SYNTHESIS,CHARACTERIZATION AND INVESTIGATION ON OPTICAL PROPERTIES OF SODIUM CERIUM DOUBLE TUNGSTATE [$NaCe(WO_4)_2$] NANOMATERIALS

Thesis submitted for partial fulfillment for the
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LAW AND MANAGEMENT
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BY

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DECLARATION OF ORIGINALITY AND COMPLIANCE OF ACADEMIC ETHICS

I do hereby declare that this dissertation contains literature survey and original research work by the undersigned candidate, as part of my ***Master of Technology*** *in* ***Nanoscience and technology*** *studies during academic session 2021-2023.*

All information in this document has been obtained and presented in accordance with academic rules and ethical conduct.

I also declare that I have fully cited and referred all material and results that are not original to this work.

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CERTIFICATE FROM THE SUPERVISORS

This is to certify that the thesis entitled "SYNTHESIS,CHARACTERIZATION AND INVESTIGATION ON OPTICAL PROPERTIES OF SODIUM CERIUM DOUBLE TUNGSTATE [NaCe(WO4)2] NANOMATERIALS" has been carried out by Ms. Koninika Biswas (University registration no-160438 of 2021-2022) of Jadavpur University under my guidance and is absolutely based on her own work. This thesis is in partial fulfilment of the requirement for the degree of Master of Technology in Nanoscience and technology under the supervision of Dr. Chandan Kumar Ghosh and neither her thesis nor any part of the thesis has been submitted for any kind of degree/ diploma or any other academic award anywhere before.

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CERTIFICATE OF APPROVAL

The forgoing thesis entitled "SYNTHESIS,CHARACTERIZATION AND INVESTIGATION ON OPTICAL PROPERTIES OF SODIUM CERIUM DOUBLE TUNGSTATE [NaCe(WO4)2] NANOMATERIALS" is hereby approved as credible study of the subject carried out and represented in a manner of warrants its acceptance as a prerequisite to the degree for the undersigned does not necessarily endorse any statement made, opinion, opinion expressed or conclusion drawn there in but approved the thesis only for the purpose for which it has been submitted.

The final examination for evaluation of the thesis

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Signature of supervisor

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ABSTRACT

The study given in the thesis “Synthesis, Characterization and Investigation on Optical Properties of Sodium Cerium Double Tungstate [$NaCe(WO_4)_2$] Nanomaterials” is primarily concerned with two segment: first, the synthesis of scheelite material $NaCe(WO_4)_2$ and second finding the changes in optical properties.

Rare earth oxide materials have potential applications in optoelectronics owing to their unique optical properties that arise from $4f$–$5d$ electronic transitions. Optical properties such as Photoluminescence (PL) of these oxide materials are found to be determined by their crystallographic features as well as type of activator ion and sensitizer ion residing in the host lattice. Alkali rare earth double tungstate with the general formula $ARE(WO_4)_2$, where A is an alkali metal ion, *RE* is a rare earth ion, and M = W/Mo, were known to adopt the Scheelite-like crystal structure. These materials have received a lot of interest owing to their structural stability and tenable optical properties. The primary goal is to synthesize $NaCe(WO_4)_2$ using Hydrothermal Method. Their structural and optical properties have been researched and characterized. The control of its size and form was achieved by adjusting the preparation parameter.

INDEX

List of Acronyms

Abbreviation	**Full From**
XRD	X-ray Diffraction
θ	Bragg’s angle
FTIR	Fourier-Transform Spectroscopy
NCWO	Sodium Cerium Double Tungstate
Eg	Band Gap Energy
PL	Photoluminescence Spectroscopy
UV-Vis	Ultra Violet Visible Spectroscopy
CIE	Commission Internationale de l'Elcairage
I_{max}	Maximum Intensity
I_{int}	Initial Intensity

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Outline of the Thesis

The thesis is organized as follows:

- **Chapter 1: Introduces about nanotechnology and nanomaterials**
- **Chapter 2: Introduction about the type of material used in this work.**
- **Chapter 3: Review of the various kind of work done on scheelite type materials containing rare earth elements.**
- **Chapter 4: Provides information regarding the synthesis of nanoparticles and steps for preparation of the compound.**
- **Chapter 5: Discussed about the different kind of instruments used for the purpose of different characterization.**
- **Chapter 6 : Discussed about results of the different characterization outputs.**
- **Chapter 7: Conclusion of the thesis.**

CHAPTER-1

NANOTECHNOLOGY AND NANOMATERIALS

[1.1] Nanotechnology and nanomaterials:

Nanotechnology means matter on a ‘nano’ scale, is considered to be a key enabling technology. The Greek word "nano" (meaning dwarf) refers to a reduction of size, or time, 10-9 fold, which is one thousand times smaller than a micron [1] .One manometer (nm) is one billionth of a meter, and it is also equivalent to ten Angstroms. The properties of matter at the nanoscale are different from those at a larger scale [2]. When the dimensions of materials are reduced from a large size, the properties remain the same at first, then small changes occur.

