Effects of Solvent and Particle Size on Photoluminescence Properties of Double Tungstates $NaRE(WO_4)_2$ ($RE = Sm^{3+}$, Ho^{3+} and Pr^{3+})

A dissertation submitted in partial fulfilment of the Award degree

MASTER OF SCIENCE

IN

PHYSICS

BY

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18th May 2022

Certificate

This is to certify that the project entitled

Effects of Solvent and Particle Size on Photoluminescence Properties of Double Tungstates NaRE(WO$_4$)$_2$ (RE = Sm^{3+}, Ho^{3+} and Pr^{3+})

Is a bona fide work carried out by

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Under the Guidance of Dr. Venkatesha R. Hathwar

As a part curriculum for the degree in

Master of Science

In physics during the academic year 2021-2022

Dr. Venkatesha R. Hathwar
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Programme Director

DECLARATION

We declare that this project has been completed by Ms. Tanvi T. Naik and Ms. Rutuja N. Sawant Dessai and to the best of our knowledge, it has not been previously formed the basis for the award of any degree or diploma by any other university.

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Abstract

Sodium rare earth double tungstates are attracting a lot of researchers due to their unique luminescent properties. They are found to have good application as phosphor coated white light LEDs which have advantages like low power consumption, good lifetime, high luminous efficiency and environment friendly. Using a proper synthesis technique is important in the development of phosphors. In this project, $NaRE(WO_4)_2$, (RE=Sm, Ho and Pr) were synthesised via three different synthesis methods: solid state synthesis, hydrothermal synthesis and solvothermal synthesis. Compounds synthesised via different synthesis routes were compared and analysed for their particle sizes, morphology, luminescent properties and bandgap using different analytical techniques such as X-ray diffraction, Scanning electron microscopy, Photoluminescence spectroscopy and UV-Visible spectroscopy. It was found that compounds synthesised via solvothermal method had smaller particle size compared to compounds synthesised using other two synthesis methods and were observed to have higher luminescence output and higher energy band gap.

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Chapter1: Introduction

1.1 Early history and evolution of light

Since the discovery of light, illumination techniques have evolved alongside human civilization. From ancient fire torches to modern light bulbs, lighting is an integral part of human life. However, with the progression in technology, lighting no longer remains a means of just lighting up the dark.[4]

Before the invention of incandescent light, humans used oil lamps, firewood and candles for lighting. After invention of electricity and after it was made available to homes and businesses, traditional methods of illumination slowly lost their market. They weren't a reliable option until and after 1880 when Thomas Edison invented a bulb that could last for 1500 hours. Slowly over 20th century, light bulbs evolved to become more efficient.[5] An incandescent bulb had many disadvantages like they required high maintenance, high energy to run thus not environment friendly. Also, there were not much colour options.

Figure 1.1: Evolution of light bulb. Adopted from the reference [6]

Since then, there have been numerous improvement that has made the bulb light longer, brighter, and cheap to buy. Other technologies have been discovered in the field of electric lighting, this includes compact fluorescent and LED bulbs. Although the LED bulbs have turned to be the favourite because of its low power consumption. LED is a kind of solid-state lighting where a semiconductor converts electricity to light (without producing heat).

Electroluminescence, the principle behind LEDs was first discovered in 1907 by Henry Joseph Round in Silicon Carbide. But unfortunately, the yellow light that he created was too dim to be of any real use. Scientists continued to study electroluminescence, but wasn’t until 1962 that visible LEDs were created as we know today. LEDs uses semiconductors (generally Gallium Arsenide) to emit light. From street lights and calculators to TV remotes and traffic signals, nowadays, LEDs are all around.[7]

1.2 Phosphor coated white light LEDs

Phosphor is a substance that displays property of luminescence. In case of LED lighting, the type of luminescence is specifically fluorescence, the emission of light caused by absorption of blue light energy emanating from LED chip. By carefully tuning the composition and structure of phosphor, one can play with the spectral content of the emitted light, one can meet the desired performance criteria. For this reason, phosphors are widely used in electronics and lighting industry to enable applications such as displays, fluorescent lighting and white LEDs.

Most white light LEDs consists of a LED chip which emits blue light with a narrow spectrum between 440 nm to 470 nm and a coating of yellow, green or red phosphors. The phosphors are designed to absorb some of blue light from LED die. The light emitted by phosphors, in combination with remaining blue light leaking through phosphor layer, results in the light which is perceived as white light by human eye.[8]

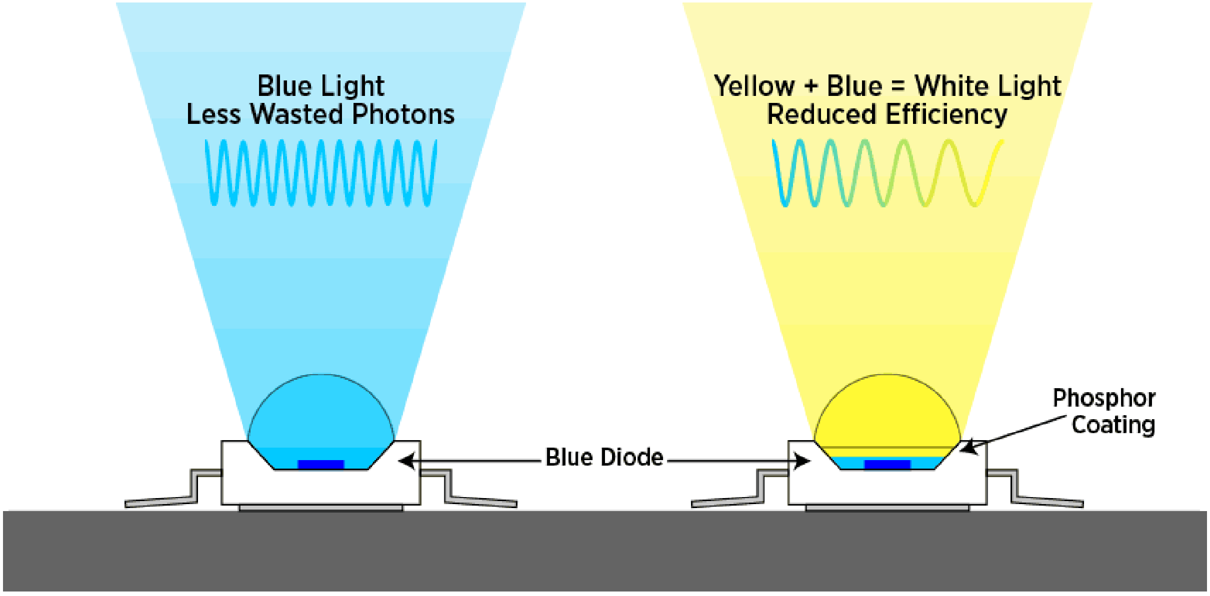


Figure 1.2 : Blue LED diode is coated with a phosphor to shift photon wavelengths making white light. Adopted from the reference [9]

1.3 Solid state lighting

Solid-state lighting (SSL) is a rapidly emerging field. it promises to reduce power consumption as much as 50%, significantly reduce carbon dioxide emission and inspires the development of completely new lighting industry. SSL uses semiconductor light emitting diodes (LEDs), organic light-emitting diodes (OLED), or polymer light-emitting diodes (PLEDs) as a source of illumination rather than electrical filaments, plasma or gas. Solid state electroluminescence is used in SSL opposite of incandescent bulbs (in which use thermal radiation) or fluorescent tubes. Compared to incandescent lighting, SSL creates visible light with reduced heat generation and less power dissipation. Most common white LEDs convert blue light from a solid-state device to an approximate white light spectrum using photoluminescence, the same principle used in conventional fluorescent tubes.

Figure 1.3 : solid state lighting devices Adopted from the reference [1]

Due to their small mass, solid-state lighting devices have greater resistance to shock and vibration compared to brittle glass tubes/bulbs and long, thin filament wires. They also eliminate filament evaporation, thereby increasing the life span of the illumination device. [10]

1.4 Luminescence

Electrons have been excited, the distribution of electrons is no longer in equilibrium, and they eventually decay into lower states, emitting radiations in the process. This emission is referred to as luminescence. Luminescence is therefore the inverse of absorption. It is thus a form of cold body radiation. It can be caused by chemical reactions, electrical energy, subatomic motions or stress on a crystal. This distinguishes luminescence from incandescence, which is light emitted by a substance as a result of heating.

Types:

A) Chemiluminescence: the emission of light as a result of a chemical reaction.

B) Crystallo-luminescence: produced during crystallization.

C) Electroluminescence: a result of an electric current passes through a substance.

D) Photoluminescence: a result of absorption of photons.

Likewise, there are many but we have focused only on photoluminescence.[11]

Figure1.4 : Fluorescent solutions under UV light (a form of photoluminescence). Adopted from the reference [12]

1.5 Rare earth elements and their properties

The rare earth elements are 17 metallic elements found in the middle of periodic table. Some of the rare earth elements have unusual, magnetic, luminescent and electric properties that make them very useful for industrial applications and in manufactured products. But because these elements have a very similar electron structure, separating them from each other is difficult. Although mineral ores containing rare earths can be found on every continent, most production of rare earths today happens in China.

Magnetic properties: some rare earth elements like Nd, Dy and Sm are valued for their magnetic properties. Magnetic fields are generated by unpaired electrons aligned so they spin in the same direction. The orbital electron structure of these elements contains many unpaired electrons, which means these rare earth materials can store large amounts of magnetic energy. Rare earth magnets are widely used today in many applications like wind turbines, guidance systems on aircraft and missiles, etc.

Electrical properties: The electronic structure of rare earths makes them useful for nickel-metal hydride (NiMH) batteries. The anodes of these batteries are made up of mischmetal, a mixture of cerium, lanthanum, neodymium and praseodymium which is cheaper to make because the rare earth metals do not have to be completely separated from each other. The rare earths give batteries a higher capacity to store energy in the given weight. And a better ability to retain capacity after many discharge-recharge cycles.

Catalytic properties: The electron structure of the rare earths makes them useful as accelerators for chemical reactions. Cerium and lanthanum are the main rare earths used in catalytic applications because of their abundance and cheaper rate. Cerium is used in catalytic convertors on gasoline powered cars and Lanthanum is commonly used in fluid catalytic cracking, the process of refining crude oil into specific useful hydrocarbons such as gasoline.

Luminescent properties: Some rare earth elements give off light when stimulated by electromagnetic radiation. These elements are used as phosphors (light emitting substances) in energy efficient light sources such as LEDs and compact fluorescent bulbs. Europium phosphors produce red light that proved crucial for development of colour TVs in 1960s. The fluorescent properties of Erbium ions make them useful for amplifying signals transmitted through glass fibres. Lasers represent another use of luminescent properties of various rare earths. Yttrium-Aluminium-garnet (YAG) is a common medium for solid state lasers. When doped with erbium, YAG lasers produce wavelengths of focused light useful for oral surgery and dentistry. When doped with Neodymium, YAG lasers are widely used in manufacturing, medicine and military applications.[13]

The lanthanide ions are characterized by an incompletely filled 4f shell shielded from surroundings by the filled 5s2 and 5p6 orbitals, resulting in the sharp and narrow lines of the emission spectra of transitions within the 4f configuration. The emission spectra arising from 5d-4f transitions are bread as the 5d electrons are unshielded and hence are heavily influenced by their surroundings. The lifetimes of emissions due to 4f-4f transitions are substantially long lived, mostly in the range of milliseconds because of the forbidden character of f-f transitions in free 4f ions.

