

Synthesis and characterization of $\text{Sc}_2\text{W}_3\text{O}_{12}:\text{Yb}^{3+}/\text{Er}^{3+}$

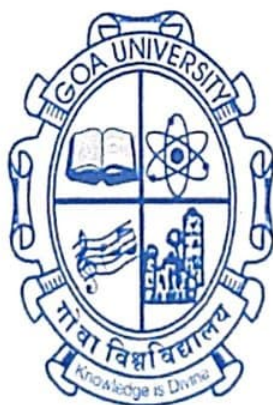
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DECLARATION BY STUDENT

I hereby declare that the data presented in this Dissertation report entitled, "**Synthesis and characterization of $\text{Sc}_2\text{W}_3\text{O}_{12}:\text{Yb}^{3+}/\text{Er}^{3+}$** " This is based on the results of investigations carried out by me in the Masters of Physics at the School of Physical and Applied Science, Goa University, under the Supervision of UGC Assistant Prof. Dr Venkatesha Hathwar. I have not submitted the same elsewhere for a degree or diploma award. Further, I understand that Goa University or its authorities will not be responsible for the correctness of observations / experimental or other findings given the dissertation.

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COMPLETION CERTIFICATE

This is to certify that the dissertation report "**Synthesis and characterization of $\text{Sc}_2\text{W}_3\text{O}_{12}:\text{Yb}^{3+}/\text{Er}^{3+}$** " is a bonafide work carried out by Miss. Vijaymala V. Parab under my supervision in partial fulfilment of the requirements for the award of the degree of Master of Science in Physics at the School of Physical and Applied Science, Goa University.



Signature of Dean of the School

Date: 8 May 2024

Place: Goa University



School stamp



Signature of Supervising Teacher

Dr. Venkatesha Hathwar

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With great pleasure, I provide the report of my final year M.Sc. project work. Despite my best efforts, this project would not have been successful without the support and advice of a few individuals. For that reason, I would like to sincerely thank those people.

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ABSTRACT

This project report presents a comprehensive investigation into the synthesis, characterisation, and application of $\text{Sc}_2\text{W}_3\text{O}_{12}:\text{Yb}^{3+}/\text{Er}^{3+}$ using the hydrothermal method. The synthesized material was systematically studied using X-ray diffraction (XRD) and scanning electron microscopy (SEM) to analyze its structural and morphological properties. Furthermore, the potential application of the synthesised material in dye degradation was explored.

The efficiency of the hydrothermal synthesis process in yielding phase-pure and precisely specified crystalline minerals led to its selection. Under carefully regulated hydrothermal conditions, it was possible to synthesise Yb- and Er-doped Scandium tungstate, which resulted in the production of crystalline structures with the appropriate compositions. The produced material's crystal structure and phase purity were determined by XRD analysis, which also verified that ytterbium and erbium ions had been incorporated into the scandium tungstate lattice. The manufactured particles' homogeneity and shape were highlighted by SEM imaging, which also shed light on their surface characteristics.

Dye degradation studies were conducted to investigate the synthesized material's potential for environmental remediation, in addition to structural and morphological characterization. The model organic dye pollutant used as methyl orange, and under visible light irradiation, the synthesised scandium tungstate doped with Yb and Er showed encouraging photocatalytic activity for dye breakdown.

In general, this research advances knowledge of hydrothermally produced rare-earth doped materials and their possible uses in environmental remediation. The results highlight the significance of customizing material characteristics for particular uses and provide new directions for the study of advanced materials for environmental sustainability.

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CHAPTER 1

1 Introduction

1.1 Early history and evolution of light

Lighting has been evolving for roughly two million years. For most of our history, we have depended on the sun and stars as natural light sources. It was essential when we lived in the country, but today our cities and businesses are always open. Our current lifestyle would not be possible without adequate lighting.

In the UK, lights use more than 58,000 terawatts of electricity each year. In Britain, we use this kind of light in every home, business, and street. Among the first things humans invented was manufactured light. Instead of waiting for lightning to ignite ancient wood and brush, our ancestors used simple tools to start a fire whenever they needed it. By 125,000 BC, it had become widespread and allowed humans to live in caves, their very first shelter.

Lighting and shelter evolved simultaneously. Mankind would not have been able to live off a light source without manipulating it until 4500 BC. This marked the invention of the first oil lamp, which was followed in 3500 BC by the creation of the candle. Lamps were the main product of the development efforts of innovators before electricity. Invented in 1780, the Argand lamp quickly rose to prominence as a must-have item in 18th-century Paris. This was due to the higher efficiency of the lamp, which produced 10 times more light than a single candle.

William Murdoch created the first gas lamp in 1792, which completely changed the way people used and developed lighting outside their homes. Before 1800, factory work was dangerous. Early cotton mills used steam or water engines, and any misplaced equipment could injure workers if it could not be properly repaired. Using gas lighting, the Salford cotton mill owned by Philips and Lee began to modify this. The mining industry was pushed forward by similar innovations. Invented by Humphrey Davy, the safety mine lamp helped coal miners prevent the ignition of naturally occurring flammable methane in the mine.

1.2 Phosphor-coated white light LEDs

The development of white LED bulbs was made possible in 1992 by the Nobel Prize-winning innovation of the blue LED, which started a revolution in lighting. Commercial white LEDs combine a blue LED with a phosphor conversion layer to produce white light emission. However efficiency is lost during the conversion process and the phosphor ages over time, reducing the life of the bulb. The process of creating traditional white LEDs involves phosphor-coating the blue LED. The phosphor absorbs some of the blue light and changes it to another colour. The combination of hues creates what our eyes interpret as white light.

Previous research has attempted to engineer layers of compound semiconductors with different emission wavelengths to form a single structure to produce phosphor-free white LEDs. Because they don't emit enough red light, these gadgets have a low colour rendering index (CRI), which measures how realistic the colours of things look with a particular light source. An LED is made up of many components, one of which is phosphor, which is necessary to produce the vital white light that an LED produces. The substance that is placed on the surface of the blue LED is called phosphor and has nothing to do with the element phosphor. A portion of the phosphor is converted to the appropriate complementary hues when struck by a blue light source, so the entire output appears white. Coating LEDs with phosphors to make them appear whiter is nothing new. However, a number of methods that have attempted to achieve this are limited by efficiency issues.

For example, much of the light that is released is reflected to the chip in one common way, causing it to be wasted and distributed. While other coating methods are more efficient, they also suffer from significant losses due to total internal reflection and quantum conversion. One material that exhibits luminescence is phosphorus. When it comes to LED lighting, fluorescence—the type of luminescence produced when blue light energy from LED chips is absorbed—is the specific luminescence that occurs. The structure and composition of the phosphor can be carefully tailored to manipulate the spectrum of emitted light and achieve the required performance standards. Therefore, phosphors are often used in the electronics and lighting industries to facilitate the use of devices such as screens, fluorescent lights, and white LEDs.

1.3 Solid state lighting

Instead of electric filaments, plasma (used in arc lamps such as fluorescent lamps), or gas, solid-state lighting (SSL) uses semiconductor light-emitting diodes (LEDs), organic light-emitting diodes (OLEDs), or polymer light-emitting diodes (PLEDs). as lighting sources. Unlike fluorescent or incandescent lamps that use thermal radiation, SSL uses solid-state electroluminescence. SSL produces visible light with less heat generation and energy dissipation than incandescent lighting. Most "white LEDs" are made of a solid-state semiconductor that uses photoluminescence, the same technology that powers conventional fluorescent lights, to convert blue light into a roughly white light spectrum.

Compared to long thin wires and fragile glass tubes or light bulbs, solid-state electronic lighting devices are more resistant to shock and vibration due to their generally modest weight. They also prevent filament evaporation, which could extend the life of the lighting fixture. Solid-state lighting is often found in traffic signals, as well as in contemporary automotive lights, parking, and street lights, railroad marker lights, building exteriors, remote controls, and other applications. Non-imaging optical concepts may be the most effective means of controlling LED light emission. Solid-state lighting has advanced significantly in this industry. Semiconductor lamps are gradually replacing classic tungsten-halogen lamps in the entertainment lighting sector.

Solid-state lighting, or SSL, is a fast-growing industry. It claims to drastically reduce carbon dioxide emissions, save up to 50 per cent in energy consumption, and stimulate the growth of a whole new lighting industry. Instead of using electric filaments, plasma, or gas as a light source, SSL uses semiconductor light-emitting diodes (LEDs), organic light-emitting diodes (OLEDs), or polymer light-emitting diodes (PLEDs). Unlike fluorescent or incandescent lamps that use thermal radiation, SSL uses solid-state electroluminescence. SSL produces visible light with less heat generation and energy loss than incandescent lighting. On the same principle as conventional fluorescent lamps, photoluminescence is used by most common white LEDs to convert blue light from a semiconductor device into an approximate white light spectrum.