Nanotechnology encompasses nanomanufacturing and application of physical, chemical, and biological systems at scales ranging from individual atoms or molecules to submicron dimensions, as well as the integration of the resulting nanostructures into larger systems. Nanotechnology revolves across scientific fields, including chemistry, physics, material science, engineering, and manufacturing. Its impact on our society and economy in the twenty-first century is comparable to that of semiconductor technology, information technology, or cellular and molecular biology in the twentieth century.

The involvement of nanotechnology into larger systems has given some break-through solutions to many current environmental, medical, and industrial problems, including smart materials, nanomanufacturing, electronics, drug delivery, energy and water, biotechnology, information technology, and national security[3].

Nanotechnology and nanoscience are those fields of study which concentrate on things at a nanoscale scale and involves items smaller than a hundred nanometer and falls under the preview of nanotechnology or nanoscience. These topics are combining various disciplines such as physics, chemistry, engineering, and biology.

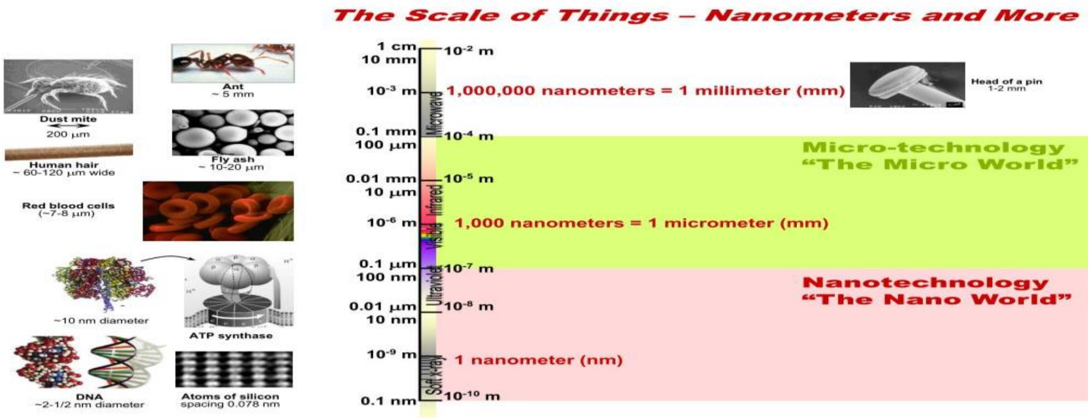

Figure 1: Definition of nanotechnology

[1.2] Properties of Nanomaterials:

[1.2.1] Physical Properties:

(1) Zero dimensional (0D) : Zero-dimensional (0D) nanomaterials represent materials wherein all the dimensions (x,y,z) are measured within the nanoscale of 1–100 nm. The most common representation of zero dimensional nanomaterials are mostly spherical nanoparticles. However, cubic and polygonal shapes with nano dimensions are also found under this class. They can be amorphous, single crystalline, or polycrystalline. Uniform materials with nano dimensions, such as molecules, clusters, fullerenes, rings, particles, and grains, are considered under this class.

(2) One-dimensional (1D) : One-dimensional (1D) nanomaterials possess nanometer size in two directions but larger length (>100 nm) in the third which leads to needle-like shaped nanomaterials. Carbon nanotubes , metals or metal oxides nanowires, polymer nanowires or nanofibers, and hybrid materials are the common representatives of one dimensional nanomaterial. These nanomaterials have unique properties due to their inherent high-aspect-ratio structural feature and with superior mechanical, electrical, and optical properties.

(3) Two-dimensional (2D) : The two-dimensional (2D) nanomaterials are thin sheets at atomic level at two dimensions and the other one of the dimensions is not confined to the nanoscale. Nanofilms, nanolayers, and nano coatings are the common representations of two-dimensional nanomaterials that exhibit plate-like shapes. Graphene is one of the most recent examples of this class, which is a single carbon layer of the honeycomb graphite structure.

(4) Three-dimensional (3D) : Three-dimensional nanomaterials are those that are not confined to the nanoscale in any dimension. They possess three arbitrarily dimensions above 100 nm. However, these nanomaterials generally have a nanocrystalline structure or involve the presence of features at the nanoscale. In terms of the nanocrystalline structure, bulk nanomaterials can be composed of multiple arrangements of nano size crystals in different orientations. With the respect to the presence of features at the nanoscale, 3D nanomaterials can contain dispersion of nanoparticles, bundles of nanowires, and nanotubes as well as multi- nanolayers.

[1.2.2] Optical Properties:

The optical properties like reflection, transmission, absorption and light emission of the nanomaterials are fully dependent on their electronic structure that significantly differs from various morphologies since electronic structure of the nanomaterials are mostly dependent on surface atoms. Two factors which increased energy level spacing that is quantum effect and surface plasmon resonance due to contribution of the size-dependent optical properties of nanomaterials. Size has effect on optical properties are observed when the particle size is reduced to 10 nm. At nanoscale level, particles are so small that electrons in them are not as much as free to move as in case of bulk material.