Ln^{3+} doped phosphors are found to show excellent up-conversion luminescence and/or down-conversion luminescence ranging from ultraviolet (UV) to infra-red region. Up-conversion is a process in which the sequential absorption of two or more photons leads to the emission of light at shorter wavelength than the excitation wavelength. Whereas down-conversion is the opposite, in which one high energy photon which is inefficiently absorbed is converted into two or more lower energy photons.[14]

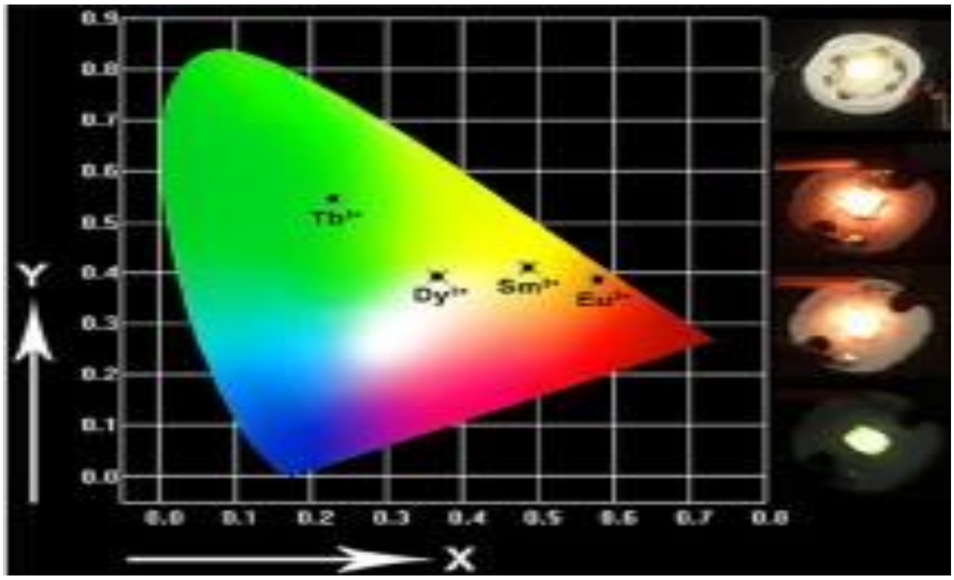


Figure 1.5 : CIE chromaticity diagram of some rare earth elements. Adopted from the reference [15]

Chapter 2: Experimental section

2.1 Materials

Na_2CO_3, WO_3, Sm_2O_3, Ho_2O_3, Pr_2O_3, $Na_2WO_4.2H_2O$, $Sm(NO_3)_3.6H_2O$, $Ho(NO_3)_3.5H_2O$, $Pr(NO_3)_3.H_2O$, Milli-Q water, Ethylene Glycol, HCl solution, NaOH solution. All the materials are purchased from Alfa Aesar and Sigma-Aldrich of analytical grade and used as such without further purification

.2.2 Synthesis

2.2.1 Solid state synthesis

Solid state reaction method also known as ceramic method is the oldest and most effective method widely used to make inorganic solids. Stoichiometric amounts of powdered reactants are mixed and are heated in furnace at high temperatures for prolonged periods. The final products include single crystals, polycrystalline solids, glasses and thin films which are widely applicable in the field of energy and electronics.

Procedure:

Stoichiometric amounts of Na_2CO_3, WO_3 and, $(RE)_2O_3$ (RE=Sm,Ho,Pr) were weighed and mixed using agate mortar for 60 minutes. The mixture was transferred into an alumina crucible boat and was kept in furnace for pre-heating at 350˚C for 2 hours. The compound was taken out, grounded for few minutes and was again kept in furnace for calcination at 800 ˚C for 10 hours. Pallets were made ansintered at 800 ˚C for 12 hours.

2.2.2 **Hydrothermal synthesis**

In hydrothermal synthesis, the reactants are heated in water/steam at high pressures and temperatures. The water acts as pressure transmitting medium and as a solvent. Solubility of the reactants is pressure and temperature dependent. The reactants are placed in teflon lined autoclave and heated in oven. The autoclave maintains high temperature and pressure for the reaction to take place.

Procedure:

Stoichiometric amounts of $Na_2WO_4.2H_2O$ and $RE(NO_3)_3.H_2O$ (RE= Sm, Ho, Pr) were weighed and dissolved in a beaker containing 10 ml milli-Q water seperately. Magnetic stirrer was used to stir and dissolve the reactants. $Na_2WO_4.2H_2O$ solution was poured into $RE(NO_3)_3.H_2O$. The mixture was stirred again for 30 minutes. The neutral pH was maintained for the reaction. The mixture was made upto 40 ml by adding milli-Q water and was transferred into a teflon lined autoclave, sealed and kept in oven for heating at 200 ˚C for 24 hours. The formed compound was washed and centrifuged several times with milli-Q water and dried. Pallets were made and sintered at 800 ˚C for 12 hours.

2.2.3 **Solvothermal synthesis**

Solvothermal synthesis is similar to hydrothermal synthesis, -where other supercritical solvents are used instead of water. This method has increasing applications.

Procedure:

Stoichiometric amounts of $Na_2WO_4.2H_2O$ and $RE(NO_3)_3.H_2O$ (RE= Sm, Ho, Pr) were weighed and individually dissolved in a beaker containing 10 ml Ethylene glycol. Magnetic stirrer was used to stir and dissolve the reactants. $Na_2WO_4.2H_2O$ solution was poured into $RE(NO_3)_3.H_2O$ solution. The mixture was stirred again for 30 minutes. The neutral pH was maintained for the reaction. The mixture was made upto 40 ml by adding Ethylene glycol and was transferred into teflon autoclave, sealed and kept in oven for heating at 200 ˚C for 24 hours. The formed compound was washed and centrifuged several times with double distilled water and dried. Pallets were made and sintered at 800 ˚C for 12 hours.

Chapter 3: Characterization

Characterization is very important for development of good quality materials. The complete characterization of any material consists of phase analysis, structural and compositional characterization, micro-structural analysis and spectroscopic analysis. One single technique is not capable for providing complete characterization of a solid. In this chapter different analytical instrumental techniques are discussed which were used to characterize the samples prepared.

3.1 X-ray Diffraction

X-ray diffraction (XRD) has been used over a century for the identification of crystalline - phases as a fingerprint technique in the synthesis and structure determination.

3.1.1 Generation of X-rays

X-rays are electromagnetic radiation having wavelength ~1Å. X-rays are produced when high energy particles such as electrons are accelerated through high potential collide with target material. The resulting X-ray spectra usually have two components: broad spectrum of wavelengths known as white radiation and a number of fixed or monochromatic wavelengths. X-rays which are used in Xray diffractometers are monochromatic X-rays. A beam of electrons when accelerated through high potential difference are allowed to strike a metal target such as Cu. The incident electron beam has sufficient energy to ionise some of the Cu K shell electrons. An electron in the outer orbit (such as L, M) can fill the vacancy created in the K shell and the energy released in the transition appears as X-radiation. For Cu, transition from L-shell to K-shell appears as K_α radiation and transition from M-shell to K-shell appears as K_β radiation.

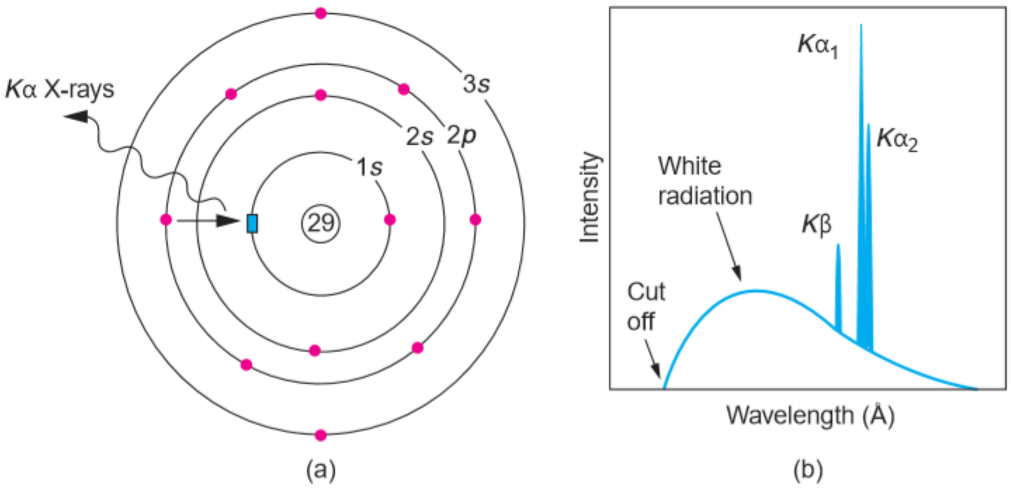


Figure 3.1: a) Generation of Cu Kα X-rays, b) X-ray emission spectrum of Cu. Adopted from the reference [2]

3.1.2 Interaction of X-rays with matter

Bragg approach to diffraction is to regard the crystals is build up in layers or planes and each plane acts as semi-transparent mirror. When X-rays with wavelength similar to atomic spacings are incident upon a crystalline material, some of the x-rays are reflected off the plane with and of incidence equal to angle of reflection and the rest are transmitted to be subsequently reflected by succeeding planes.

Bragg’s Law

$$2d\ Sin\theta = n\lambda \qquad [3.1.2]$$

Where;

d is interplanar spacing, θ is Bragg's angle or diffraction angle, λ is Wavelength of X-rays used and ***n*** is order of diffraction. [2]

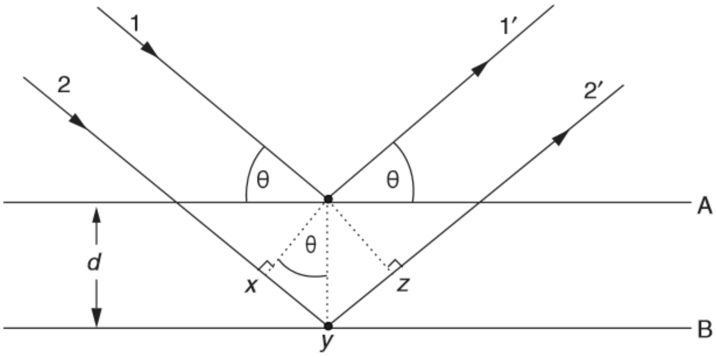


Figure 3.2: Schematic representation of Bragg's Law. Adopted from the reference [2]

When Bragg's law is satisfied, the reflected beams are in phase and they interfere constructively. For angles other than Bragg's angle, they are out of phase and interfere destructively. Bragg's law imposes a strict condition on the angles at which reflection may occur.[2]

3.1.3 Powder XRD method

In this method, a monochromatic beam of x-rays strikes a finely powdered sample in which there is random orientation of crystals in every possible direction. In such powdered sample, various planes are also present in every possible orientation. Foe each set of planes, at least some crystals must be oriented in at Bragg's angle, to the incident beam and thus Bragg's law satisfied for those crystals and planes. The diffracted beam is then detected by the detector. For any set of lattice planes, the diffracted radiation from the surface of a cone. The only requirement for diffraction is that the planes should be at Bragg's angle with respect to the incident beam and no restriction is placed on the angular orientation of the planes about the axis of incident beam. In finely powdered sample, crystals are present at every possible angular position about the incident beam so the diffracted radiation appears to be emitted from the sample as cones of radiation. Each set of planes give its own cone of radiation.[2]

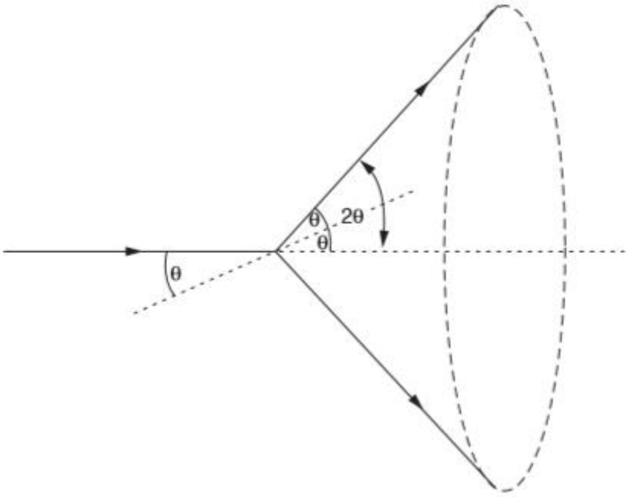


Figure 3.3: Formation of cone of diffracted beam. Adopted from the reference [2]

3.1.4 - Powder X-ray Diffractometer

Powder X-ray Diffractometer consist of following components:

X-ray Source: High energy electrons are produced from heated tungsten filament and this is allowed to impinge on small metal target example Copper in a sealed diffraction tube.

