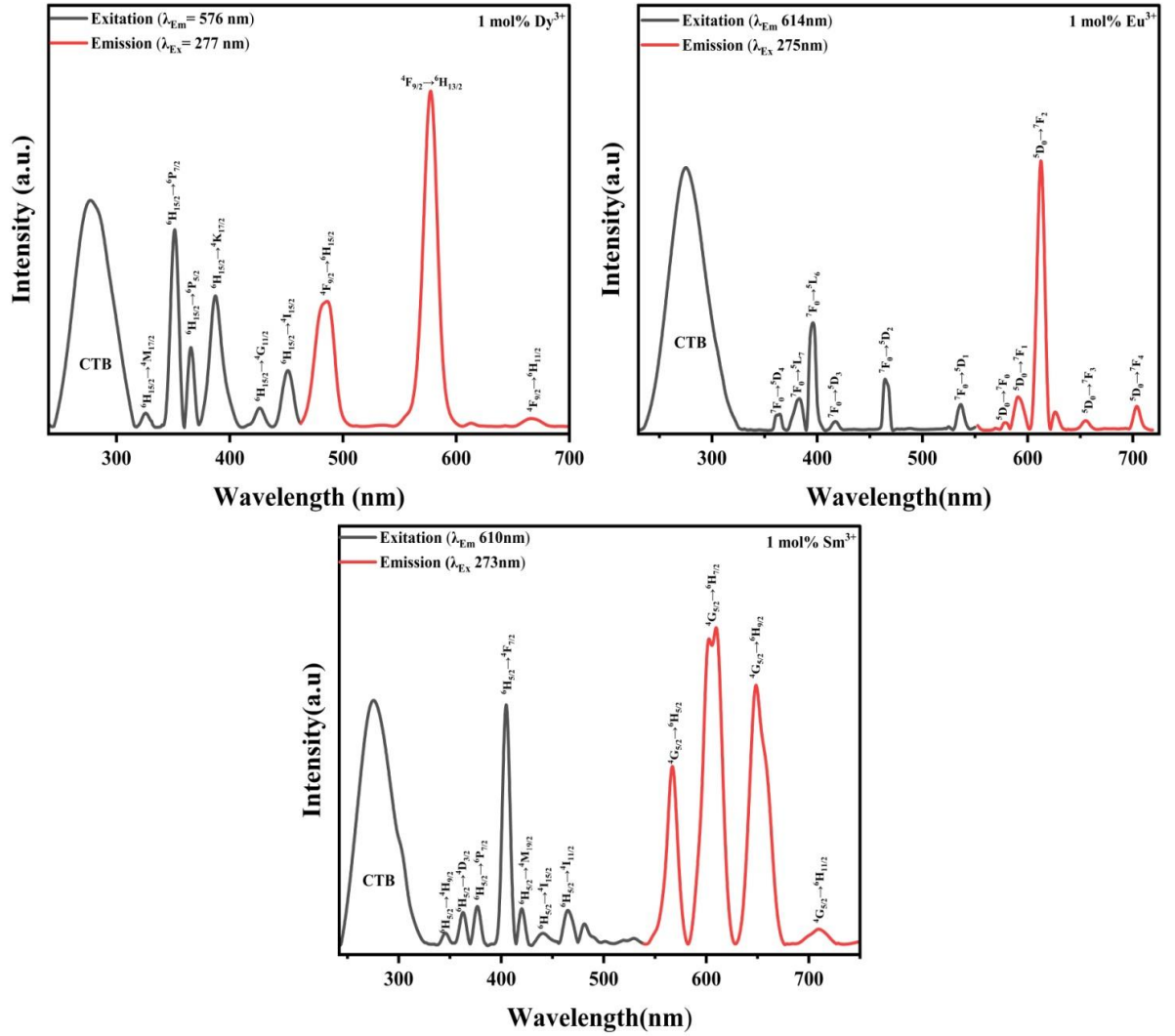
Fig.4.4. PL emission and excitation spectra of tungstate host doped with 1 mol % of Dy^{3+}, Eu^{3+} and Sm^{3+} ions.