[1.2.3]Interfacial Properties:

Surface properties of metal and semiconductor nanoparticles are quite different from that of bulk material and in-depth understanding of these aspects is essential for the utilization of various nanomaterials for optoelectronic devices. However, it is difficult to probe the surface properties of nanomaterials by adopting conventional methods. Photo responsive molecules have been widely used as a ruler for probing the physical properties of micro heterogeneous environment. Although exciting advances have been made in recent years in the design of nanomaterials, investigations on the surface properties of such systems using fluorophores are rather few. This was based on a general belief that the metal surfaces strongly quench the singlet-excited state of fluorophores through an energy transfer process [3].

[1.3] Application of Nanotechnology:

Figure 2: Application of nanotechnology

(1) Energy ： Energy is one of the greatest importance in human life because of its benefits as the main resource for human activity. Since demand of energy will never decrease, it is extremely necessary to develop modern technology like nano based technology, in order to obtain a more effective and efficient process to produce more energy. The use of nano technology or nano materials in the field of energy, which involves lithium-ion battery, light emitting diode, super-capacitor and solar cell is recently a hot topic in many scientific researches. Although current development is hampered by the expensive cost of production compared to conventional technologies. Priority should be given to nano technology in the energy sector in order to obtain higher efficiency, lower production cost, and easier in application [4].

(2) Defense and security ： The developments in nanotechnology especially in nanostructures and nanocomposites are being done for the following military applications - Lightweight protective clothing, chemical and biological warfare protection and self-decontaminating nano fibre -fabrics. Also, adaptive suits which have switchable fabrics for improved thermal control, switchable camouflage. Micro sensors used for body and brain sensing, environmental and situational awareness, integrated into a smart suit or a smart helmet. Wearable and flexible displays for visual feedback auxiliary supports. Flexible or rigid textiles for additional strength, exoskeletons, and robotics to assist the human tasks [5].

(3) Medicine and drug ： Nanotechnology is being applied extensively to provide targeted drug therapy, diagnostics, tissue regeneration, cell culture, biosensors and other tools in the field of molecular biology. Various nanotechnology phenomenon like fullerenes, nanotubes, quantum dots, nanopores, magnetic nanoprobes and radio -controlled nanoparticles are being developed. Development of newer drug delivery systems which are based on nanotechnology methods is being tried for medical conditions like cancer, diabetes, fungal infections, viral infections and in gene therapy. The main advantages of these type of treatment like targeting of the drug which enhanced safety profile. Nanotechnology has also founded its use in diagnostic medicine in the form of contrast agents, fluorescent dyes and magnetic nanoparticles [6].

CHAPTER-2

INTRODUCTION

[2.1] Nanostructure:

Nanostructured materials are those materials whose structural elements - crystallites or molecules - have dimensions in the 1 to 100 nm range. The discovery of nanostructured material increased the interest in both academic and industrial was remarkable[7-8].

[2.2] History of Scheelite Material:

Scheelite first got its recognition in 1751 for an occurrence in Mount Bispbergs klack, Säter, Dalarna, Sweden, and named after Carl Wilhelm Scheele (1742–1786).

[2.3] Scheelite Material:

Since there always had been a demand for sustainable development, energy consumption, greener, and safer technology, researchers are motivated to find the best materials in the field of optics and rare-earth oxides is one of them. Scheelite material is a vast range of group of material which is based on the formula ABO_4. Scheelite material have a tetragonal structure having space group I41/a. This material is used for a wide variety of applications for good photoluminescence, display technology, solid-state lighting, optoelectronic devices, luminescent diodes, solar cells etc. Among all the type of them alkali rare earth double tungstate material which have the general formula of $ALn(WO_4)_2$ have been at the peak of attraction and a lot of experiments are being carried out in the recent years. Since scheelite materials have excellent optical properties which leads its use in many application based on optical properties. These Scheelite materials have narrow emission bands where 4f - 5d transitions [9]. Ln^{3+} have excellent structural and optical properties. The fluorescence in lanthanides occurs through f → f transitions within the 4f orbital. The 4f shell is shielded results in zero phonon lines in the emission spectra of lanthanides. Herein, Ce^{3+} shows a different character due to its f-d transitions. The emission is broad shows a strong dependency on the crystal filed environment [10].

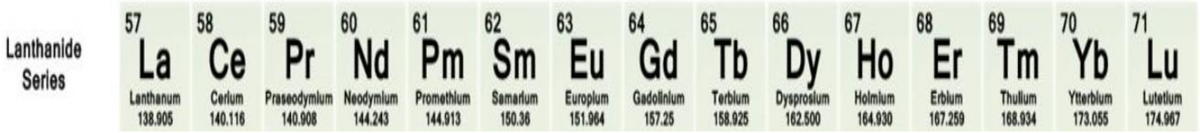

Figure 3: Lanthanide series

Lanthanide which are doped in divalent metal tungstate have emerged as a new class of nanophosphors which owes to excellent chemical and thermal stability along with the ability to tune its optical properties [11].

[2.4] Nanomaterials Optical Application:

(1) Hybrid semiconductor nanomaterials have interesting optical properties that find important applications in emerging technologies. Hybrid nanomaterials are composite materials which has physical dimensions which is relevant for the interface region between different components [12].