Collimator: X-rays are generated by target material and then it passes through collimator. It consists of set of two metal plates which are closely packed and separated by a small distance. The collimator absorbs all the x-rays except the narrow beam that passes through it.

Monochromators: Monochromators separates polychromatic light into range of individual wavelength. Graphite Monochromator is used in Rigaku Smart Lab X-ray diffractometer. The graphite monochromator optimizes sensitivity by lowering the background level. It improves signal-to-noise by eliminating fluorescence from Co, Ni, Fe, Mn containing materials.

Filters: Filters absorbs undesirable radiations but allow the radiation of desired wavelength to pass. Example nickel filter is used to remove K_β radiations of copper. These filters are used as an alternate to monochromators.

Detector: The D/TEX Ultra 250 is used to detect the diffracted beam in Rigaku Smart lab powder X-ray diffractometer. It is a 1D Silicon strip detector that decreases data acquisition time by 50% compared to competitive detectors. This is achieved by increasing the active area of the aperture and thus increasing the count rate. D/TEX ultra has smaller pixel pitch and longer in direction of 2θ.[16]

Figure3.4: Rigaku Smart Lab Powder X-ray diffractometer at ULMC of Goa University.

3.2 Scanning Electron Microscopy

Scanning electron microscope is one of the most versatile or multifaceted instrument which use to observe the structure morphology at higher magnification and chemical composition characterization.

3.2.1 Principle

The Scanning electron microscope works on the principle of applying kinetic energy to produce signals on the interaction of the electrons. These electrons are secondary electrons, backscattered electrons, and diffracted backscattered electrons which are used to view crystallized elements and photons.

Backscattered electrons: Backscattered electrons are reflected back when primary electron beam the sample. These are elastic interactions. Backscattered electrons come from deeper areas of samples. Its image display high sensitivity in difference in atomic numbers which will show up as brighter or darker

Secondary electrons: The secondary electrons are from atoms of the sample and they are inelastic interactions. It comes from surface regions. Scattered electrons give information about nano and micro structure of the samples in form of image.

Scintillator is used as a detector which is held at a high positive potential of several KV and the secondary electrons are accelerated into scintillator to give visible light which is then detected by photomultiplier.

At each point signals are emitted from specimen and is collected by detectors. The detector signal is synchronized with known location of the beam on the specimen and signal intensity used to modulate the corresponding image pixel. The signals collected in series are combined to form an Image whose dimension distribution depends upon the scan pattern chosen.[17]

3.2.2 Instrumentation

The scanning electron microscope instrument consists of the following components:

Electron source: The electron source generates electrons at top of the microscope column. The electrons are emitted by heated filament of Tungsten or Lanthanum Hexabromide by thermionic emission.

Anode: Anode has a positive charge, which attracts the electrons to form an electron beam.

Magnetic lens: Magnetic lens controls the size of the beam and determines number of electrons in the beam. The size of the beam will decide the resolution of the image. Apertures can be also used to control size of the image.

Scanning coils: The scanning coils deflects the electrons along x and y axes. To ensure it scans in a raster fashion over surface of the sample.

Objective lens: The objective lens is the last lens among lenses that creates the electron beam. Since this lens is very close to sample, it focuses the beam to a very small spot on the sample.

Since electrons cannot pass through glass, so SEM glass are electromagnetic. They made up of coil of wire inside metal poles. When current passes through these coils, they generate magnetic field. Since electrons are highly sensitive to magnetic field which allows the lenses in the microscope to control them.[18]

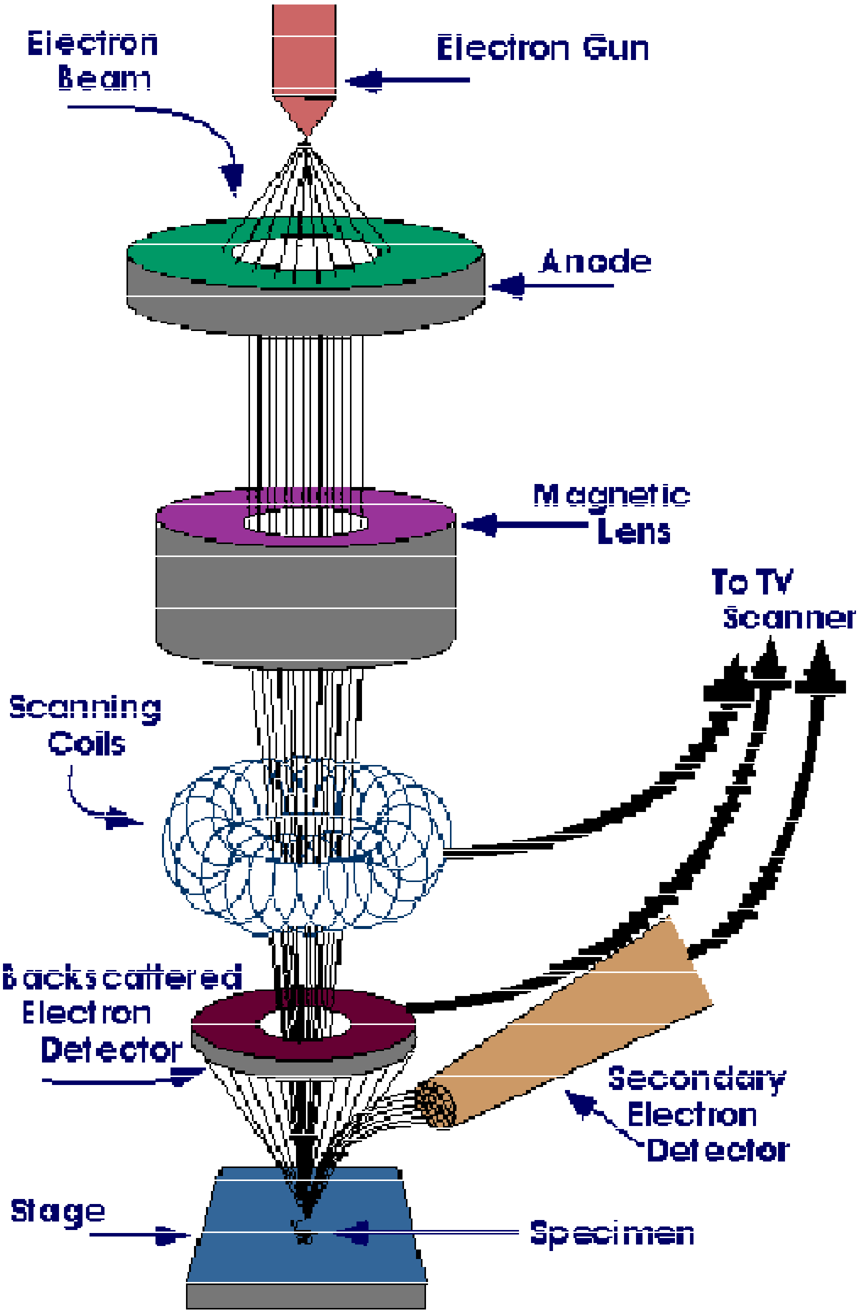


Figure3.5: Schematic diagram of a Scanning electron microscope. Adopted from the reference [3]

3.2.3 Applications

The main application of SEM is for determine materials under high magnification and providing information about sizes, shapes and compositions as seen from solid surfaces. The results complement those obtained from optical microscopy by providing information on submicron-sized features, but can also extend to features up to hundreds of microns across. Images may be recorded using both secondary electrons and back-scattered electrons, with instrumental conditions optimised for good topographic contrast.[17]

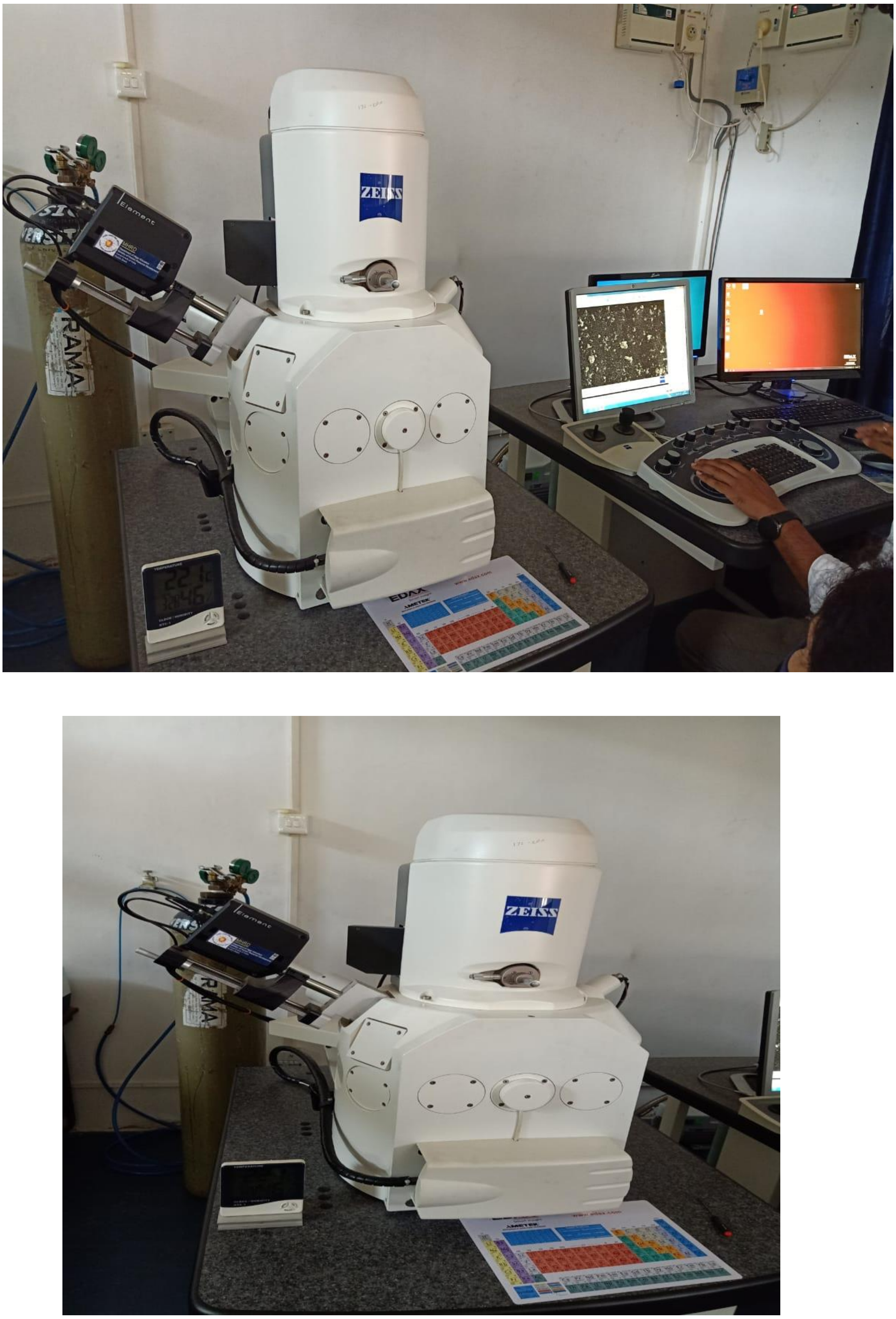


Figure3.6: Carl Zeiss Scanning Electron Microscope at USIC of Goa University.

3.3 UV Visible Spectroscopy

The wavelength of ultraviolet and visible radiation falls in the range of 200 to 800 nm of the electromagnetic spectra. Ultraviolet is from 200 nm to 400nm and visible is from 400 nm to 800 nm. Energy of this radiation is sufficient enough to cause electronic transition of outer valence electrons. In both organic and inorganic compounds, the electrons from bonding (outermost) orbitals are promoted to antibonding orbitals or higher energy levels by absorbing radiation from UV-Visible region. These electronic transitions are associated with vibrational and rotational transitions.