1.4 Luminescence

Luminescence is a term used to describe the light emitted by some relatively cool materials. This is not the same as the light given off by hot objects such as burning coal or wood, molten iron or wire that has been heated by an electric current. Examples of objects are neon and fluorescent lighting, television, radar, and X-ray fluoroscopic screens, organic materials such as luminol or luciferins in fireflies and fireflies, specific pigments used in outdoor advertising, and naturally occurring electrical phenomena such as lightning and the aurora borealis, which exhibit luminescence. Luminescence is sometimes referred to as "cold light" because it does not come from a material that is above room temperature in any of these processes. Luminescent materials are useful because they can convert invisible energy sources into visible light.

After a suitable material has received energy from a source—such as UV or X-ray radiation, electron beams, chemical processes, etc.—luminosity emission happens. All discrete energy states, including the ground state of an atom, are defined as quantum states. The energy raises the material's atoms into an excited state, but excited states are unstable, so the material goes through another transition, returning to its unexcited ground state. The absorbed energy is released as heat, light, or both. Only the outermost electrons that orbit atom nuclei are involved in the excitation. The degree to which excitation energy is transformed into light determines luminescence efficiency, and only a few materials have luminescence efficiencies high enough to be useful in real-world applications.

After excitation, the electrons no longer have an equilibrium distribution and gradually decay to lower states, producing radiation in the process. Luminescence is the term used to describe this emission. Thus, luminescence is the opposite of absorption. As a result, it is a type of cold body radiation. Chemical interactions, electrical energy, subatomic vibrations, or crystal stress are some of the possible causes. This distinguishes luminescence from incandescence, which is the light a substance emits when heated.

Types of luminescence:

A) Chemiluminescence: Light is released as a result of a chemical reaction known as chemiluminescence. Some substances react to form molecules in an excited state, which emits light energy after returning to the ground state. Luciferase catalyzes the reaction between luciferin and oxygen in fireflies, resulting in the emission of light, a phenomenon that is well known. This phenomenon is used in real-world products such as glow sticks that light up when chemicals are mixed. Chemiluminescence is used analytically in methods such as chemiluminescence immunoassays (CLIA) to identify and measure chemicals in samples. With advantages such as ease of use, speed, and minimal background interference, its high sensitivity enables the identification of minute amounts of drugs. Chemiluminescence is widely used in environmental monitoring, medical diagnostics, and forensic science. Its ability to produce light without the need for external sources is extremely beneficial for scientific research and technological advancement.



Figure 1: Chemiluminescence (Direct and Indirect Chemiluminescence: Reactions, Mechanisms and Challenges. Molecules. 2021 Dec 17)

B) Crystalloluminescence: Mechanoluminescence, another name for crystalloluminescence, is a term used to describe the light emission that occurs from certain crystals when subjected to mechanical stress. This process occurs as a result of pressure-induced changes in the atomic structure of the crystal, which cause light to be released as stored energy. One well-known crystal that exhibits crystalloluminescence is quartz. Flashes of light are created by quartz crystals that are broken or deformed. Unlike other types of luminescence, crystalloluminescence is not dependent on external energy sources such as heat or light. This property makes it useful in several fields, such as geology, materials science, and luminescence dosimetry, which measures radiation exposure. Knowing how crystalloluminescence behaves under stress can help in the development of new materials, sensors, and structural health monitoring, among other things.

C) Photoluminescence: When a material absorbs photons or light energy, it releases light, a process known as photoluminescence. Higher energy electrons are produced in the substance when photons are absorbed. These excited electrons release light energy when they settle down to their ground state. Numerous materials, such as semiconductors, fluorescent dyes, and certain crystals, exhibit photoluminescence. It is essential to many applications, including optoelectronic devices, lighting technology, and fluorescence microscopy. Light-emitting diodes (LEDs) and other devices that use semiconductor materials that emit light when excited make use of photoluminescence. This phenomenon has broad applications in domains ranging from consumer electronics to scientific research, supporting improvements in communication, healthcare, and energy-efficient lighting. It is essential for comprehending the characteristics and behaviours of materials.

D) Electroluminescence: A material that undergoes electroluminescence emits light when an electric current is passed through it. The recombination of electrons and electron holes in the material causes this event, which releases energy in the form of photons. Light-emitting diodes (LEDs), which use semiconductor materials that glow when exposed to an electric field, are common devices using electroluminescence. LEDs are widely used in many different applications such as solid-state lighting, displays, and indicator lights.

1.5 Rare earth elements and their properties

A class of chemical elements known as rare earth materials is present in the earth's crust and is characterized by special properties and a wide range of industrial applications. Despite their name, rare earth elements (REEs) are relatively common in the Earth's crust, but they are often scattered and difficult to extract economically. The seventeen elements in the group are yttrium, scandium, and fifteen lanthanides. Because of their electrical structure, these elements have comparable chemical properties, making them useful for a variety of technical and commercial applications.

The magnetic behaviour of rare earth minerals is one of their most important characteristics. The production of permanent magnets requires several rare earth elements, especially neodymium, samarium, and dysprosium. These magnets are essential for many different applications, including computer hard drives, wind turbines, electric car motors, and medical devices such as MRI machines. Due to their exceptional magnetic stability and strength, rare earth magnets are essential for today's technologies.

The luminescence of rare earth minerals is another remarkable characteristic. Several rare earth elements are used as phosphors in lighting and imaging technologies, including yttrium, terbium, and europium. These components are essential for LED lighting, fluorescent lights, televisions, and smartphone screens because they emit visible light when stimulated by an external power source. Bright colour displays and energy-efficient lighting solutions are made possible by rare earth phosphors. In the subject of catalysis are vital elements of rare earth. Rare earth elements such as cerium, lanthanum, and others are used as catalysts in various chemical processes such as environmental remediation, automobile emission control, and oil refining. They can easily support chemical reactions due to their different electrical structures and surface properties, improving process efficiency and reducing environmental impact. In addition to industrial use, rare earth minerals are essential for the creation of high-end electronics and telecommunications equipment. For example, gadolinium is a component of magnetic resonance imaging (MRI) contrast agents that allow accurate imaging of internal body structures for diagnostic purposes. Fibre optic communication uses yttrium and erbium to facilitate high-speed data transmission over long distances. In

addition, rare earth elements are essential for the production of rechargeable batteries, especially nickel-metal hydride (NiMH) batteries. Lanthanum, cerium, and praseodymium are important elements in the electrodes of these batteries that increase their performance and energy storage capacity. NiMH batteries are often found in portable electronics and hybrid electric vehicles (HEVs). Rare earth elements are widely used in aerospace and defence sectors because of their special qualities. For instance, neodymium is used to create high-performance magnets for aircraft and missile guidance systems. Radar devices, satellite communications technology, and precision-guided weapons all use rare earth metals.

The seventeen metallic elements in the middle of the periodic table are known as the rare earth elements. Because of their unique electrical, magnetic, luminescent, and magnetic properties, several rare earth elements are highly valuable in manufactured goods and industrial environments. However, separating these elements from each other is challenging due to their strikingly similar electronic structures. Although rare earth mineral ores are found on every continent, China currently produces most of the world's rare earths.

Magnetic properties: The magnetic properties of some rare earth elements such as Nd, Dy, and Sm are valuable. Unpaired electrons that are oriented to rotate in the same way create magnetic fields. These elements have many unpaired electrons in their orbital electron structures, which allows these rare earth materials to store large amounts of magnetic energy. Today, rare earth magnets are widely used in various applications such as wind turbines and rocket and aircraft guidance systems.

Electrical properties: Rare earths are advantageous for nickel-metal hydride (NiMH) batteries because of their electrical structure. Since rare earth metals do not have to be completely separated from each other, the anodes of these batteries use a mixed metal - a mixture of cerium, lanthanum, neodymium and praseodymium, as it is a cheaper material to manufacture. Batteries using rare earth elements have a greater capacity to store energy per unit weight. and better retention of capacity even after many discharge and recharge cycles.

Catalytic properties: Rare earth can be used as catalysts for chemical reactions due to their elec-

tron configuration. The most common rare earths used in catalytic applications are lanthanum and cerium due to their lower cost and abundance. Catalytic converters in gasoline-powered vehicles use cerium, while fluid catalytic cracking—a common method of refining crude oil into particularly useful hydrocarbons such as gasoline—uses lanthanum.