(2) TiO_2 was used for tailoring the intrinsic properties and chemical stoichiometry for optimum performance in any light–matter-related application [13].

(3) ZnO which is also an industrially important material with a direct band gap near the UV range of 3.37 eV and an exciton binding energy of 60 meV at room temperature [14].

(4) Nonlinear optics is given increasing attention due to its wide application in the area of laser technology, optical communication and data storage technology [15].

(5) Nanomaterial optical sensors are among the most important types of chemical sensors that have been produced in the recent years [16].

(6) Nanomaterials based on carbon and noble metals, such as reduced graphene oxide and gold nanoparticles have gained space in scientific research due to their distinct properties, such as high electrical and thermal conductivities, surface-to-volume ratio, electron mobility at room temperature, a high mechanical resistance and large surface area [17].

[2.5] Motivation for the work:

Through the recent advancement in the field of nanotechnology, nanomaterials are widely being used in the illumination industry due to its large surface area and ability for the enhancement optical properties. Therefore, a detailed study has been done in this thesis, of the optical properties of NCWO by applying the concept of nanotechnology. Thus, the aim of the thesis work is to monitor results of different characterization are how much sensitive to the variation in concentration of one of the prime materials used for the preparation of the compound.

CHAPTER-3

LITERATURE REVIEW

[3.1] Evolution of materials used in optoelectronics:

[3.1.1] Semiconductor materials:

Early in 1960's semiconductor laser optoelectronic devices was first demonstrated which have been produced in millions, and involved our everyday lives in communications, computing, entertainment, lighting and medicine. The majority of these electronic devices are silicon based, some are made using III–V semiconductor compounds such as GaAs, InP, GaN and GaSb and their alloys due to their direct band gap[18].

[3.1.2] Semiconductor nanomaterials:

When the size of semiconductor materials is reduced, their physical and chemical properties change drastically, resulting in properties due to their large surface area or quantum size effect. Further development of nanotechnology have certainly led to significant breakthroughs in the semiconductor industry[19].

[3.1.3] Rare earth nanomaterials:

In recent years, the third-generation semiconductor materials represented by ZnO, SiC, and GaN have opened up a new situation in the semiconductor industry. Doping rare earth elements in semiconductor materials can adsorb impurities, thereby effectively improving the purity and integrity of semiconductor materials. Rare earth oxide semiconductors, as a special kind of semiconductor material, have the advantages of rich spectral lines, high color purity, and high luminous efficiency. In addition, due to its special 4f energy band, it has a similar light-emitting mechanism to semiconductors. Rare earths are key materials for solid-state lasers and have important applications in laser weapons, thermonuclear fusion, laser communications, laser processing, and medical treatment.

[3.1.4] Rare earth and scheelite nanomaterials:

Shifa Wang et al. reported $Ca(WO)_4$ which is a scheelite material for having variation in UV-Vis and PL characteristics due to change in temperature. When the material was calcinated at 400℃ the reflection was at lowest due to low crystallinity. Below 600° Eg increases as calcinating temperature increases but from 700° to 900° Eg decreases as calcinating temperature increases. It was observed that the reflectance is increasing first then decreasing with the increase in calcination temperature. As for PL characteristics the emission increases first then decreases with the increase of calcination temperature. So it was concluded that at higher calcination temperature the fluorescent groups and oxygen vacancy are small and shows excellent luminescence properties[20]. As reported in [21] that the only peak appeared was at 265nm in the PL graphs of $CaWO_4$ .As for the UV-Vis graph the band gap appeared at 3.31 and 3.27 eV.

When rare earth elements were doped with scheelite materials different photoluminescence characteristics can be found. As per reported in [22] Dy^{3+} a rare earth element was doped in $CaWO_4$ and $CaMoO_4$ and the excitation spectra for the first one was found around 243nm and for the second one around 277nm.The emission color were found from blue, blue-green to yellow and white by decreasing the doping concentration of the dopant. Similarly when $SrMoO_4$ was doped with Tb^{3+} we found that doping shifted the band gap energy to higher energies than the pure compound [23].

[3.2] Scheelite nanomaterials:

Scheelite crystallizes are a tetragonal crystal system, which means it has four-fold rotational symmetry along the c-axis. The crystal structure can be classified as scheelite-type structure or the calcium tungstate structure. Here in this type of structure, tungsten atoms occupies the center of the unit cell, surrounded by oxygen atoms forming a distorted octahedral coordination. In this type of structure, it exhibits perfect cleavage on {110} planes, which is a plane perpendicular to the c-axis.

Scheelite materials are used over the years for various prospectives. It is a kind of material that can be used without much adverse effects like green energy material. The structure of scheelite material can be tetragonal or triclinic.

[3.3] Different synthesis method for preparation of scheelite nanomaterials:

[3.3.1] Solid state method: Solid state method consists of two type of methods. First, physical vapor deposition method and second chemical vapor deposition method.

[3.3.1.1] Physical vapor deposition method: In physical deposition method, materials get deposited on the surface either as a thin film or as nanoparticles. Highly controlled vacuum technique such as thermal evaporation and sputtered deposition causes vaporization of material, which is then further condensed on a substrate. It is a simple method but expensive.