3.3.1 Principle

A compound appears coloured if it selectively absorbs light from the visible region. The absorbed energy raises the molecule from ground energy state (E_0) to higher excited energy state (E_1).

$$\Delta E = E_1 - E_0 = h\nu = hc/\lambda \qquad [3.3.1]$$

The difference in energy ΔE depends on how tightly the electrons are bound to the bonds, and accordingly absorption will occur in UV or visible range. In compounds having sigma bonds, the electrons in the molecule are tightly bound so radiation from UV region will be absorbed. No absorption occurs in visible region, so the compound appears colourless. If the electrons in the molecule are loosely bound, absorption occurs in the visible region and the compound appears coloured.

There are three types of ground state orbitals in molecules:

a) σ (bonding) molecular orbital – Electrons in this orbital are tightly bound and require high energy for their excitation and thus don't show absorption near UV region.

b) π (bonding) molecular orbital – Electrons in this orbital are found in multiple bonds and are generally mobile. Since π bonds are weak, the energy produced by UV radiation can excite its electrons from ground level to higher energy levels.

c) n (non-bonding) molecular orbital – Valence electrons which do not participate to form a chemical bond in a molecule are called as non-bonding electrons or n electrons. These are generally lone pair of electrons and can be excited by UV radiation.

Besides these, the anti-bonding orbitals are σ* orbital and π* orbital. [19]

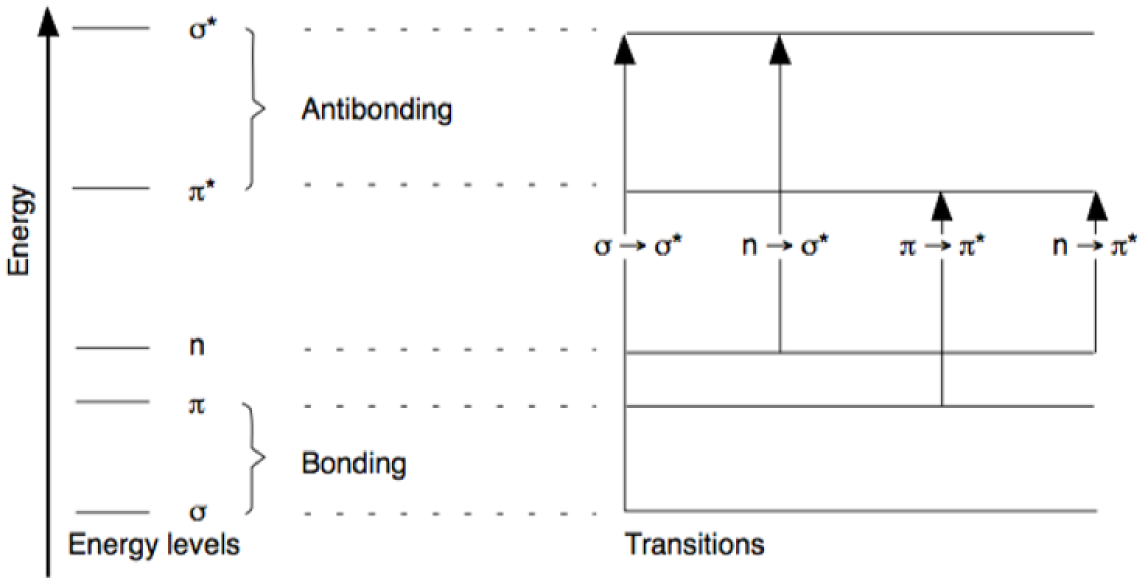


Figure3.7: Electronic transitions in UV-Visible spectroscopy. Adopted from the reference [19]

3.3.2 Beer-Lambert Law

A light beam is emitted via source and the incident beam passes through the sample and the wavelength of light reaching the detector is measured. The measured wavelength provides qualitative and quantitative information about the loaded sample such as chemical structure and number of molecules present. The information can be obtained as absorbance, transmittance or reflectance of radiation of range 160 nm to 3500 nm.

When light beam of specific energy (intensity) is focused onto a sample, the molecules absorb some energy of the incident light. A photodetector measures the intensity of light coming out of the sample and registers its absorbance. The absorption or transmission spectra of the light absorbed or transmitted by the sample against the wavelength is recorded. Beer-Lambert Law is basic principle of quantitative analysis which states that absorbance of light by the sample is directly proportional to analyte concentration and optical path length.

$$A = \varepsilon . l . c \qquad [3.3.2]$$

Where ε is molar absorption coefficient, l is optical path length and $\boldsymbol{c}$ is molar concentration.

Transmittance ($\boldsymbol{T}$) is given by

$$T = I/Io \qquad [3.3.3]$$

Where I is intensity of incident light and Io is the intensity of light detected

and absorbance is the inverse of transmittance given by

$$A = \log\left(\frac{1}{T}\right) = \log\left(\frac{I}{Io}\right) = -\varepsilon c l \qquad [3.3.4]$$

3.3.3 Instrumentation

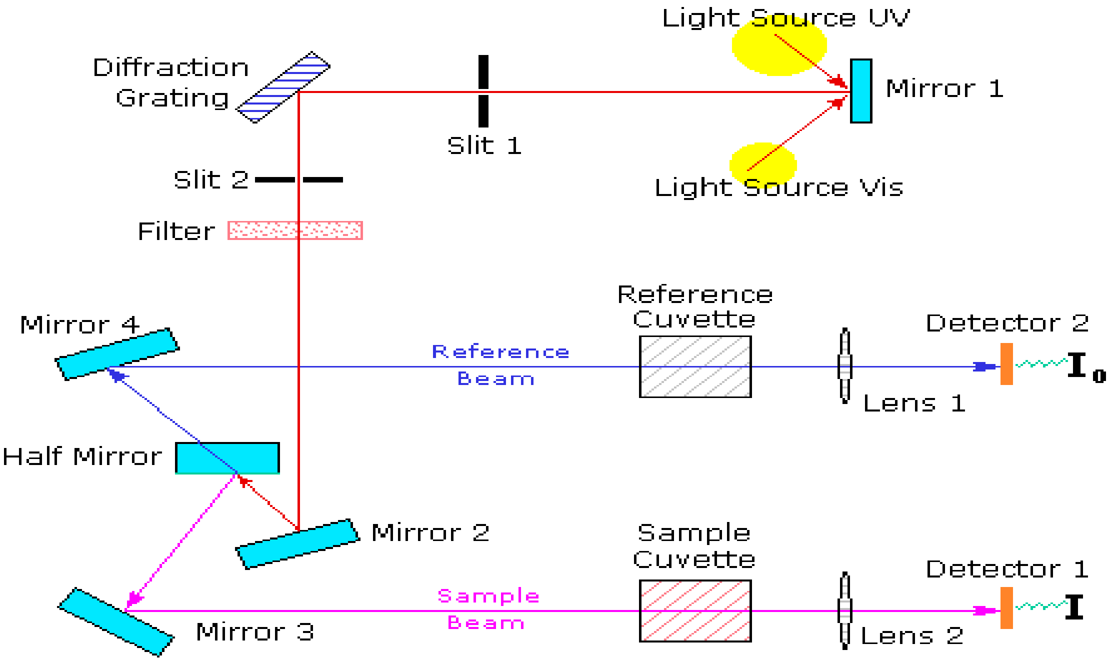


Figure 3.8: Schematic representation of UV- Visible Spectrometer. Adopted from the reference [19]

The instrument consists of a UV source which produces continuous UV spectrum by electrically exciting deuterium or hydrogen at low pressures, a visible light source which is generally a Tungsten filament lamp, a monochromator and before reaching the sample, the light is divided into two parts of similar intensity with a half mirror splitter. One part travel via cuvette having solution of material to be examined in a transparent solvent and the second beam or reference beam travels through cuvette having only solvent.

The detector detects the intensity of light transmitted by both the cuvettes and sends that data to a meter to record and display the values. Electronic detectors calculate and compare the intensities of the light beams. [20]

3.3.4 Calculation of band gap from reflectance

Band gap energy is the energy needed to excite an electron from the valence band to the conduction band. Band gap energy is crucial in predicting photophysical and photochemical properties of some materials. In 1966, Tauc proposed a method to determine the band gap energy of materials using optical absorption spectra.

Tauc method is based on assumption that the energy-dependent absorption coefficient α can be expressed as

$$(\alpha . h\upsilon)^{\frac{1}{\gamma}} = B(h\upsilon - E_g) \qquad [3.3.6]$$

Where h is Plank constant, υ is frequency of photon, E_g is band gap energy and $\boldsymbol{B}$ is constant. γ depends on nature of electronic transition and is equal to ½ or 2 for direct and indirect transition band gaps respectively.

The measured reflectance spectra can be transformed to the corresponding absorption spectra by applying the Kubelka-Munk function

$$F(R_\infty) = \frac{K}{S} = \frac{(1-R_\infty)^2}{2R_\infty} \qquad [3.3.7]$$

Where $R_\infty = R_{sample}/R_{standard}$ is the reflectance of an infinitely thick specimen, while ***K*** and ***S*** are the absorption and scattering coefficients respectively. Putting $F(R_\infty)$ instead of α in equation [3.7] we get,

$$(F(R_\infty). h\upsilon)^{\frac{1}{\gamma}} = B(h\upsilon - E_g) \qquad [3.3.8]\ [21]$$

Figure3.9: Shimadzu UV-2401PC UV- spectrometer at SPAS of Goa University.

3.4 Photoluminescence spectroscopy

Photoluminescence is a process in which a molecule absorbs a photon in the visible region, exciting one of its electrons to higher electronic excited states and radiates a photon while coming down to lower energy state.

There are two types of photoluminescence: fluorescence and phosphorescence.

A pair of electrons occupying the same electronic ground state have opposite spins and are said to be in a singlet state. When an analyte absorbs an ultraviolet or visible photon, one of its valence electrons moves from ground state to an excited state with a conservation of electron spin. Emission of a photon from the singlet excited state to singlet ground state or between any two energy levels with the same spin is called fluorescence. The probability of fluorescence is very high and average lifetime of an electron in the excited state is only 10^{-5} to 10^{-8} s.

In some cases, an electron in a singlet excited state is transformed to a triplet excited state in which its spin is no longer paired with the ground state. Emission between a triplet excited state and a singlet ground state or between any two energy levels that differ in their respective spin states is called phosphorescence. The average lifetime for phosphorescence ranges from 10^{-4} to 10^{4} s.

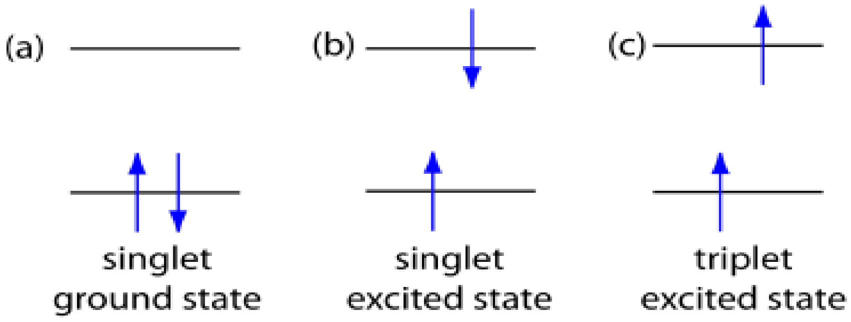


Figure3.10: Electronic configurations for a) a singlet ground state, b) a singlet excited state, c) a triplet excited state. Adopted from the reference [22]

The luminescence of inorganic materials is composed of following processes: i) absorption and excitation, ii) energy transfer, and iii) emission. Most luminescent materials consist of a host material to which certain dopant ions (activators) are added. In such cases, the host material plays two distinct roles. a) It acts a passive matrix to define the spatial locations of the activator ions. Here It exerts its own scientific influence spectroscopic behaviour of the activator. And b) it also acts as an active participant in the luminescence process; it helps to shape the structure of energy levels of the activator and also introduces vibrations of various energies (phonons) which influence the kinetics of the luminescence phenomena.