Luminescent properties: Some rare earth elements emit light when exposed to electromagnetic radiation. These materials are used in energy-efficient light sources such as LEDs and compact fluorescent lamps as phosphors or compounds that emit light. The red light produced by europium phosphors was essential to the development of colour television in the 1960s. Erbium ions can be used to amplify signals transmitted through glass fibres due to their fluorescence. Another application for the light qualities of certain rare earths is in lasers. For solid-state lasers, the typical medium is yttrium-aluminium-garnet (YAG). YAG lasers can produce focused wavelengths of light that are useful for oral surgery and dentistry when doped with erbium. YAG lasers are widely used in manufacturing, medical and defence applications when doped with neodymium.

The sharp and narrow lines of the emission spectra of transitions within the 4f configuration are caused by the incompletely filled 4f shell of lanthanide ions, which is shielded from its surroundings by the filled 5s² and 5p⁶ orbitals. The reason for the broad emission spectra from 5d-4f transitions is that the 5d electrons are not isolated and are therefore greatly affected by their environment. Since f-f transitions in free 4f ions are forbidden, the lifetime of emissions originating from 4f-4f transitions is quite long, typically measured in milliseconds.

Excellent up-conversion luminescence and/or down-conversion luminescence from ultraviolet (UV) to infrared region are observed in Ln³⁺ doped phosphors. Up-conversion is the process by which light with a wavelength shorter than the excitation wavelength is released due to the subsequent absorption of two or more photons. On the other hand, down-conversion is reversed when one inefficiently absorbed high-energy photon is transformed into two or more lower-energy photons.

CHAPTER 2

2 Literature review

This thesis presents research on potassium double tungstate waveguides with high ytterbium concentrations designed for optical amplification applications. Within the scope of the research, spectroscopic and optical gain properties in epitaxy layers with trivalent ytterbium (Yb^{3+}) concentrations up to 76 at per cent or $5 \times 10^{21} \text{ cm}^{-3}$ will be investigated. The temperature dependence, luminescence duration, and transition cross-sections of the high ytterbium concentration epitaxy layers are all closely and thoroughly investigated. To counteract the radiation trapping effect that causes the measured lifetime to increase, a unique confocal measurement setup is suggested. It is confirmed that potassium double tungstate epitaxial layers with high Yb^{3+} concentrations exhibit relatively mild concentration-dependent lifetime quenching. The existence of the energy transfer upconversion (ETU) process is shown by additional examination of the power-dependent luminescence decay curves. The potassium double tungstate epitaxy layers with a high ytterbium concentration have cross-section spectra that resemble bulk crystals. Two factors are responsible for the observed significant changes in cross-section spectra with increasing temperature: the linewidth of the corresponding transition at a given temperature and the fractional population at the initial Stark level. Both numerical and experimental methods are used to study the material gain in thin film configurations. Overall, the work presented in this thesis contributes to our understanding of the properties of potassium double tungstate waveguide layers at high Yb^{3+} concentrations. The experimental findings demonstrate that the epitaxial layers maintain advantageous spectroscopic characteristics. However, other effects have also been identified and examined, including the ETU process, quenched ions, and localized heating inside the pumped zone. In particular, the behaviour of absorption and emission would be significantly impacted by increased temperature on the gain medium.

This work involved the preparation of $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped and $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Li}^{+}$ co-doped $\text{NaSc}(\text{WO}_4)_2$

at varying concentrations using a high-temperature solid-state technique. The findings demonstrated that $\text{NaSc}(\text{WO}_4)_2$ differs from other $\text{NaLn}(\text{WO}_4)_2$ in that it is a member of the monoclinic system. By increasing concentration, the significant polarizability of Li^+ ions altered the W–O bonds and expanded the crystal lattice parameters, resulting in a more than three-fold increase in luminescence intensity. Under 980 nm pumping, the Er^{3+} ions released strong green light and faint red light; the two-photon process was included in the luminescence mechanism. The emission chromaticity of $\text{NaSc}(\text{WO}_4)_2$ remained constant with varying pumping powers, suggesting that $\text{NaSc}(\text{WO}_4)_2$ could be an effective material for green UC luminescence. The development of up-conversion materials is supported by the data and theory presented in this paper.

Materials that experience negative thermal expansion (NTE) have an open, low-density structure that can react to high pressure, producing new compounds and/or distinct physical characteristics. Here, we report that when treated at 4 GPa and 1400°C, one such NTE material, white, insulating, orthorhombic $\text{Sc}_2\text{W}_3\text{O}_{12}$, changes into a black compound. The high-pressure phase, $\text{Sc}_{0.67}\text{WO}_4$, crystallizes as a dense, monoclinic structure (space group P2/c) with a defect-rich wolframite-type structure that contains 1-D chains of edge-sharing WO_6 octahedra. The Sc defect structure provides insight into the chemical bonding between $\text{Sc}_{0.67}\text{WO}_4$ and the ambient pressure $\text{Sc}_2\text{W}_3\text{O}_{12}$ phase. According to tests of thermoelectric power, resistivity, magnetic susceptibility, and infrared spectroscopy, the $\text{Sc}_{0.67}\text{WO}_4$ sample is a paramagnet with metal-like conductivity in the presence of weak localization and electron-electron interactions.

This work uses a one-pot hydrothermal procedure to manufacture $\text{Sc}_2\text{M}_3\text{O}_{12}$. A thorough investigation was conducted into the impacts of process conditions on the crystal structure, morphology, photocatalytic activity, and negative thermal expansion (NTE) behaviours of flower-like $\text{Sc}_2\text{Mo}_3\text{O}_{12}$. The findings show that a one-pot hydrothermal reaction can be used to create orthorhombic flower-like $\text{Sc}_2\text{W}_3\text{O}_{12}$ constructed by nano-size flaky crystal grains in as little as two hours at a temperature as low as 120 °C. The hydrothermal reaction temperature and time have no obvious effects on the crystal structure and morphology. However, the photocatalytic property of synthesized $\text{Sc}_2\text{W}_3\text{O}_{12}$ is sensitive to the above parameters. The sample synthesized at 200 °C for

2 h shows the best photocatalytic degradation of methyl orange, and the degradation rate is 73.32 per cent in 2 h.

The implementation of temperature sensing in the high-temperature zone is severely hampered by the temperature-quenching luminescence impact of optical materials utilized for fluorescence intensity ratio temperature sensing. A lot of attention has been paid recently to some atypical thermal enhancement up-conversion materials because of their remarkable potential for temperature sensing in high-temperature zones. There are currently not many documented up-conversion luminescence thermal enhancement materials, and the thermal enhancement luminescence process has not been sufficiently explored. This work prepared new up-conversion luminescent materials $\text{Sc}_2\text{W}_3\text{O}_{12}:\text{Yb}^{3+}, \text{Er}^{3+}$, and successfully controlled the thermal enhancement effect by varying the Yb^{3+} concentration.

CHAPTER 3

3 Materials

3.1 Materials required

$\text{Sc}_2(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, NaWO_4 , $\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$

3.2 Procedure:

Stoichiometric amounts of $\text{Sc}_2\text{W}_3\text{O}_{12}$: $\text{Yb}^{3+}/\text{Er}^{3+}$ were separately weighed and dissolved in a beaker with 10 ml of milli-Q water. The reactants were mixed and dissolved using a magnetic stirrer. The mixture is stirred once more for thirty minutes. The pH value was kept neutral during the procedure. After adding milli-Q water to a volume of 60 mL, the mixture was placed in a Teflon-lined autoclave, sealed, and heated for 24 h at 180 °C in an oven. After the chemical was formed, centrifuged several times using milli-Q water and was dried at 90° for 4 hours.



Figure 2: Autoclave used in hydrothermal method (SPAS Goa University)

CHAPTER 4

4 Characterization

In materials science, the term "characterization" refers to the wide and generic process of examining and measuring a material's structure and qualities. Without it, a scientific understanding of engineering materials could not be determined. It is an essential procedure in the field of materials science. The term "materials analysis" has varying definitions. While some restrict its use to techniques that examine the microscopic structure and properties of materials, others include macroscopic techniques like mechanical testing, thermal analysis, and density calculation.

When it comes to the imaging of individual atoms and chemical bonds, for example, or the imaging of coarse grain structures in metals, the scale of the structures seen in materials characterization spans from angstroms to centimetres.

While certain characterization methods, including basic optical microscopy, have been used for centuries, new methods and approaches are always being developed. The field has undergone a significant revolution with the introduction of the electron microscope and secondary ion mass spectrometry in the 20th century. These advancements have made it possible to image and analyze structures and compositions on much smaller scales than was previously feasible, which has greatly increased our understanding of why different materials exhibit different properties and behaviours.[4] Recently, the highest resolution achievable for the examination of specific samples over the previous 30 years has been further enhanced using atomic force microscopy.