[3.3.1.2] Chemical vapor deposition method: In chemical method of deposition, thin film of target material is deposited on the surface through the chemical reaction of gaseous molecule containing atoms useful for film formation. The target material is then released in the form of volatile molecule and works as precursor and then series of chemical reactions take place between the precursor fragment, precursor and substrate surface to produce a thin film.

[3.3.2] Sol gel method: In this method, a network formation is introduced using colloidal suspension (sol) and gelatin to form a network in continuous liquid phase (gel). This process involves four main steps; hydrolysis, condensation, particle growth and agglomeration of particle.

[3.3.3] Coprecipitation method: Coprecipitation is a method of adding raw materials into the mixed metal salt solution. The metal ions gets precipitated to form the precipitation mixture or precursor in the metal ion solution. After the precipitation the mixture is stirred and washed several times, and dried leading to a high-quality product.

[3.3.4] Hydrothermal method: Hydrothermal method is basically the reaction of aqueous solution vapors with solid material at high pressure and temperature, and leads to deposition of small particles. In this method cation precipitate in polymeric hydroxide form and further these hydroxides would get dehydrated and accelerate the formation of metal oxide crystal structure.

[3.4] UV and PL characteristics of cerium doped or cerium containing scheelite nanomaterials:

In this chapter we are going to discuss about UV and PL characteristics of cerium doped or cerium containing scheelite nanomaterials which already have been reported.

Fang *et al.* reported that when Ce^{3+} was doped in $PbWO_4$ the adsorption edge is shifted toward higher wavelength that is red shift [24].Although in another work [25] it was also reported that when Ce^{3+} doped $PbWO_4$ blue -green emission and blue emission was observed due to WO_4^{2-} groups . In another work [26] it was reported that when $CoWO_4$ doped with Ce^{3+} its PL peak was around blue-green and green spectra. K.V. Dabre *et al.* reported that when Ce^{3+} was doped in MWO_4 (M=Ca, Sr and Ba) the intensity in the excitation band was decreasing with increase in ionic radius (Ca<Sr<Ba) and a red shift occurred with increase in ionic radius. The intensity of PL emission increased with Ce^{3+} concentration which showed the contribution of 5d-4f transition of Ce^{3+} in emission spectra [27].

Another work based on M_{1-X} WO_4: xCe^{3+} (M=Ca,Sr,Ba) also stated blue emission at 440nm [28]. In another work [29] it was reported $AgTb(WO_4)_2$ when doped with Ce^{3+} it showed blue shift in the band as Ce^{3+} concentration was increased. The shift in wavelength showed the characteristics which could be used for tunable detector applications and design of diodes and laser . M. S. Sena *et al.* reported $Ce_2(MoO_4)_3$ uv-vis graph showed that band gap energies of 2.26 eV,2.43eV and 2.34eV at 500℃, 600℃ and 800℃ [30].

Mei Li *et al.* reported the energy gap around 4.03 eV for $NaLa(WO_4)_2$:$0.02Sm^{3+}$ and when dopped with Ce^{3+}, 4.06eV was the energy gap and close to optical band gap. After doping the emission peak was between 300 and 550 nm due to immigration of charge from O^{2-} to W^{6+}. It was found that at low doping content Ce^{3+} act as energy transfer donor and on high doping content Ce^{3+} had a quenching effect on Sm^{3+}. $NaLa(WO_4)_2$:Sm^{3+}:Ce^{3+}phosphor showed good thermal stability and could be used as red phosphor for LED [31].

At another work [32] when Ce^{3+} doped in $SrMoO_4$ the compound could be used in converter from ultraviolet to visible light converter and other photonic applications was reported. Similar compounds like $Ce_{2x}Sm_x(WO_4)_3$ were used to form tunable radiation sensors, used in medical imaging and low-cost lightning [33] was also reported and $Ce_2(MoO_4)_3$ photoluminescence spectra showed that maximum intensity appeared at blue-green region. The behavior can be explained by multiphonon and multilevel process which involves precipitation of many states within the gap [34]. In the compound $Ce_2(WO_4)_3$ uv-vis showed blue shift and the PL graph showed intensity decreased with increase in crystal size [35].

A similar compound showed that the optical properties of $NaCe(MoO_4)_2$ showed attribution to an O2p-Ce4f charge transfer and became responsible for yellow color [36].Another similar compound $LiCeW(O_4)_2$ showed blue emission due to Ce^{3+} and WO_4^{2-} [37]. When NCW was doped with Er and Yb an efficient laser can be realized[38]. C. Rakhi et al. reported that their compound showed peaks around blue-green region on excitation at 400 nm in their PL graph. The material had good characteristics required for use in optoelectronics devices, semiconductor devices and light emitting diodes [39].