3.4.2 Radiation-less deactivation

When a molecule relaxes to a lower energy without emitting photon, it is called as radiation-less deactivation. One example is vibrational relaxation in which a molecule in excited vibrational energy level comes down to lower vibrational energy level in the same electronic state. The average lifetime of vibrational relaxation is less than 10^{-12} s.

Another form of radiation-less deactivation is internal conversion in which a molecule in ground vibrational level of an excited state passes directly into a higher vibrational energy level of a lower energy electronic state of the same spin state. By combination of vibrational relaxations and internal conversions, a molecule in excited electronic state may return to ground electronic state without emission of photon. A similar form of radiation-less deactivation is an external conversion in which excess energy is transferred to the solvent or to another component of the sample’s matrix.

A final form of radiation-less deactivation is intersystem crossing. In this, a molecule in its ground vibrational energy level of an excited electronic state passes into a higher vibrational energy level of a lower energy excited state with a different spin state.

Fluorescence and phosphorescence spectra is shown in the figure.

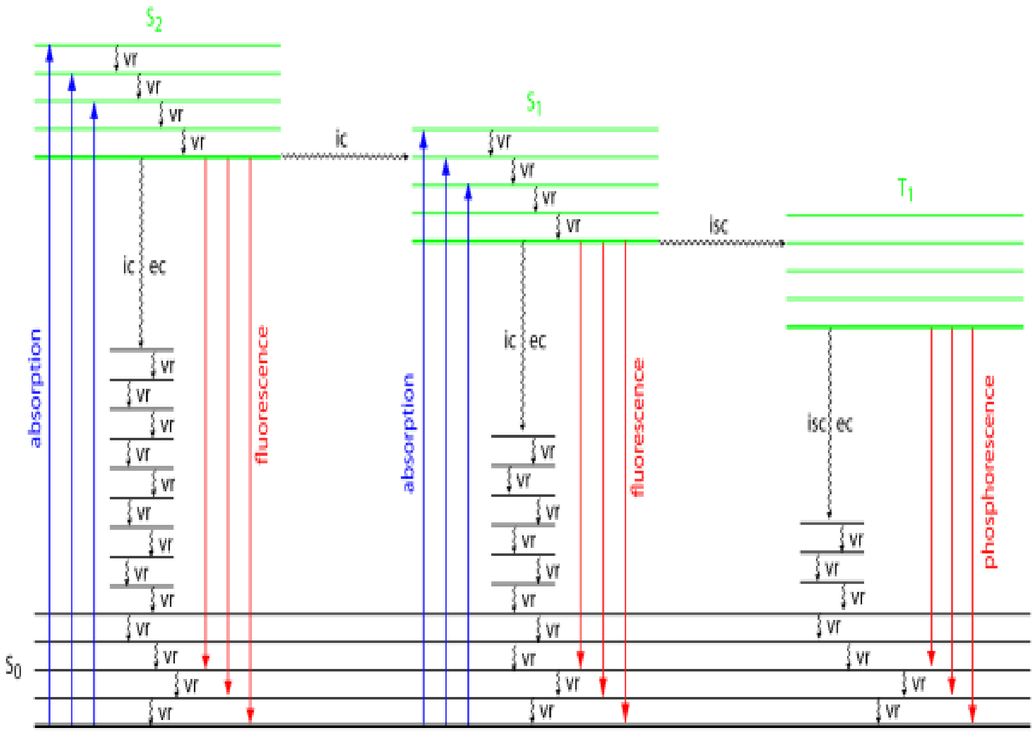


Figure3.11: Energy level diagram for a molecule showing pathways for deactivation of an excited state. Adopted from the reference [22]

Vr is the vibrational relaxation; ***ic*** is internal conversion; ***ec*** is external conversion and ***isc*** is an intersystem crossing. The lowest vibrational energy for each electronic state is indicated by the thicker line. The electronic ground state is shown in black and the three electronic states are shown in green. The absorption, fluorescence and phosphorescence of photons ae also shown.

3.4.3 Relaxation by fluorescence

Fluorescence quantum yield (φ_f) is the ratio of photons emitted to photons absorbed by the sample. Fluorescence quantum yield ranges from 0 to 1. In other words, it gives the probability of fluorescence.

Intensity of fluorescence $\boldsymbol{I_f}$ is proportional to amount of radiation absorbed by the sample ($\boldsymbol{P_o}$-$\boldsymbol{P_T}$) and fluorescence quantum yield (φ_f).

$$I_f = k.\varphi_f.(P_O - P_T) \qquad [3.4.1]$$

Where k is a constant accounting for efficiency of collecting and detecting the fluorescent emission.

From Beer's law,

$$\frac{P_T}{P_o} = 10^{-\varepsilon lc} \qquad [3.4.2]$$

Where c is the concentration of the sample. From 1 and 2 we get,

$$I_f = k.\varphi_f.P_O(1 - 10^{-\varepsilon lc}) \qquad [3.4.3]$$

When εlc <0.01 (when concentration is very less), equation [3.4.3] simplifies to

$$I_f = 2.303k\varphi_f \ \varepsilon lcP_O = k'P_O \qquad [3.4.4]$$

Where k' is collection of constants. Therefore, the intensity of fluorescence emission increases with increase in quantum efficiency, power of incident source, molar absorptivity and concentration of the sample.

A molecule's fluorescence quantum yield is also influenced by external variables such as temperature and solvent. Increase in temperature generally decreases φ_f because frequency of collisions between the molecule and the solvent increases external conversion.

Fluorescence is generally observed when lowest energy absorption of the molecule is a π to π* transition. Also, some **n** to π* transitions show weak fluorescence.

3.4.4 Relaxation by phosphorescence

The intensity of phosphorescence is given by an equation similar to equation 4 for fluorescence

$$I_p = 2.303k\varphi_p\, \varepsilon lcP_O = k'P_O \qquad [3.4.5]$$

Where φ_p is phosphorescent quantum yield.

Phosphorescence is most favourable in molecules with **n** to π^* transitions which have higher probability for an intersystem crossing than π to π^* transitions.

3.4.5 Excitation versus emission spectra

Photoluminescence spectra are recorded by measuring the intensity of emitted radiation as a function of either excitation wavelength or emission wavelength. Excitation spectra is obtained by monitoring emission at a fixed wavelength while varying the excitation wavelength. A sample's excitation spectrum is nearly identical to its absorbance spectrum when corrected for variations in the intensity of source and response of detector. The excitation spectra provide convenient means for selecting best excitation wavelength for a quantitative or qualitative analysis.

In emission spectrum, in order to excite the sample, a fixed wavelength is used and the intensity of emitted radiation is monitored as a function of wavelength. Although a molecule has only one excitation spectra, it has two emission spectra, one for fluorescence and one for phosphorescence. [22]

3.4.6 Instrumentation

The fluorescence from a sample is recorded and measured by an analytical device called spectrofluorometer. Scanning of excitation and emission wavelengths is done to record fluorescence. Fluorescence spectrometers use laser sources which has monochromator (to select wavelength), laser source (for sample illumination), detectors and corrected spectrum.

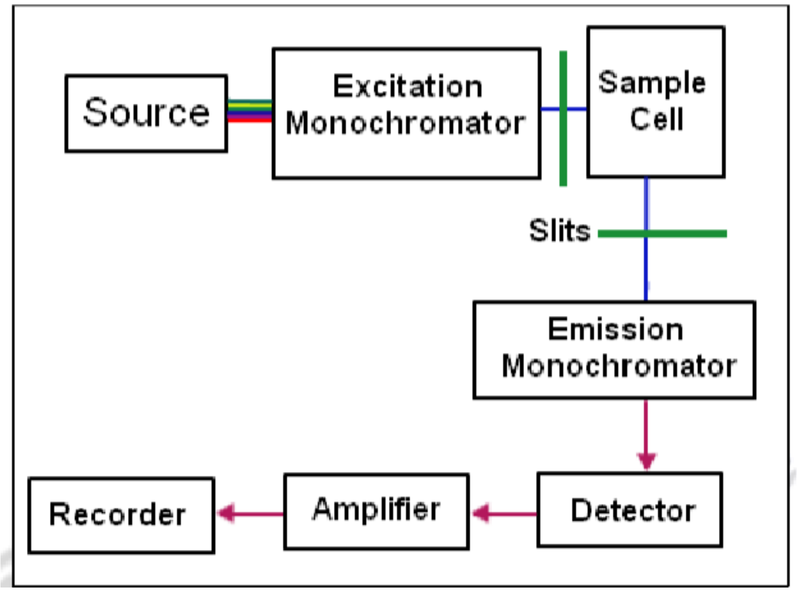


Figure3.12: Block diagram of fluorescence spectrometer. Adopted from the reference [11]

a) source of light: the source of light used is of continuous type, xenon arc lamp.

b) Monochromators: there are two types of monochromators, excitation and emission type.

c) Gratings: Reflection grating is the crucial part of monochromator, whose purpose is to disperse the incident light through grooves which are positioned vertically.

d) Slits: Very flexible slits are used at the entrance and exit points of the monochromator. Bandpass of the incident light is determined by the skit width on the excitation monochromator. The emission monochromator slits control the fluorescence intensity signal. When setting the slit width, the trade-off is intensity of signal versus spectral resolution. When slit width is wider, there is decrease in resolution because of extra light falling on the sample and detector. When the slits are narrow, higher resolution is obtained but at the cost of signal.

e) Shutters: Beneath the slit of excitation monochromator exit, an excitation shutter is placed whose purpose is to shield the sample from photo bleaching or photo degradation by long exposure to light. The detector is protected from the bright light by the emission shutter which is positioned just prior to the entrance of emission monochromator.

f) Sample compartment: in sample compartment, several optional attachments are present along with a bunch of fibre optics to take the excitation beam to the sample which is placed remotely and bring back the emission beam to emission monochromator.

g) Detector: There are two types of detectors, signal and reference detector. The signal detector is based on photon counting. Whereas the purpose of reference detector is to monitor the Xenon lamp for correction of wavelength and its time dependent output.[11]

Figure3.13: Cary Eclipse Fluorescence Spectrophotometer in SPAS.

Chapter 4: Results and discussion

4.1 X-ray diffraction analysis

X-ray diffraction patterns of the synthesised samples were analysed using Rietveld analysis in FullProf software. The XRD patterns of NaRE(WO_4)$_2$,(RE= Sm, Ho, Pr) are shown in figure4.1, 4.2 and 4.3 respectively.