Characterization is essential to create high-quality materials. Phase analysis, structural and compositional characterization, microstructural analysis, and spectroscopic analysis make up the entire characterization of the material. It is impossible to fully characterize a body with a single technique. This chapter describes in detail the various analytical instrumental techniques that were used to characterize the prepared samples.

4.1 X-ray Diffraction

The experimental science of identifying a crystal's atomic and molecular structure is known as X-ray crystallography. The crystalline structure of a crystal causes an incident X-ray beam to diffract into numerous distinct directions. A three-dimensional image of the electron density inside the crystal can be created by a crystallographer by determining the angles and intensities of these diffracted beams. The locations of the atoms in the crystal, their chemical relationships, the degree of crystallographic disorder, and other details can all be inferred from this electron density. Many materials, including salts, metals, minerals, semiconductors, and other types of inorganic, organic, and biological molecules, can form crystals. For this reason, X-ray crystallography has been essential to the advancement of numerous scientific disciplines. During the initial decades of its application, this technique was used to ascertain atom sizes, chemical bond lengths and kinds, and atomic-scale variations among different materials, particularly minerals and alloys. Many biological compounds, including vitamins, medications, proteins, and nucleic acids like DNA, were also shown to have clear structures and functions thanks to this technique. The main technique for identifying materials that seem similar in prior studies and assessing the atomic structure of novel materials is still X-ray crystallography.



Figure 3: Rigaku Smart Lab Powder X-ray diffractometer at ULMC of Goa University

4.1.1 Generation of X-rays

An X-ray tube is a type of vacuum tube that produces X-rays by rapidly accelerating the electrons produced from a hot cathode using a high voltage. The X-rays are produced when the high-velocity electrons smash with the anode, a metal target. The target material in medical X-ray tubes is often tungsten or an alloy of rhenium and tungsten which is more resistant to cracks. Molybdenum is occasionally used for more specialized uses, such as mammography, which calls for softer X-rays. The most common target in crystallography is copper; cobalt is frequently employed when fluorescence from the iron concentration of the material could cause issues.

An 80 kV tube cannot produce X-rays with an energy higher than 80 keV because the maximum energy of the produced X-ray photon is restricted by the energy of the input electron, which is equal to the voltage on the tube times the electron charge. Two distinct atomic processes produce X-rays when the electrons strike their target:

Bremsstrahlung is the name for the radiation that is released by electrons in the vicinity of nuclei when they are scattered by a strong electric field. The spectrum of these X-rays is continuous. The energy of the incident electrons sets a limit on the Bremsstrahlung frequency. Therefore, a tube's output is made up of many spikes at the characteristic lines together with a continuous Bremsstrahlung spectrum that drops off to zero at the tube voltage. The greatest energy of the X-ray photons ranges from approximately 20 keV to 150 keV because the voltages employed in diagnostic X-ray tubes range from about 20 kV to 150 kV.

The majority of the electrical power needed by the tube is discharged as waste heat in both of these inefficient X-ray production techniques, which only convert around 1 per cent of the electrical energy used by the tube into X-rays. To generate a useful amount of X-rays, the X-ray tube needs to be built with a heat-dissipating capacity. Synchrotron radiation, produced by particle accelerators, is a specialized source of X-rays that is increasingly being employed in research. Its wide X-ray spectra, good collimation, linear polarization, and X-ray outputs that are many orders of magnitude larger than those of X-ray tubes are its unique qualities.

It is possible to successfully produce short millisecond bursts of X-rays with a peak energy of 15

keV by peeling pressure-sensitive adhesive tape from its backing in a moderate vacuum. This is most likely the outcome of electrical charges from triboelectric charging recombining. X-ray triboluminescence has a high enough intensity to be an image source for X-rays.

electromagnetic radiation with a wavelength of around 1 \AA is known as X-rays. When high-energy particles such as electrons collide with a target material after being accelerated by a high potential, X-rays are released. The resulting X-ray spectra typically consist of some fixed or monochromatic wavelengths and a broad band of wavelengths known as white radiation. Monochromatic X-rays are those used in X-ray diffractometers. When the strong potential difference accelerates the electron beam, it can strike a metal target such as copper. There is enough energy in the incident electron beam to cause the ionization of some Cu K shell electrons.



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

4.1.2 Interaction of X-rays with matter

There are three primary ways that X-rays interact with matter: photoabsorption, Compton scattering, and Rayleigh scattering. Since the energy of the X-ray photon is far higher than the energy of chemical binding, the intensity of these interactions is mostly determined by the energy of the X-rays and the elemental composition of the material, with little influence from chemical characteristics. The predominant interaction mechanism for the lower hard X-ray energies and in the soft X-ray range is photoelectric absorption, also known as photoabsorption. Compton scattering takes centre stage at higher energy.[6]

In medical imaging, the most common interaction between X-rays and soft tissue is called Compton scattering. An outer shell electron's inelastic scattering of an X-ray photon is known as Compton scattering. The scattering electron receives a portion of the photon's energy, ionizing the atom and lengthening the X-ray's wavelength. Although the dispersed photon can travel in any direction, it is more likely to travel in the same direction as it started, particularly in the case of high-energy X-rays. The Klein-Nishina formula uses various scattering angles to describe the probability. The conservation of momentum and energy allows for the direct determination of the transferred energy from the scattering angle.[4]

In the X-ray range, Rayleigh scattering is the predominant elastic scattering mechanism. The refractive index is the result of inelastic forward scattering and is only marginally lower for X-rays. According to Bragg's approach to diffraction, crystals are arranged in layers or planes, with each plane serving as a semitransparent mirror. When incoming X-rays with wavelengths comparable to atomic distances strike a crystalline material, part of the radiation is reflected from the plane at an angle of reflection equal to the incidence, and the remaining radiation is carried to reflection by the planes that follow it. The reflected rays interfere constructively when Bragg's law is satisfied and they are in phase. They are destructively out of phase for angles other than the Bragg angle. Bragg's law places strict limits on the angles at which reflection is allowed.

4.1.3 Powder XRD method

While some features of powder diffraction using neutrons are discussed, the main focus of this page is on X-ray powder diffraction, which is the most prevalent type. (Dynamical diffraction makes powder electron diffraction more complex; it is not covered in this article.) Common diffractometers use electromagnetic radiation (waves) whose source determines their wavelength and frequency. X-rays are frequently the source, although neutrons are also frequently used sources, with their frequency being established by their de Broglie wavelength. As soon as these waves hit the sample, the incoming beam may penetrate the lattice and be diffracted by the atoms within, or it may be reflected off the surface.

When atoms are symmetrically organized with a separation distance of d , these waves will only constructively interact in the locations where the path-length difference $2d \sin \theta$ is greater than or equal to an integer multiple of the wavelength. This will result in a maximum of diffraction according to Bragg's law. There are no bright spots in the diffraction pattern as a result of these waves' destructive interference at the places where they are out of phase between the crossings. This gap is known as the atomic spacing since the sample is functioning as the diffraction grating.[13]

Using this technique, a finely powdered material with a random crystal orientation is exposed to a monochromatic X-ray beam in all directions. Such a powder sample also has different planes in all possible orientations. For Bragg's law to be satisfied for these crystals and planes, at least a portion of the crystals in each set of planes must be oriented relative to the incident beam at the Bragg angle. The detector then captures the diffracted beam. Diffracted radiation from the surface of the cone for any set of grating planes. There is no restriction on the angular orientation of the planes concerning the axis of the incident beam; the only prerequisite for diffraction is that they are at the Bragg angle. Since in a finely powdered sample, there are crystals at all conceivable angular points relative to the incident beam, the diffracted radiation appears to be emitted from the sample as cones of radiation. Each set of planes creates a unique cone of radiation.

4.1.4 Powder X-ray Diffractometer

The parts of a powder X-ray diffractometer are as follows:

X-ray source: A heated tungsten filament produces high-energy electrons, which can then strike, for example, a small metal target. Sealed diffraction tube containing copper.

Collimator: The target material generates X-rays, which are then directed through the collimator. It consists of a pair of closely spaced metal plates that are only slightly apart. All X-rays are absorbed by the collimator, except for a narrow beam that passes through it.

Monochromators: Monochromators separate different wavelengths from polychromatic light. The X-ray diffractometer manufactured by Rigaku Smart Lab uses a graphite monochromator. Graphite monochromator reduces background noise and maximizes sensitivity. Removing fluorescence from materials containing Co, Ni, Fe, and Mn, increases the signal-to-noise ratio.

Filters: Filters pass radiation of the desired wavelength and block unwanted radiation. An example of a nickel filter used to eliminate copper radiation. Monochromators are replaced by these filters.