It was found that all the following compounds $LiCe(WO_4)_2$, $NaCe(WO_4)_2$ and $KCe(WO_4)_2$ exhibited broad light emission bands corresponding to the excitation at 360nm. It was also found that emission intensity decreased in the order $KCe(WO_4)_2$> $NaCe(WO_4)_2$> $LiCe(WO_4)_2$ in accordance with the decrease in ionic radii of K^+151pm>Na^+118pm>Li^+92pm [40]. UV-vis spectra of different $Na_{0.5}Ce_{0.5}WO_4$ morphologies showed sharp absorption peak from 375 which gives the idea if transition from O2P to Ce 4f+5d and W4f states. The bandgap energy value is a function of size. The sample showed fluorescence peak at blue region and red region. The blue emission is for WO_6 octahedra groups and Ceo_8 polyhedral which depends on the oxygen vacancies in the semiconductor. Due to these effects bond energy decreased and red colour emission was found. The charge transfer happened to W-O bonds within $(WO_4)^{2-}$ compound and 5d transition of Ce^{3+} [41].

[3.5] Advantages and disadvantages of cerium containing scheelite compound:

From the basis of different works which are mentioned above it can be concluded that on addition of rare earth elements like cerium to scheelite compounds have the following advantages:

1) The optical properties would be enhanced from the properties of a pure scheelite compound.
2) With nanomaterials containing these properties would find its application in various optoelectronic devices having blue emission.

But, the disadvantage is that the processing time and condition are difficult to obtain in large scale and the yield of the compounds are very less .

Chapter-4

Experimental Process

[4.1] Hydrothermal Process:

Researchers have always been in search of new material synthesis method which have less pollution, easy operation, low production cost and good product performance. But most solid phase method which results in high yield and large- scale production arises a problem to control particle size, purity and morphology of powder. Among these methods the hydrothermal method is further researched as it is a soft synthesis method [42-43].Previously hydrothermal method which be ginned during mid-19th century were used to apply for formation of single crystal growth[44-45].Water in hydrothermal reaction can act as solvent or chemical component. But with high temperature and pressure water can lead to different changes such as the increase in ionization constant, decrease in viscosity and surface tension of water which in turn leads to increase in mobility of molecules and ions and thus the crystal growth continues. Also the dielectric constant is low thus decreasing the ability of water to act as solvent. With the increase in water vapor, diffusion coefficient decreases and reaction increases due to collision among the molecules [46-48].

Some compound has very less solubility in water to increase the solubility the role of ‘mineralizers’ is introduced. Mineralizers are those compounds whose solubility in water increases with the gradually increase in temperature in water. With addition of these compounds not only the solubility of solute is increased but the temperature coefficient is also changed, while some will form complexes with the crystals to increase its nucleation rate. Also they have a great impact on the quality and growth rate of the crystals [49-52].Hydrothermal method can be divided into many parts based on categories it is measured like as for based on research object and purpose it can be divided into synthesis, reaction, treatment and crystal growth. Now based on reaction temperature it can be divided into low-temperature hydrothermal method and supercritical hydrothermal method.

As for based on equipment it is divided into ordinary hydrothermal method and special hydrothermal method. As for the special hydrothermal method which includes direct current electric, magnetic and microwave. In case of microwave hydrothermal method the interaction between microwaves and matter leads to dielectric loss, conduction loss and magnetic loss. In this mechanisms several type of heating takes place like joule, induction and medium heating [53-54].

Figure 4 : Hydrothermal autoclave

The steps of crystal growth in ordinary hydrothermal method are:

(1) The reactants are dissolved in hydrothermal medium in the form of ions or molecular groups.
(2) Then the ions and molecules will be separated by temperature difference in upper and lower portion with in the kettle.
(3) Then the ions or molecules or molecular groups are transported to low temperature region that is the region in which seed crystals is grown.
(4) Then the ions or molecular groups will be adsorbed decomposed and desorbed at the crystal interface.
(5) Then the adsorbed materials will move to the surface.
(6) Hydrothermal conditions make the making or crystal growth dependent on it [55-57].

Hydrothermal method was be used in formation of different scheelite material like $FeWO_4$,$CoWO_4$ [58].

$PbMoO_4$ when synthesized in conventional hydrothermal method showed tetragonal structure without any secondary phases and are well-ordered at long and short range and have self-organized along [001] direction [59].

More tungstate oxides like $SrWO_4$,$CaWO_4$,$PbWO_4$ and $ZnWO_4$ are prepared by conventional hydrothermal method [60-61].