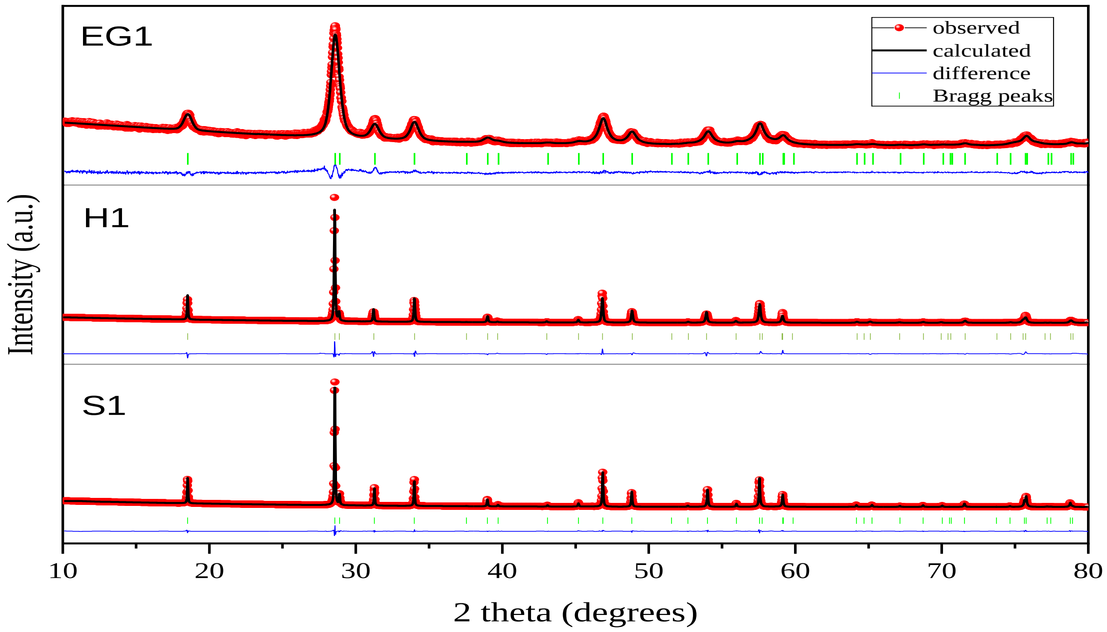


Figure4.1: Comparison of - X-ray diffraction patterns of NaSm(WO_4)$_2$ with different synthesis methods

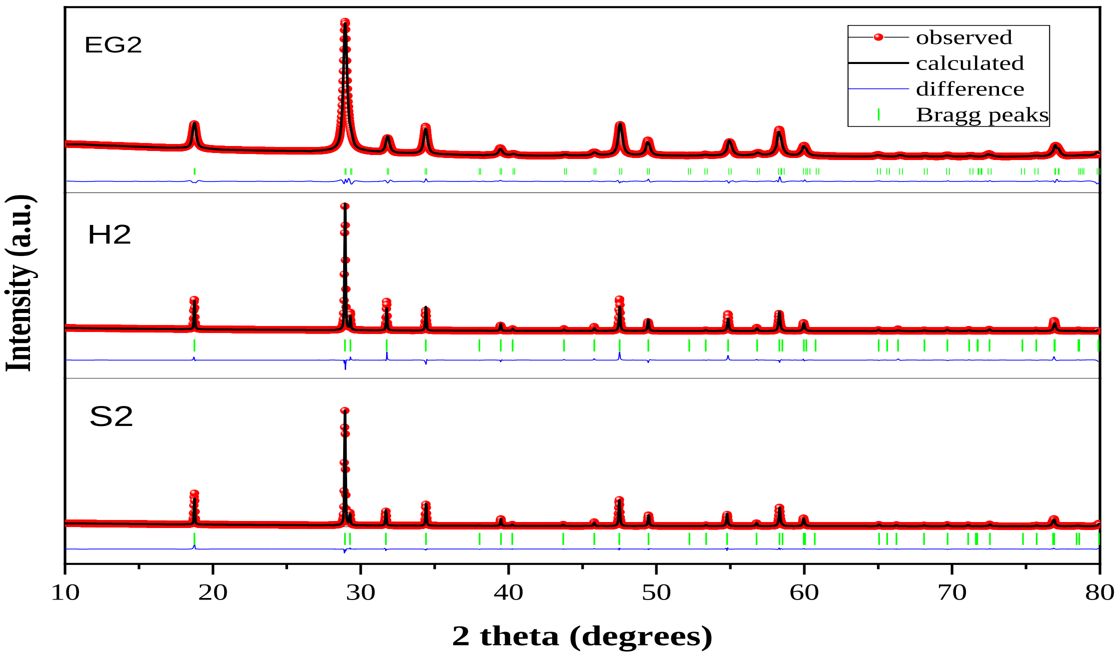


Figure4.2: Comparison of X-ray diffraction patterns of NaHo$(WO_4)_2$ with different synthesis methods

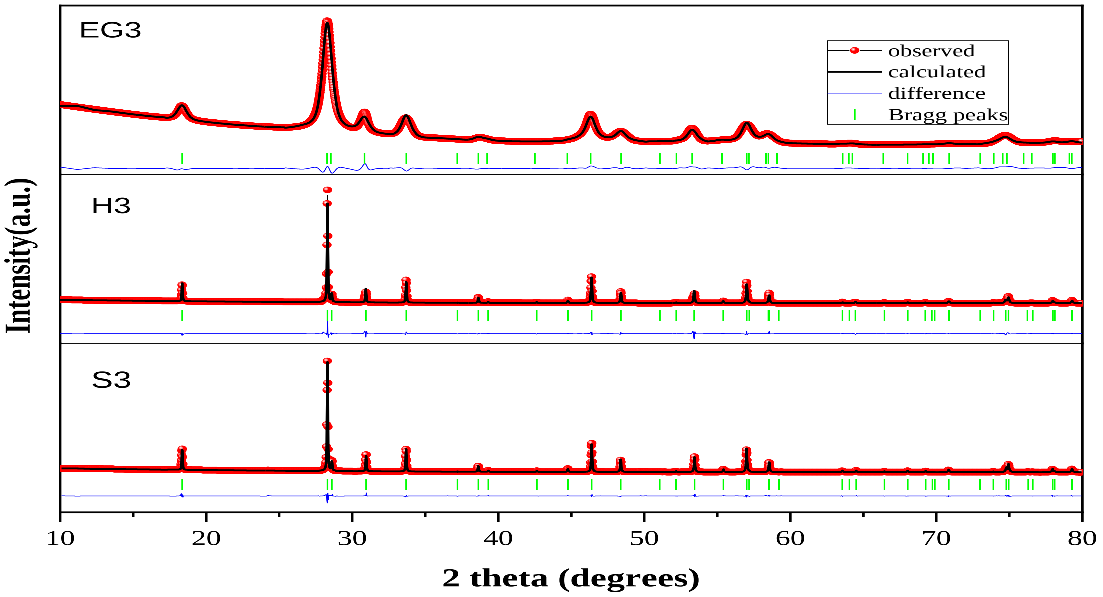


Figure4.3: Comparison of X-ray diffraction patterns of NaPr$(WO_4)_2$ with different synthesis methods

XRD pattern confirms the formation of pure phase compounds without any impurities or any secondary phases as shown in Figures 4.1, 4.2 and 4.3. Thus, samples are pure in phase and are in good agreement with previously reported data having Scheelite structure with the tetragonal space group $I4_1/a$. The lattice constant of samples was determined and listed on table 1.

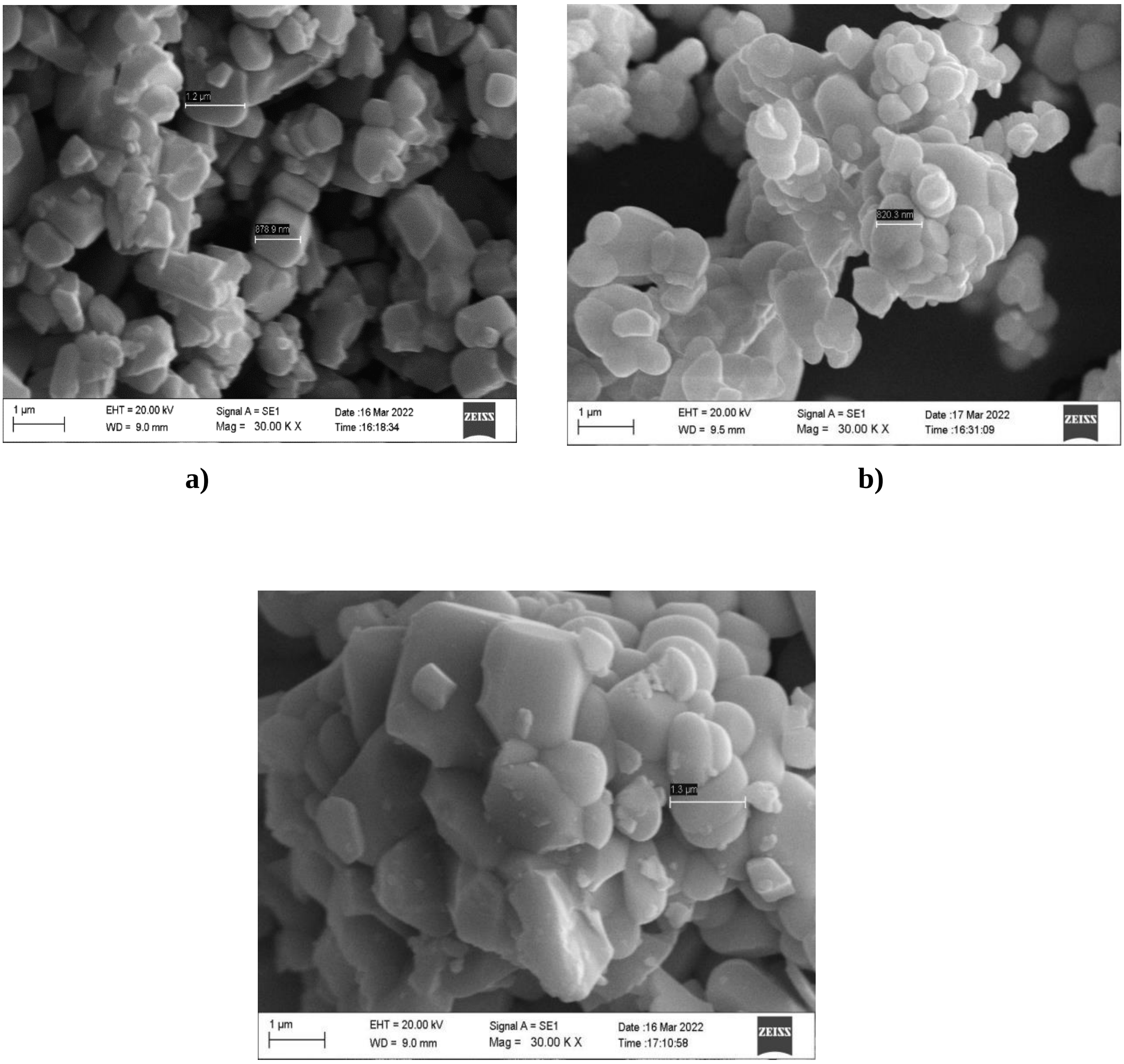
It can also be seen that compounds synthesised via solid state method and hydrothermal method have intensities and peak shapes of similar size compared to that of synthesised via solvothermal method with ethylene glycol as solvent in which lower intensity and peak broadening is observed. Thus, it is evident that solvent plays an important role in controlling particle size and morphology. Smaller sized particles can be synthesised by playing with different solvents. It is observed that the lattice parameters remain same for all compounds independent of their synthesis methods.

samples	**a** (A˚)	**c** (A˚)	**Volume**	**R$_B$-** **factors**	**Chi2**	**Rp**	**Rwp**
S1	5.2704	11.4318	317.453	2.11	0.968	9.26	8.77
H1	5.2679	11.4507	317.777	3.65	3.77	14.9	16.2
EG1	5.2675	11.4209	316.897	5.09	2.33	16.1	15
S2	5.2068	11.2794	305.805	2.81	2.62	8.86	9.19
H2	5.2091	11.2630	305.629	4.56	8.86	15.2	18
EG2	5.2146	11.2459	305.806	1.90	0.786	10.3	9.98
S3	5.2315	11.5466	326.287	3.17	2.28	11.4	10.8
H3	5.2314	11.5534	326.346	4.35	5.75	15.6	17.7
EG3	5.3135	11.5884	327.189	1.90	0.786	10.3	9.98