Detector: In the Rigaku Smart lab X-ray powder diffractometer, the diffracted beam is detected using a D/TEX Ultra 250. Compared to competing detectors, this 1D silicon strip detector reduces data acquisition time by 50 per cent. This is achieved by expanding the active area of the aperture, which increases the pulse rate. D/TEX Extreme features a longer 2 theta direction and lower pixel pitch.[2]

4.2 Scanning Electron Microscopy

A concentrated electron beam is used to scan a sample's surface in a scanning electron microscope (SEM), creating images of the material. The sample's atoms and electrons interact to produce a variety of signals that reveal details about the sample's composition and surface topography. An image is created by combining the intensity of the detected signal with the position of the electron beam as it scans in a raster scan pattern. In the most used SEM mode, a secondary electron detector (Everhart–Thornley detector) is used to detect secondary electrons released by atoms stimulated by the electron beam. Specimen topography affects the quantity of detectable secondary electrons and, thus, the signal strength. Resolutions better than one nanometer can be attained by certain SEMs.[3] Using specialized instruments, specimens are examined under a variety of cryogenic or higher temperatures, high vacuum, low vacuum, or wet environments in variable pressure or environmental SEMs. One of the most adaptable or multi-purpose tools for characterizing chemical composition and observing structure shape at higher magnification is the scanning electron microscope.

4.2.1 Principle

The interactions of the electron beam with atoms at different depths within the sample provide the signals that an SEM uses to create an image. A variety of signals are generated, such as transmitted electrons, absorbed current (specimen current), distinctive X-rays, light (cathodoluminescence) (CL), reflected or back-scattered electrons (BSE), and secondary electrons (SE). All SEMs come equipped with secondary electron detectors as standard equipment, however, it is uncommon for one device to contain detectors for every other type of signal.

The mean free route of secondary electrons in solid matter is limited by their extremely low energies, which are on the scale of 50 eV. As a result, SEs are limited to escaping from a sample's surface to the upper few nanometers. At the primary electron beam's point of impact, secondary electron signals are typically highly localized, allowing for the collection of sample surface pictures with a resolution of less than 1 nm. Elastic scattering causes beam electrons to reflect from the sample; these electrons are known as back-scattered electrons or BSEs. BSE images have a lower resolution than SE images because they arise from deeper regions inside the specimen due to their higher energy compared to SEs.[10]

However, because the intensity of the BSE signal is closely correlated with the specimen's atomic number (Z), BSE is frequently employed in analytical SEM along with spectra created from distinctive X-rays. BSE pictures can reveal details about the distribution of various sample elements, but not their identities. BSE imaging can scan colloidal gold immuno-labels with a diameter of 5 or 10 nm in samples that are mostly made up of light elements, such as biological specimens. These labels would be difficult or impossible to detect in secondary electron pictures. When the electron beam removes an electron from the sample's inner shell, a higher-energy electron fills the shell and releases energy, resulting in the emission of characteristic X-rays.

A scanning electron microscope works on the principle of kinetic energy, which generates signals based on the contact of electrons.[1] These electrons, which are used to see photons and crystalline components, are secondary electrons, diffracted backscattered electrons, and backscattered electrons. Electrons that have been backscattered are those that bounce back when the initial electron

beam hits the sample. These interactions are flexible. Electrons reflected from deeper areas of the samples are created. Its image has a great degree of sensitivity to changes in atomic number so that it appears lighter or darker.[9, 15] Secondary electrons: These electrons come from the atoms of the sample and are the result of inelastic interactions. Its source is surface areas. The images created by scattered electrons provide information about the nano and microstructure of the samples. A photomultiplier is used to detect the visible light produced when secondary electrons are driven into a scintillator which is held at a high positive potential of several KV. The detectors collect the signals emitted by the sample at each location. The detector signal is modulated by the corresponding image pixel by being synchronized with the known beam location on the sample and signal intensity. A sequence of signals is combined to form an image, and the selected scan pattern determines the dimensional distribution of the image.

4.2.2 Instrumentation

The equipment of the scanning electron microscope consists of the following parts: Electron source: At the top of the microscope column, the electron source produces electrons.[5] Thermionic emission occurs when a heated filament of tungsten or lanthanum hexabromide releases electrons. Anode: The positive charge on the anode attracts electrons to it, creating an electron beam. Magnetic lens: This device regulates the size of the beam and counts the electrons in it. The size of the beam determines the resolution of the image. The image size can also be adjusted using aperture. Scanning coils: Scanning coils deflect electrons along the x and y axes. to ensure that the sample surface is scanned in a raster pattern. The objective lens is the final lens in the series of lenses used to form the electron beam. The beam is focused on a very small area of the sample by this lens because it is close to the sample. Glass is impermeable to electrons, so SEM glass is electromagnetic. They consisted of wire coils enclosed in metal columns. A magnetic field is produced by these coils when current flows through them. Because electrons are so sensitive to magnetic fields, microscope lenses can regulate them.

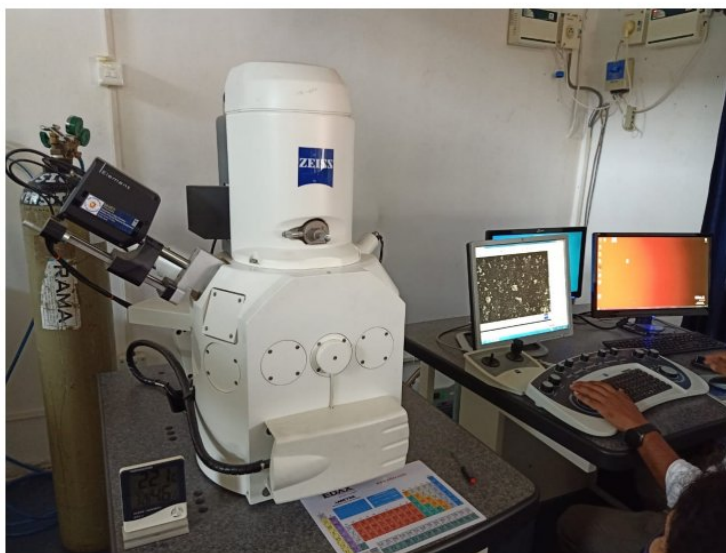


Figure 5: Carl Zeiss Scanning Electron Microscope at USIC of Goa University

4.2.3 Applications

SEM is primarily used to identify materials at high magnification and to provide details of their sizes, shapes, and compositions as observed from solid surfaces. Information on submicrometer features, as well as features up to hundreds of microns across, provides results that complement those from optical microscopy. To achieve strong topographic contrast, both secondary electrons and backscattered electrons can be used to record images. SEMs are employed in materials science for failure analysis, research, and quality assurance.[19, 7]

SEMs are used extensively in modern materials science research and inquiry into mesoporous structures, high-temperature superconductors, alloy strength, and nanotubes and nanofibres. In actuality, SEMs have proved essential to the growth of almost every material science business, from chemistry and aerospace to electronics and energy use. By advancing current production techniques and creating new ones, scientists are investigating novel applications for nanowires as gas sensors. To characterize nanowires and comprehend their gas-sensing behaviour, electron microscopy is essential.

Reliable semiconductor performance necessitates precise topographical data. The semiconductor's composition may be quickly and precisely determined because of the high-resolution three-dimensional images that SEMs generate. SEMs are one of the three primary tools used for quality control in almost all wafer fabrication processes. Larger monitors (19 inches) have been demonstrated to lessen inspectors' visual fatigue when it comes to routine daily quality control tests.[14]

4.3 UV Visible Spectroscopy

Absorption spectroscopy or reflectance spectroscopy in portions of the ultraviolet and the entire, nearby visible parts of the electromagnetic spectrum is referred to as ultraviolet (UV) spectroscopy or ultraviolet-visible (UV–VIS) spectrophotometry. This methodology is frequently employed in a variety of practical and basic applications due to its ease of implementation and relative affordability. All that is needed for the sample to be a chromophore is for it to absorb in the UV-Vis range. Fluorescence spectroscopy is enhanced by absorption spectroscopy. Aside from the measurement wavelength, the parameters of interest are absorbance (A), transmittance, or reflectance, and how they vary over time.

An analytical tool called a UV-vis spectrophotometer calculates how much ultraviolet (UV) and visible light a sample absorbs. It is a commonly used method for identifying and quantifying chemicals in a range of samples in the domains of chemistry, biochemistry, and other sciences.[12] A light beam is passed through the sample using a UV-vis spectrophotometer, which measures the amount of light absorbed at each wavelength. The concentration of the absorbing chemical in the sample determines how much light is absorbed.