4.2.3. CIE

CIE chromaticity coordinates and CCT values are the important parameters to characterize a phosphor. The respective emission spectra of RE ions doped tungstate phosphor are used to evaluate CIE colour coordinates as shown in Fig.5. CCT values are calculated using the McCamy relation [67]. The light which has a CCT value higher than 4000K is called cold light and if it has a CCT value lower than 3200K it's called warm light. Tungstate hosts doped with Dy^{3+} ions are emitting cold light whereas, Eu^{3+} or Sm^{3+} ions doped tungstate hosts are emitting warm light. The CIE was in the white region when doped with Dy^{3+} ions, red region when doped with Eu^{3+}

ions and orange-red region when doped with Sm^{3+} ions. Colour purity (CP) is a necessary factor in LEDs, which was calculated using the formula [68]:

$$\text{Colour Purity} = \frac{\sqrt{(x-x_{ee})^2+(y-y_{ee})^2}}{\sqrt{(x_d-x_{ee})^2+(y_d-y_{ee})^2}} \times 100\% \qquad (4.4)$$

Here, (x, y) are colour coordinates of phosphor, (x_d, y_d) are coordinates of dominating wavelengths and (x_{ee}, y_{ee}) represents illumination points. The following values of CIE colour coordinates, CCT and CP values of prepared phosphors are shown in the table 1.

Table 4.1. CIE, CCT and CP of tungstate host doped with 1 mol % of Dy^{3+}(D1), 1 mol % of Eu^{3+} (E1), and 1 mol % of Sm^{3+}(S1) ions:

Composition	CIE		CCT	CP
			(K)	(%)
	x	**y**		
D1	0.338	0.363	5305	12.78
E1	0.626	0.373	1931	86.42
S1	0.542	0.449	2109	71.72
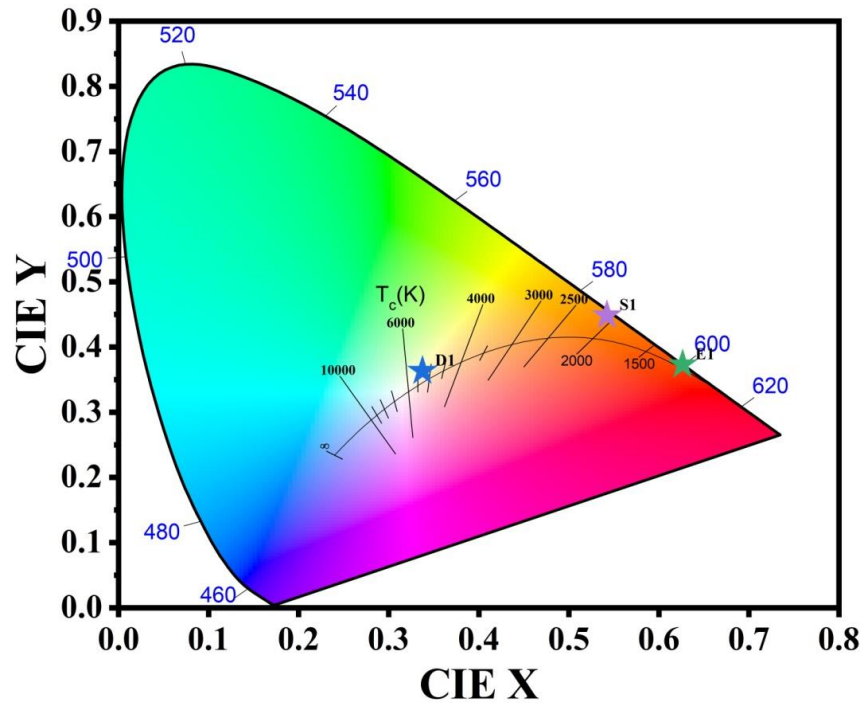
Fig.4.5. CIE chromaticity coordinates and CCT of tungstate host doped with 1 mol % of Dy^{3+} (D1), Eu^{3+} (E1) and Sm^{3+} (S1) ions.

CHAPTER 5
CONCLUSION

CHAPTER 5: CONCLUSION

The 1.0 mol% Dy^{3+} ions, Sm^{3+} ions and Eu^{3+} ions activated tungstate phosphor was prepared using solid state method and analysed using structural, optical & PL observations. The peaks in the XRD pattern of un-doped tungstate host were well matched with its JCPDS data. The direct energy band gap was estimated to be equal to 4.03 eV for Dy^{3+}, 4.07 eV for Eu^{3+} and 4.07 eV for Sm^{3+} using Uv-Vis spectroscopy. The PL emission spectrum of tungstate phosphor activated by (i) Dy^{3+} ions demonstrate intense peak at 576nm under 277nm excitation, (ii) Eu^{3+} ions demonstrate intense peak at 614nm under 275nm excitation and (iii)Sm^{3+} ions 610nm under 273nm excitation. Based on the evaluated CIE chromaticity coordinates and CCT values, RE^{3+} (Dy^{3+}, Eu^{3+} and Sm^{3+}) ions doped tungstate phosphor emerges as a promising option for light-emitting diodes (LEDs) due to their favourable colour characteristics.