Table 1: **Rietveld analysis parameters**

4.2 Morphological study

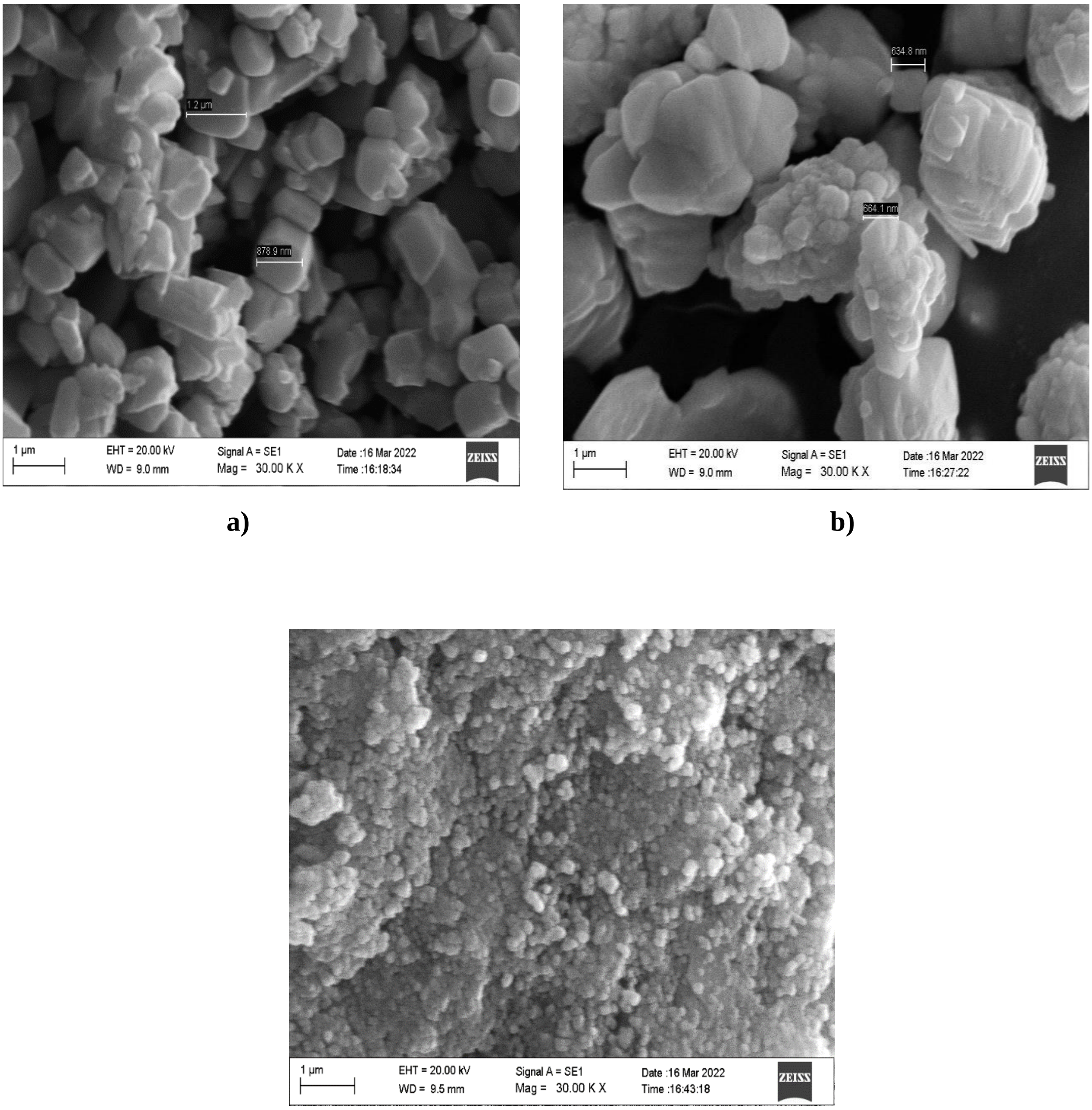
Scanning electron microscope images of the synthesised samples were taken using Zeiss Scanning Electron Microscope. Morphology and particle sizes of $NaRE(WO_4)_2$ RE=Sm, Ho, Pr) were compared and analysed using the SEM images.



a) **b)**

c)

Figure4.4: SEM images of compounds a) S1, b) S2 and c) S3



a) **b)**

c)

Figure4.5:SEM images of compounds a) S1, b) H1 and c) EG1

Figure 4.4 shows SEM images of S1, S2, and S3. It can be seen that the particle sizes are almost homogeneous. Figure 22 shows SEM images of $NaSm(WO_4)_2$ synthesized via solid state method (S), hydrothermal method (H) and solvothermal method (EG) . In figure 4.4 and figure 4.5 all images are of same scale (2µm). From figure2 it can be seen that the particle sizes are different for different synthesis methods. The size of particles of synthesized by solid state method was larger (~870nm), slightly smaller for hydrothermal method (~660nm) and very small particle size (~140nm) was observed for compounds synthesized via solvothermal method.

4.3 UV-Visible Spectroscopy

UV-Visible spectra analysis was done using Shimadzu UV-2401PC UV- spectrometer.

Using UV-Vis absorption Spectra, tauc plot was plotted for (S1, H1, EG1) , (S2, H2, EG3) , (S3, H3, EG3) and their bandgap was determined. Comparison of bandgaps was made for compound synthesised via different synthesised method.