The visible and ultraviolet parts of the electromagnetic spectrum have wavelengths between 200 and 800 nm. Visible light is from 400 to 800 nm, while ultraviolet light is between 200 and 400 nm. [8]The energy of this radiation is high enough to cause the outer valence electrons to undergo an electronic transition. By absorbing radiation from the UV-visible region, electrons from bonding (outermost) orbitals in both organic and inorganic compounds are promoted to antibonding orbitals or higher energy levels. Coupled with these electronic transitions are vibrational and rotational transitions.

4.3.1 Principle

If a substance preferentially absorbs light from the visible spectrum, it appears coloured. The molecule is raised from its ground energy state (E_0) to a higher excited energy state (E_1) by the absorbed energy. Absorption in the UV or visible spectrum occurs due to the degree of electron bonding, which determines the energy difference E . Because the electrons in sigma bond compounds are tightly bound together, UV radiation will be absorbed. Because there is no absorption in the visible spectrum, the molecule appears colourless. The loosely bound electrons cause absorption in the visible spectrum, giving the combination a coloured appearance.[18]

Molecules have three different kinds of orbitals in the ground state:

- a) Molecular orbital a bonding sigma does not show absorption in the UV region because the electrons in this orbital are strongly bound and require high energy for excitation.
- b) π bonding molecular orbital: Electrons in this orbital are typically mobile and present in many bonds. Because π bonds are weak, UV energy can stimulate its electrons from lower energy levels to higher ones.
- c) Non-bonding molecular orbital or n electron is the name for valence electrons in a molecule that does not contribute to the formation of a chemical bond. These are usually lone pairs of electrons that can be stimulated by UV light.

4.3.2 Applications

The analytical method known as UV-Vis spectroscopy counts the number of distinct UV or visible light wavelengths that a sample absorbs or transmits when compared to a reference or blank sample. It aids in the understanding of the optical characteristics, band gap determination, and electrical structure of materials in condensed matter physics. Researchers can study optical transitions, charge carrier dynamics, and excitonic effects in semiconductors, quantum dots, and nanomaterials by measuring the absorption or transmission of UV-visible light.

UV-visible spectroscopy allows for the accurate measurement of molecule structure, bond energies, and electronic configurations in atomic and molecular physics. grasp processes like photoionization, photodissociation, and photoisomerization require a grasp of chemical kinetics, photochemical reactions, and molecular interactions.[17]

Furthermore, UV-visible spectroscopy makes it easier to analyze the atmospheres, temperatures, and compositions of celestial bodies in astrophysics. Through analyzing absorption and emission lines found in stellar spectra, researchers can gain an understanding of cosmic processes, nucleosynthesis, and star development. Additionally, environmental physics uses UV-visible spectroscopy to identify contaminants, track the quality of the air and water, and analyze the composition of the atmosphere. It is also essential to biophysics, helping to understand protein folding, enzymatic processes, and biomolecular structures.

4.4 Dye degradation

Common azo dye methyl orange degrades via several processes, most often brought on by exposure to heat, light, or chemicals. One well-known process is photooxidation, in which the dye molecule absorbs photons and goes through an excited state, producing singlet oxygen and other reactive oxygen species (ROS). These reactive oxygen species (ROS) target the dye molecule, disrupting its conjugated structure, resulting in colour loss, and finally disintegrating it into smaller, colourless pieces.[16] Furthermore, chemical catalysts such as strong acids or bases can catalyze hydrolysis events, which split the dye molecule's azo bonds and cause fragmentation. Harsh environments, such as high temperatures or abnormal pH levels, speed up the process.

Additionally, the breakdown of methyl orange can also be attributed to microbial degradation by specific bacteria or fungi. By using the dye molecules as a carbon source, these microbes cleave the azo bonds enzymatically and digest the bits that are left over. Overall, photooxidation, hydrolysis, and microbial activity are some of the mechanisms and environmental factors that influence the complex process of methyl orange degradation, which leads to the dye molecule's disintegration and colour loss.

4.4.1 Principle

Methyl orange deterioration is based on several concepts that are related to chemical processes and environmental variables. The dye molecule's ability to degrade through a variety of processes, including photooxidation, hydrolysis, and microbial action, is one of the main principles. One important process is called photooxidation, in which the dye molecule absorbs photons, especially those in the visible spectrum, causing electronic transitions that result in the production of reactive oxygen species (ROS). The dye molecule is attacked by these ROS, which also includes singlet oxygen, shattering its conjugated structure and resulting in colour loss. Light intensity, wavelength, and the presence of sensitizers are some of the elements that speed up the process.

Another important concept is hydrolysis, which is particularly important in situations with high

pH or strong acids or bases present. The dye molecule's azo bonds are broken during hydrolysis, which causes fragmentation and, eventually, colour loss. These hydrolytic processes can be further catalyzed by high temperatures. All of these concepts work together to cause methyl orange to deteriorate and lose its distinctive hue. To effectively remediate dye-contaminated environments, it is imperative to comprehend these principles to design strategies to mitigate dye pollution and develop efficient dye degradation processes, such as advanced oxidation processes (AOPs), biological treatments, or photocatalysis.



Figure 6: Dye degradation instrument (SPAS Goa University)

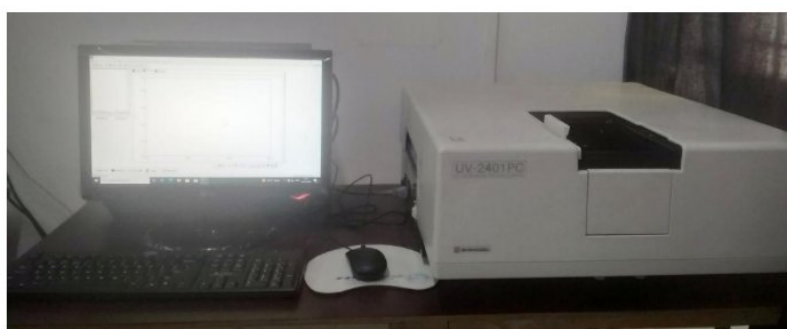


Figure 7: UV instrument (SPAS Goa University)

4.4.2 Applications

Methyl orange degradation has important uses in several industries, most notably environmental cleanup, wastewater treatment, and the creation of sustainable technologies. Environmental remediation: Polluted water bodies, textile wastewater, and industrial effluents can all be cleaned up using dye degradation techniques. Degradation methods assist reduce the negative environmental effects of dye pollution by dissolving methyl orange and other azo dyes into non-toxic pieces, protecting human health, aquatic ecosystems, and soil quality.

Wastewater treatment: To eliminate dyes from effluents released by the textile, printing, and dye manufacturing sectors, methyl orange degradation can be used in wastewater treatment procedures. Methyl orange can be effectively broken down by advanced oxidation processes (AOPs) including photocatalysis or ozonation, yielding safe byproducts like carbon dioxide, water, and mineral salts. This helps to purify wastewater so that it satisfies legal requirements for release or reuse.

Additionally, studying the methyl orange's microbial degradation routes can help create bioremediation techniques that use genetically modified microorganisms or microbial consortia for effective dye breakdown.[11] All things considered, the use of methyl orange degrading technologies is essential for tackling environmental issues, encouraging sustainable behaviour, and developing the creation of greener and cleaner industrial processes. Creation of sustainable technology: The ideas behind the breakdown of methyl orange can serve as a model for creating environmentally friendly technologies that remove pollutants and provide renewable energy. For instance, the development of clean energy technologies can benefit from the use of semiconductor materials such as titanium dioxide (TiO₂) in the photocatalytic degradation of methyl orange, which can be used not only to remove dye but also to produce hydrogen through water-splitting.

RESULTS AND DISCUSSION

5 Results and discussion

5.1 X-ray diffraction analysis

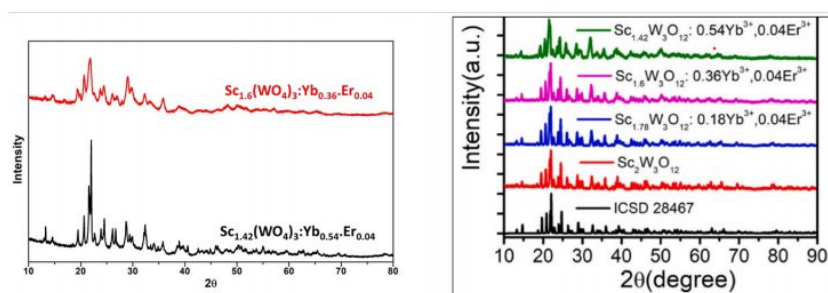


Figure 8: The XRD patterns of doped materials based on $\text{Sc}_2\text{W}_3\text{O}_{12}$

The X-ray diffraction patterns of the synthesised samples were analyzed using Rietveld analysis in FullProf software. the XRD patterns of Yb^{3+} and Er^{3+} co-doped $\text{Sc}_2\text{W}_3\text{O}_{12}$ prepared in this experiment are very consistent which indicates that Yb^{3+} and Er^{3+} co-doped $\text{Sc}_2\text{W}_3\text{O}_{12}$ materials have been successfully prepared. The XRD pattern confirms the formation of pure-phase compounds without any impurities or secondary phases. Thus, samples are pure in phase. The structure of the compound is orthorhombic and the space group is Pnca. The lattice constants of the samples were determined and listed in Table 1.