CHAPTER 6
FUTURE SCOPE

CHAPTER 6: FUTURE SCOPE

The current work is done by doping CGSW with Dysprosium (Dy^{3+}), Europium (Eu^{3+}) and Samarium (Sm^{3+}) rare earth ions which have made them an efficient, effective and high-quality phosphor which can be used for development of low cost phosphor converted white light emitting diodes (pc-w-LEDs) and red light-emitting diodes. Firstly, the luminescent property of the phosphors can be increased by co-doping Dy^{3+} with Eu^{3+} or Sm^{3+}, which increases its applications as it can be used as colour tunable LEDs and can also use for indoor purposes.

The conventional solid-state reaction technique was employed to synthesize the current phosphor, which was subsequently characterized for its photoluminescence and structural properties. Therefore, an alternative synthesis technique, such as the sol-gel method, can be investigated in order to enhance the particle morphology and decrease the particle size. Nitrates serve as metal precursors in the sol-gel combustion method, which is a combination of the sol-gel and combustion processes. In the Sol-gel approach, the metal oxides that are produced undergo a variety of processes. The process begins with the rapid hydrolysis of the metal nitrate. Subsequently, the metal hydroxide solution is condensed to form gels. Finally, the evaporation process results in the formation of xerogel, which is subsequently combusted at a high temperature. The resulting compound is a black, powdery structure that is sintered at a variety of temperatures. The luminescence properties of the phosphor as-prepared may be enhanced through the investigation of this method. These phosphors are not only applicable to w-LEDs, but they are also suitable for a variety of applications, including bio-imaging, thermal sensing, and biometric sensing.

The optimized phosphor can be employed to fabricate w-LEDs for the aforementioned applications.

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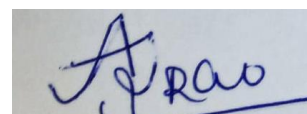
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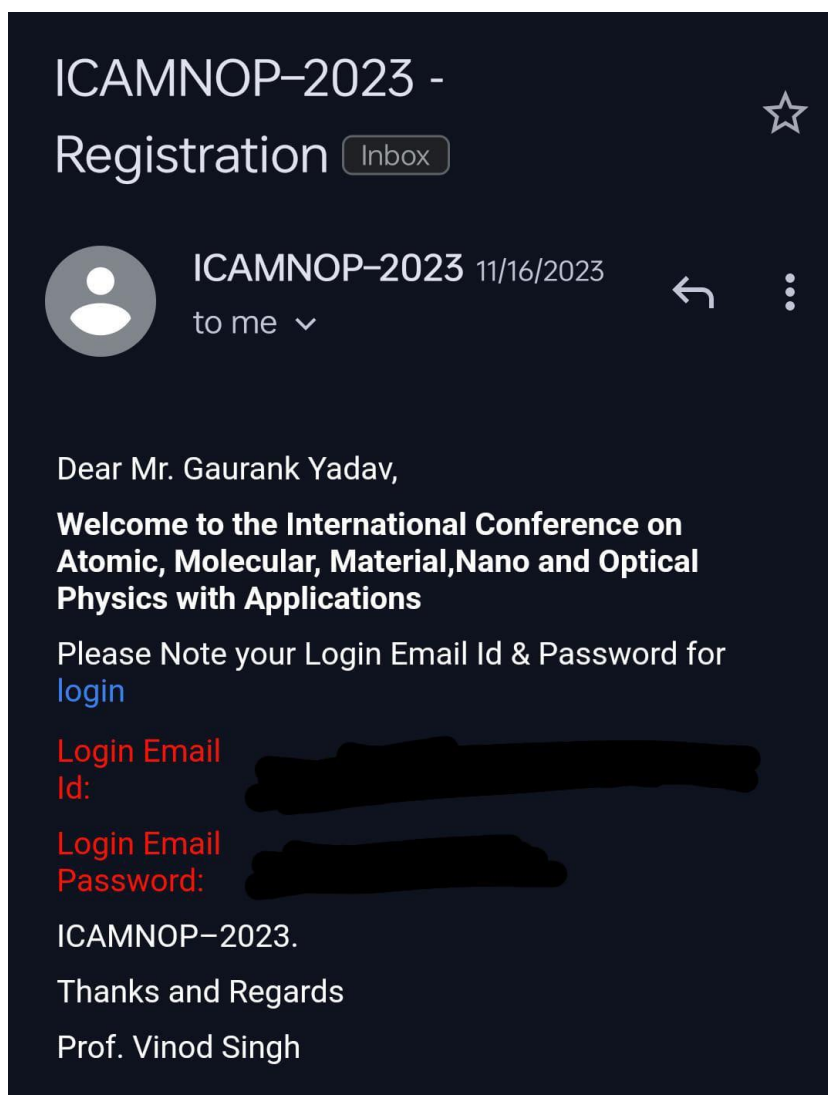
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