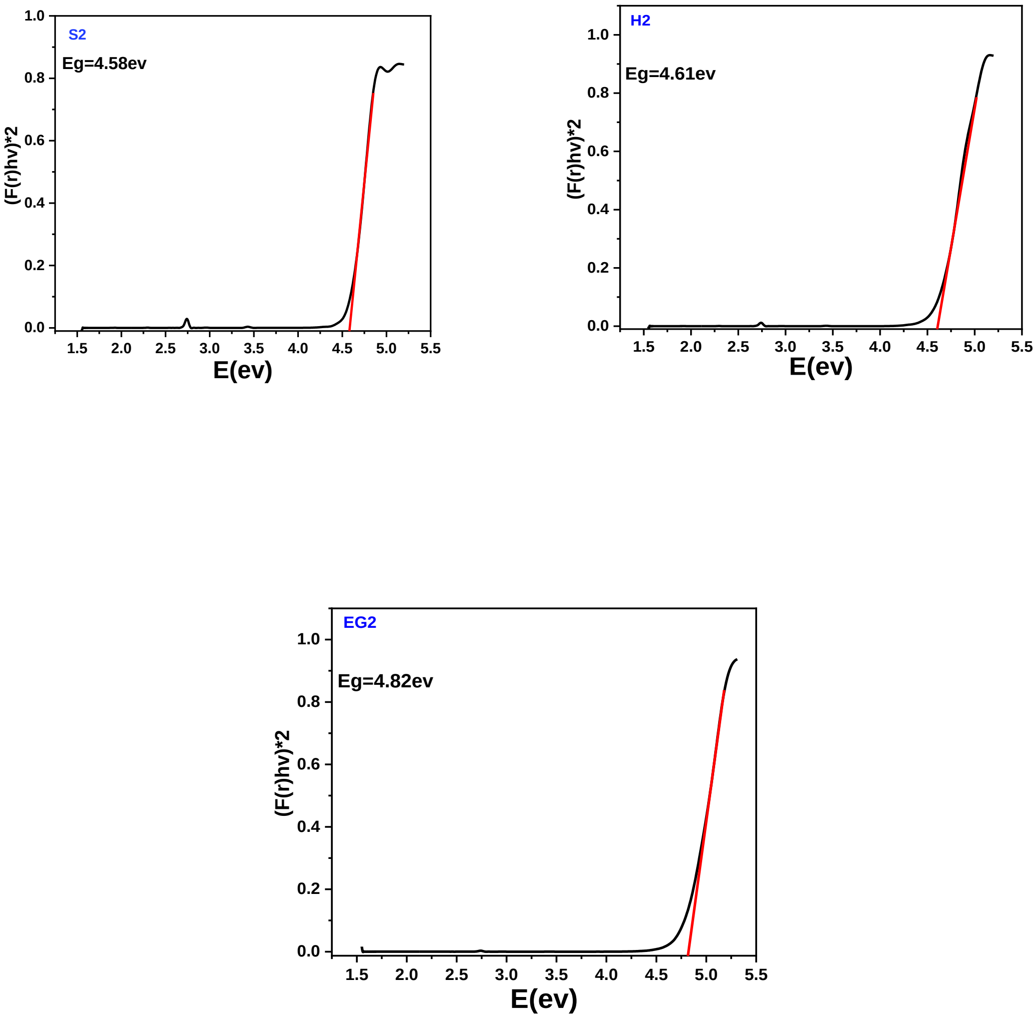


Figure4.6: Tauc plots of S2, H2 and EG2

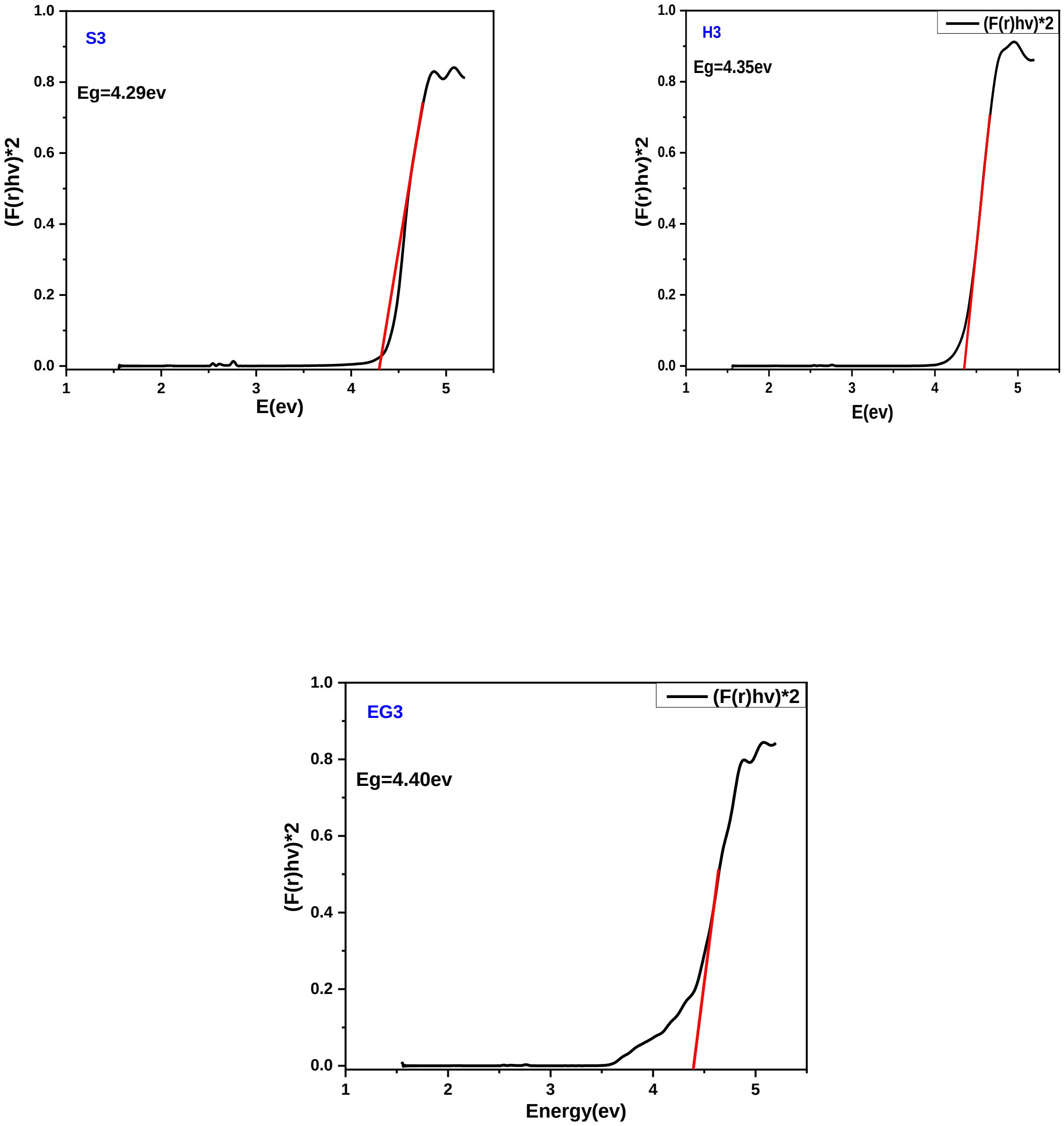


Figure4.7: Tauc plots of S3, H3 and EG3

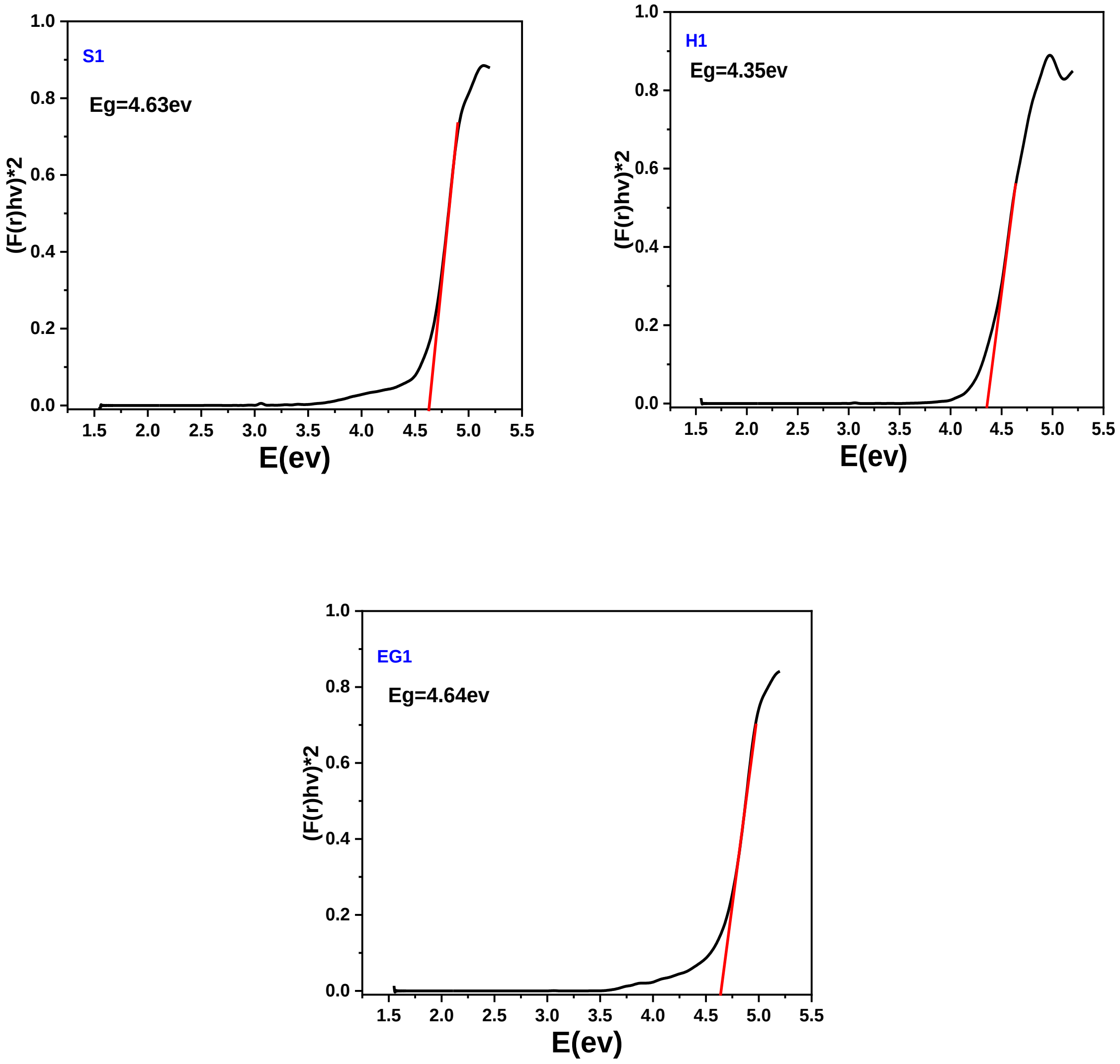


Figure4.8: Tauc plots of S1, H1 and EG1

From the Tauc plots it can be seen that energy band gap of the synthesised compounds varies with different synthesis techniques. $NaHo(WO_4)_2$ synthesised via solid state method was found to have band gap of 4.58 eV. For the same compound synthesied via hydrothermal method and solvothermal method had band gap of 4.61 eV and 4.82 eV respectively. The trend of increasing band gap with decrease in band gap was observed.

Similarly for $NaPr(WO_4)_2$ synthesised via solid state method was found to have band gap of 4.29 eV. For the same compound synthesied via hydrothermal method and solvothermal method had band gap of 4.35 eV and 4.40 eV.

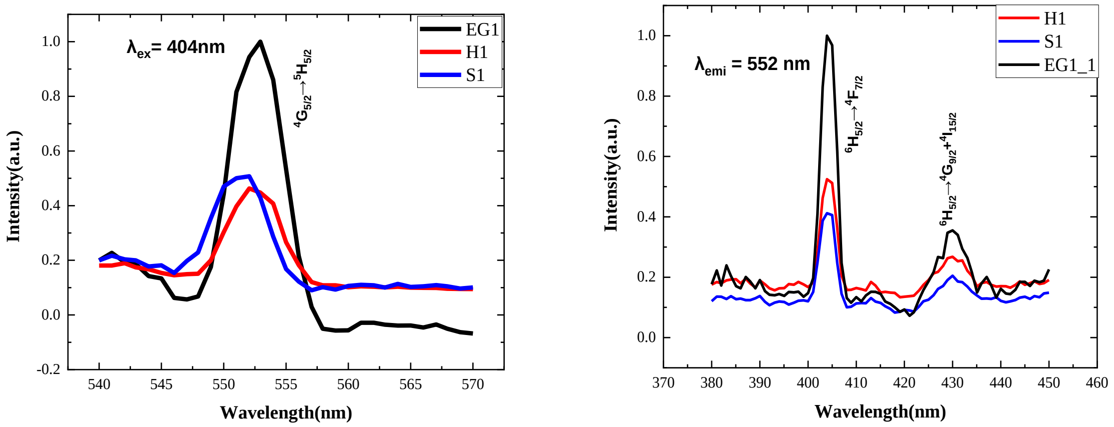
$NaSm(WO_4)_2$ synthesised via solid state method was found to have band gap of 4.63 eV. For the same compound synthesied via hydrothermal method and solvothermal method had band gap of 4.35 eV and 4.64 eV respectively.

4.4 Photoluminescence spectroscopy

The study of photoluminescence of $NaSm(WO_4)_2$; (RE=Sm, Ho, Pr) was done using Cary Eclipse Fluorescence Spectrophotometer.

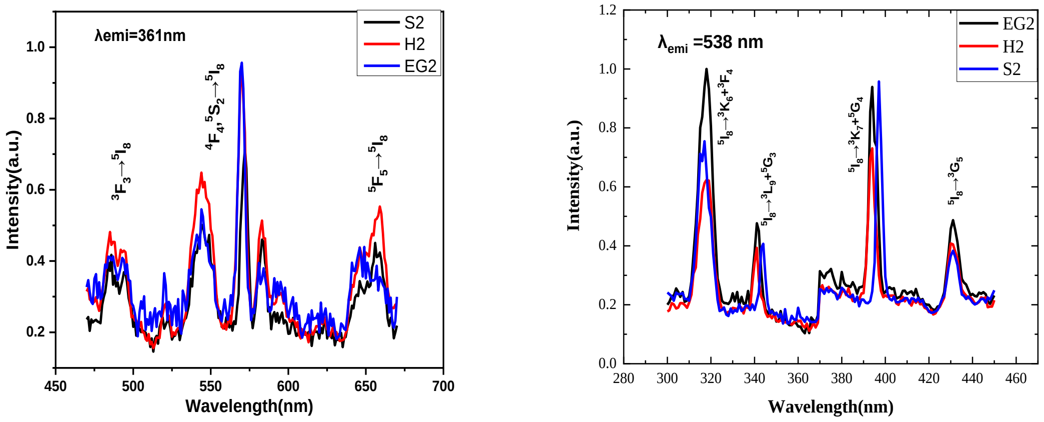
From the data collected it was seen that, $NaSm(WO_4)_2$ shows emission peak at 552nm when excited with 405nm and shows excitation peaks at 405nm and 431nm for emission at 552nm. $NaHo(WO_4)_2$ shows emission peaks at 543nm and 569nm for excitation of 361nm and excitation peaks at 318nm, 341nm, and 394nm for emission at 538nm. $NaPr(WO_4)_2$

emission peaks at 647nm and 611 nm for excitation at 448nm and excitation peaks at 448nm, 474nm and 486nm for emission of 647nm. From the PL spectra of all the compounds, it was observed that smaller the particle size, higher is the peak intensity.



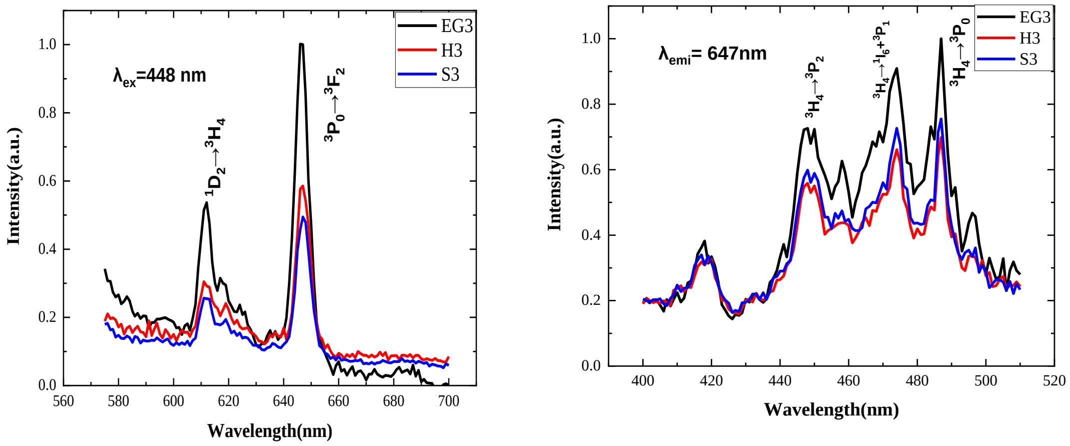
(a) (b)

Figure4.9: (a) Emission spectra and (b) Excitation Spectra for $NaSm(WO_4)_2$



(a) (b)

Figure4.10: (a) Emission spectra and (b) Excitation Spectra for NaHo(WO$_4$)$_2$



(a) (b)

Figure4.11: (a) Emission spectra and (b) Excitation Spectra for NaPr(WO$_4$)$_2$

Samples	Excitation peak wavelength (nm)	Emission peak wavelength (nm)
NaSm(WO$_4$)$_2$	404, 431	552
NaHo(WO$_4$)$_2$	318, 341, 394	543, 569
NaPr(WO$_4$)$_2$	448,474,486	647,611

Table 2: Photoluminescence excitation and emission wavelength details.

Discussion and summary

The samples were synthesised via solid states synthesis, hydrothermal and solvothermal synthesis methods. From PXRD analysis, samples were found to have space group of $I4_1/a$ and tetragonal structure. The samples were pure in phase without any impurities and secondary phases. From Rietveld analysed XRD graphs it was observed that samples synthesised via solid states and hydrothermal synthesis had similar intensity peaks whereas for compounds synthesised via Solvothermal method, peak broadening was observed. From SEM images it was observed that for compounds synthesised via solid state and hydrothermal method, particle size was almost similar. Whereas, solvothermal synthesis using ethylene glycol as solvent gave smaller particle size. Thus, it was evident that peak broadening in XRD pattern was due to smaller particle size of the analysed compounds. From PL spectra of all the compounds it was observed that smaller the particle size, higher is the peak intensity. Thus, it was evident that solvent plays important role in determining size of the particle. We can play with solvents to get desired size particles. In this project work we determined structure and -particle sizes of the synthesised compounds and compared their luminescence properties. Luminescence property of rare earth material have large application in upcoming technology due to its high efficiency, low power consumption, durability and environment friendly nature. One can study it with different rare earth material and different synthesis routes.

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