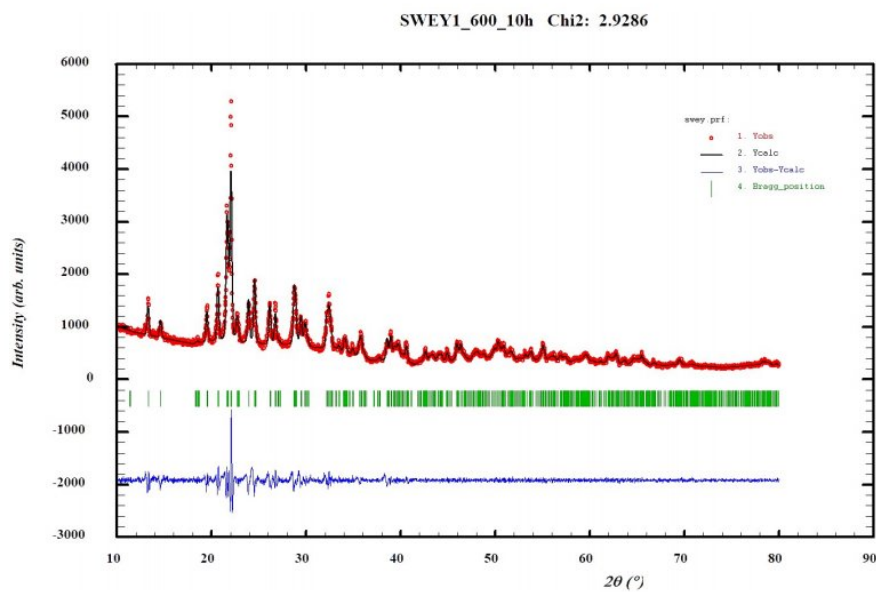


Figure 9: Profile fitting of $\text{Sc}_{1.42}\text{W}_3\text{O}_{12} : \text{Yb}_{0.54}^{3+}/\text{Er}_{0.04}^{3+}$

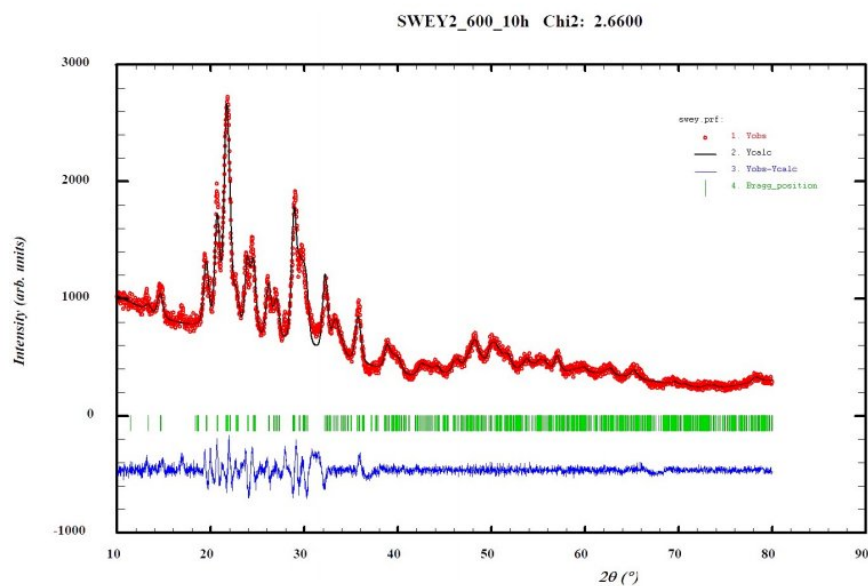


Figure 10: Profile fitting of $\text{Sc}_{1.6}\text{W}_3\text{O}_{12} : \text{Yb}_{0.36}^{3+}/\text{Er}_{0.04}^{3+}$

Compound	aÅ	bÅ	cÅ	chi ²
$\text{Sc}_{1.42}\text{W}_3\text{O}_{12} : \text{Yb}_{0.54}^{3+}/\text{Er}_{0.04}^{3+}$	9.6876	13.3415	9.5924	2.92
$\text{Sc}_{1.6}\text{W}_3\text{O}_{12} : \text{Yb}_{0.36}^{3+}/\text{Er}_{0.04}^{3+}$	9.6751	13.3209	9.5717	2.66

Table 1: Lattice parameters of compounds

5.2 SEM

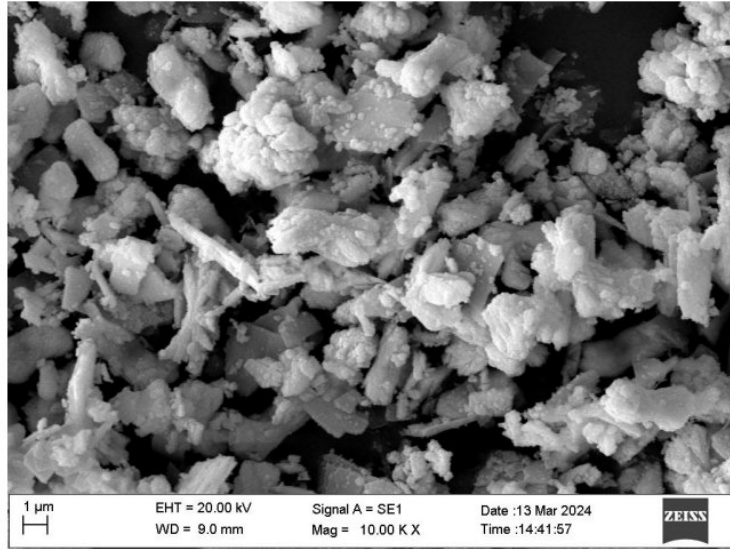


Figure 11: SEM image of $\text{Sc}_{1.42}\text{W}_3\text{O}_{12} : \text{Yb}_{0.54}^{3+}/\text{Er}_{0.04}^{3+}$

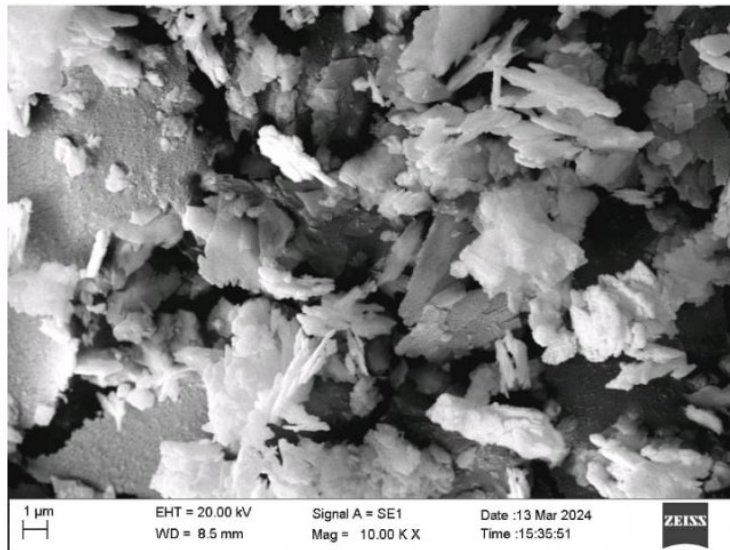


Figure 12: SEM image of $\text{Sc}_{1.6}\text{W}_3\text{O}_{12} : \text{Yb}_{0.36}^{3+}/\text{Er}_{0.04}^{3+}$

Scanning electron microscope images of the synthesized samples were taken using a Zeiss scanning electron microscope. The morphology of the samples was studied using SEM. Scanning electron microscope images show that the sample looks like flax and has identical morphology. The scale of both images is 1 micrometre.