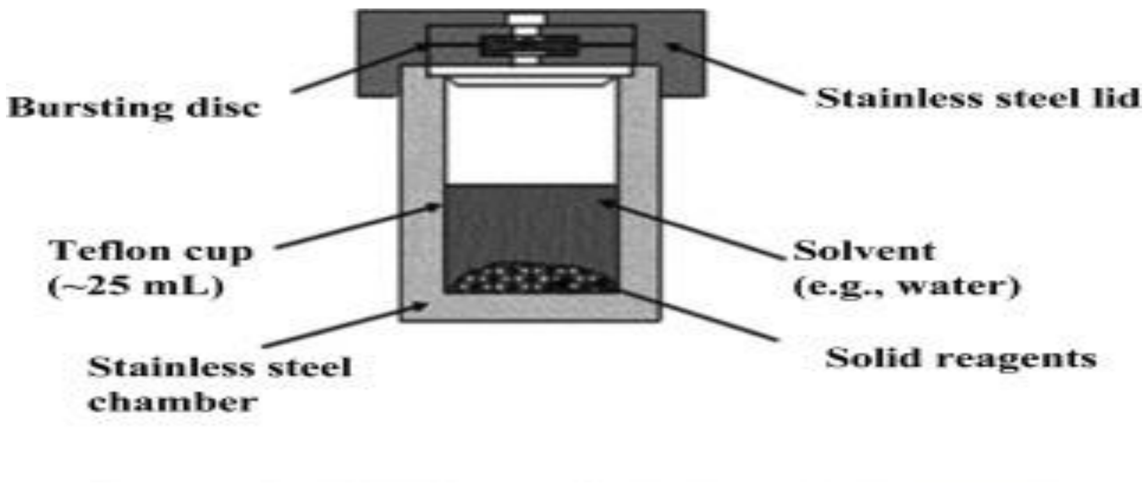

Figure 5: Hydrothermal synthesis

[4.1.2] Advantages:

Hydrothermal method has several advantages and are used for preparation of ceramic oxides, garnets, vanadates and others and helps in development of modern material science, application field and engineering research area.

[4.1.3] Drawbacks:

Hydrothermal have long reaction time compared to other methods [62].

[4.2] Preparation of NCWO:

[4.2.1] Materials:

The materials used are tri-sodium citrate dihydrate purified [$HOC(COONa)(CH_2COONa)_2 \cdot 2H_2O$, Merck, Germany], cerium nitrate [$Ce(NO_3)_3.6H_2O$, Merck, Germany], sodium tungstate [$Na_2WO_4.H_2O$, Merck, Germany].

[4.2.2] Preparation procedure:

(1) First in a beaker(A) 1 mmol of cerium nitrate and 1 mmol of trisodium citrate is taken and then 60ml of de-ionized water is added followed by 10 mins of stirring at 650 rpm.

(2) In another beaker(B) 2 mmol of sodium tungstate is taken and 20ml of de-ionized water it added .

(3) Solution in beaker (B) is added dropwise in beaker (A) for 5 mins.

(4) After that the solution is mixed through 10 mins of stirring at 650 rpm.

(5) Then the mixed solution is kept in autoclave for 21 hour at 180℃.

(6) Same process is carried on but by changing the amount of trisodium citrate into 0.75 mmol,0.50mmol and 0.25 mmol.

[4.2.3] Purification:

Purification is done by centrifugation with water and ethanol as the medium and which is followed by sonication at intervals of centrifugation to dissolve the solute in the medium for the upcoming centrifugation..

[4.2.4] Drying:

After purification first overnight drying is done at 70°C with ethanol as the medium which is followed by calcination the following day. The calcination was done with nitrogen gas flow for 24 hrs. at 800°C. Nitrogen gas was used as it is an inert gas and to remove other impurities.

Figure 6: Lab equipment's used for preparation of material

Chapter-5

Instruments & Apparatus

[5.1] Introduction to x-ray diffraction:

X-ray was discovered by Wilhelm Conrad Roentgen 1895 which helped lots of important innovations in all scientific disciplines. The research on XRD initiated by Laue, Friedrich and Knipping in 1912 helped in study of crystalline materials. X-ray have three main categories. Among them X-ray fluorescence spectroscopy is widely used for qualitative and quantitative. X-ray radiography an imaging technique based on intensity of ray through the object through the use of films or detectors making the internal structure visible by variation in absorption. Lastly the Xray methods based on availability of crystals to diffract X-ray and helps to know about crystallinity phases.

[5.1.1] Principle of x-ray:

X-ray have a wavelength between 10^{-3} and 10^{1} nm. X-ray generation can be achieved by sealed tubes, rotating anodes and also synchrotron radiation sources. Sealed tubes and anodes are used in laboratory method. X-ray produced by then are generated from electrons created by heating a tungsten filament in vacuum and accelerated through high potential field and then it is directed to a target which emits X-rays. The incident electrons have two effects which leads to generation of X-ray: First is deceleration of electrons which leads to emission of X-ray photons have a continuous distribution of wavelength and second the ionization of atoms by ejecting electrons from inner shells and to maintain stable state electrons from outer shells jump into these gaps. The difference between energies of inner shell electron and incoming electron is emitted in form of photons although there is dependency on characteristic energy between initial and final shell positions. The radiation from the tube or anode is imposition of a continuous spectrum. Generally XRD uses, Kα radiation and remove other radiation by using monochromators. Filtering is based on nonlinear absorption of filter material regarding wavelength. High energy electrons are produced by high power electron gun and injected for acceleration. Electrons which are injected in a booster ring then introduced in a storage ring where synchrotron radiation are produced. These rings are generally not circular but in polygon shape. In third generation synchrotrons a periodic arrangement of magnets consists. Then electrons forced to follow a sinusoidal path loading to emissions of photons. Emitted photon has energy to cover full spectrum from infrared to ϒ-rays.