5.3 Dye degradation

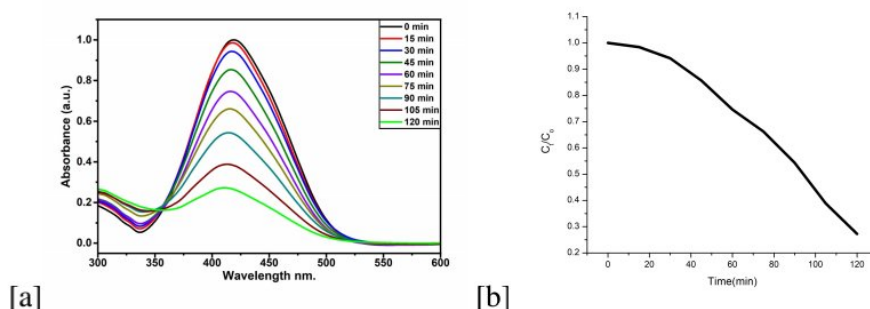


Figure 13: (a) Dye degradation of $\text{Sc}_{1.42}(\text{WO}_4)_3:\text{Yb}_{0.54}\text{Er}_{0.04}$ using methyl orange (b) Graph of (C_t/C_0)

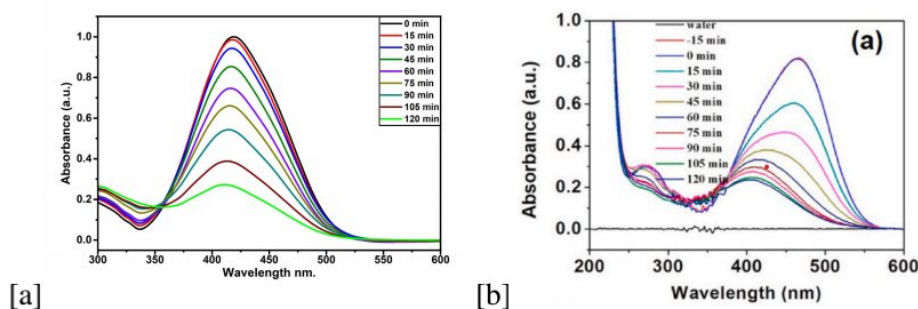


Figure 14: (a) UV-Vis absorbance spectrum of methyl orange under the irradiation of 500 W mercury lamp for different times of $\text{Sc}_{1.42}(\text{WO}_4)_3:\text{Yb}_{0.54}\text{Er}_{0.04}$ (b) UV-Vis absorbance spectrum of methyl orange under the irradiation of 500 W mercury lamp for different times of $\text{Sc}_2\text{Mo}_3\text{O}_{12}$

It can be seen that the intensity of characteristics absorption of methyl orange decreased progressively with increasing irradiation time, in addition, the position of the absorption peaks shifted to the shorter wavelengths, indicating the compound synthesized by hydrothermal reaction has an obvious degradation effect on methyl orange. The compound shows photo-catalytic properties. The compound degrades methyl orange dye by up to 75 per cent in 2 hours.

SUMMARY

6 Summary

The hydrothermal method was used to synthesize the samples. The samples formed were pure in phase, without any secondary phases. PXRD analysis revealed that the samples had an orthorhombic crystal structure and a Pnca space group. SEM images show that the samples are flax and have identical morphology. Methyl orange dye is used for a dye degradation experiment that shows the compound is undergoing a degradation process. This shows that the sample has photo-catalytic properties. The compound degrades methyl orange dye by up to 75 per cent in 2 hours.

REFERENCES

7 References

- [1] J. Li, M. Li, Z. Zhang, Z. Zheng, G. Chen, H. Wan, Y. Zhang, X. Liu, R. Ma, Luminescent yttrium oxide nanosheets for temperature sensing, *ACS Appl. Nano Mater.* 4 (2021) 12316–12324.
- [2] L. Li, C. Zhang, L. Xu, C. Ye, S. Chen, X. Wang, Y. Song, Luminescence ratiometric nanothermometry regulated by tailoring annihilators of triplet–triplet annihilation upconversion nanomicelles, *Angew. Chem. Int. Ed.* 60 (2021) 26725–26733.
- [3] Y. Ding, Y. Lu, K. Yu, S. Wang, D. Zhao, B. Chen, MOF-nanocomposite mixed-matrix membrane for dual-luminescence ratiometric temperature sensing, *Adv. Opt. Mater.* 9 (2021), 2100945.
- [4] C.D.S. Brites, S. Balabhadra, L.D. Carlos, Lanthanide-based thermometers: at the cutting edge of luminescence thermometry, *Adv. Opt. Mater.* 7 (2019), 1801239.
- [5] F. Chi, B. Jiang, Z. Zhao, Y. Chen, X. Wei, C. Duan, M. Yin, W. Xu, Multimodal temperature sensing using $\text{Zn}_2\text{GeO}_4\text{:Mn}^{2+}$ phosphor as highly sensitive luminescent thermometer, *Sens. Actual B-Chem.* 296 (2019), 126640.
- [6] W. Piotrowski, K. Trejgis, K. Maciejewska, K. Ledwa, B. Fond, L. Marciniak, Thermochromic luminescent nanomaterials based on $\text{Mn}^{4+}/\text{Tb}^{3+}$ codoping for temperature imaging with digital cameras, *ACS Appl. Mater. Interfaces* 12 (2020) 44039–44048.
- [7] A. Cirić, S. Stojadinović, Z. Ristić, I. Zeković, S. Kuzman, Z. Antić, M. D. Dramićanin, Supersensitive Sm^{2+} -activated Al_2O_3 thermometric coatings for high-resolution multiple temperature read-outs from luminescence, *Adv. Mater. Technol.* 6 (2021), 2001201.
- [8] Q. Wang, M. Liao, Q. Lin, M. Xiong, Z. Mu, F. Wu, A review on fluorescence intensity ratio thermometer based on rare-earth and transition metal ions doped inorganic luminescent materials, *J. Alloys Compd.* 850 (2021), 156744.
- [9] Y. Pan, N. Guo, L. Wang, J. Li, W. Lü, Y. Miao, Ratiometric optical thermometry in lanthanide-doped molybdate phosphors via construction of diverse charge-transfer bands, *ACS Appl. Electron. Mater.* 2 (2020) 3426–3435.
- [10] J. Qiao, J. Zhao, Q. Liu, Z. Xia, Recent advances in solid-state LED phosphors with thermally stable luminescence, *J. Rare Earths* 37 (2019) 565–572.
- [11] Y.C. Lin, M. Bettinelli, M. Karlsson, Unraveling the mechanisms of thermal quenching of luminescence in Ce^{3+} -doped garnet phosphors, *Chem. Mater.* 31 (2019) 3851–3862.

- [12] L. Wu, S. Sun, Y. Bai, Z. Xia, L. Wu, H. Chen, L. Zheng, H. Yi, T. Sun, Y. Kong, Y. Zhang, J. Xu, Defect-induced self-reduction and anti-thermal quenching in $\text{NaZn}(\text{PO}_3)_3\text{:Mn}^{2+}$ red phosphor, *Adv. Opt. Mater.* 9 (2021), 2100870.
- [13] Y. Hwa, Kim, Paulraj, Arunkumar, Y. Bo, Unithrattil Sanjith, Eden Su-Hyun Moon, A zero-thermal-quenching phosphor, *Nat. Mater.* (2017) 543.
- [14] W. Ye, C. Ma, Y. Li, C. Zhao, Y. Wang, C. Zuo, Z. Wen, Y. Li, X. Yuan, Y. Cao, Anti-thermal-quenching red-emitting $\text{GdNbO}_4\text{:Pr}^{3+}$ phosphor based on metal-to-metal charge transfer for optical thermometry application, *J. Mater. Chem. C* 9 (2021) 15201–15211.
- [15] P. Dang, W. Wang, H. Lian, G. Li, J. Lin, how to obtain anti-thermal-quenching inorganic luminescent materials for light-emitting diode applications, *Adv. Opt. Mater.* 10 (2022), 2102287.
- [16] Y. Wei, H. Yang, Z. Gao, Y. Liu, G. Xing, P. Dang, A.A.A. Kheraif, G. Li, J. Lin, R. Liu, Strategies for designing antithermal-quenching red phosphors, *Adv. Sci.* 7 (2020), 1903060.
- [17] Y. Wei, H. Yang, Z. Gao, X. Yun, G. Xing, C. Zhou, G. Li, Anti-thermal-quenching Bi^{3+} luminescence in a cyan-emitting $\text{Ba}_2\text{ZnGe}_2\text{O}_7\text{:Bi}$ phosphor based on zinc vacancy, *Laser Photon. Rev.* 15 (2021), 2000048.
- [18] Y. Bai, S. Sun, L. Wu, T. Hu, L. Zheng, L. Wu, Y. Kong, Y. Zhang, J. Xu, Oxygen vacancy content drives self-reduction and anti-thermal quenching, *J. Mater. Chem. C* 10 (2022) 4317–4326.
- [19] Y. Wang, B. Chen, F. Wang, Overcoming thermal quenching in upconversion nanoparticles, *Nanoscale* 13 (2021) 3454–3462.