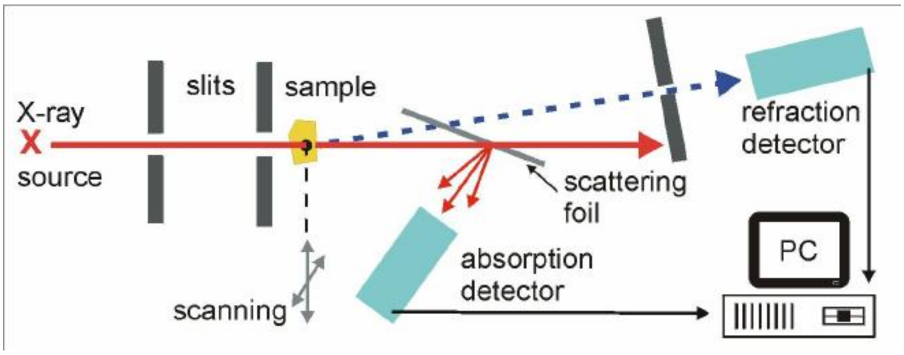

Figure 7: X-ray Diffraction

[5.1.2] Diffraction of x-ray by crystalline materials:

X-ray photon when reach matter different types of interaction takes place which leads to various absorption and scattering effects. Coherent scattering or Rayleigh scattering which occurs between photons and electrons. As a result the energy of scattered waves is unchanged and retains phase relation to the incident wave. So, X-ray photons are scattered in all directions. Although for periodic nature of crystalline structure both constructive and destructive radiation occurs which leads to characteristic phenomenon to investigate crystal structure of materials. The principle depends on diffraction of X-rays by periodic atomic planes and energy resolved detection. Geometrical interpretation of XRD is given by W.L.Bragg.

$$n\lambda = 2d_{hkl}\sin\theta$$

where n = order of diffraction, λ = wavelength and d_{hkl} = lattice spacing in nm and θ = angle of diffracted beam

The parameters which are determined are I_{max} ,I_{int} , FWHM.

$$I=I_o\times\exp(-\mu\times x)$$

The equation is used to calculate intensity loss which follows the law of Beer-Lambert.

[5.1.3] Special methods:

(1) Energy : Dispersive X-ray diffraction- Use of white beam and detection of diffraction peaks at a fixed 2θ angle by use of energy – resolved detectors.
(2) Small angle scattering : Here lattice plans are not considered for diffracting beam but small periodic structures. The diffraction takes place for variations of electron density at boundaries.

(3) In situ X- ray diffraction : This technique investigate phase – specific properties like lattice parameters , strains, orientations and phase contents.

[5.1.4] Hardware for x-ray diffraction measurements with laboratory equipment’s:

(1) X-ray source : Main aspects of X-ray production are intensity radiation and size of beam coming out of anode for the purpose of measurement. Common X-ray tubes and anodes allow the use of two types of focus shapes.

(2) Goniometer : It is the central part of the diffractometer allowing the X-ray source, the sample and the detector relatively to move in a precise manor. There are two types of goniometer – θ/θ goniometers where sample are fixed and θ/2θ goniometer where the sample and detector.

(3) Primary optics : To define the size and form of primary beam and to obtain highest signal intensity for selection of the wavelength precisely.

(4) Secondary optics : These devices placed between the sample and the detector are used to define the diffracted beam. Filters to reduce K_β can generally be placed in front of the detector.

(5) Detectors : The working principle is based on the conversion of X-ray photons into another signal which can be analyzed.

[5.1.5] Applications:

Quantitative and Qualitative phase analysis :

(1) Measurement of diffraction patterns by X-ray diffraction
(2) Qualitative phase analysis
(3) Quantitative phase analysis
(4) Method of intensity ratio
(5) Rietveld method

[5.2] Introduction to Fourier-transform spectroscopy:

Fourier-transform spectroscopy is a powerful spectral analysis technique. The output intensity of the interferometer is measured from the varying of optical path difference between the two arms of the interferometer. Wavelength-dependent pattern is obtained by scanning the interferometer optical delay, from which the input spectrum can calculated by Fourier transformation (FT). Interference-based spectroscopy was first applied by Fizeau to demonstrate that the yellow sodium radiation peak which actually was doublet the interferometric technique was further developed by Michelson, leading to the publication of the first interferogram in 1911 and finally the spectroscopic technique was established in 1957 Bellevue Colloquium, where most of the work conducted was in Fourier-transform spectroscopy. Fourier-transform spectroscopy provides highly resolved spectral measurements in the infrared, visible and ultraviolet ranges.

The performance of spectrometer may be affected due to the mechanical properties. Mechanical elements required to be realignment after continuous use, which is troublesome in some applications. A high degree of stability of the setup should be maintained in order to perform accurate spectroscopic measurements.

[5.2.1] Components:

(1) IR sources :FTIR spectrometers are mostly used for measurements in mid and near IR regions. For the mid-IR region, 2−25 μm (5,000–400 cm^{-1}). Shorter wavelengths of the near-IR region are 1−2.5 μm (10,000–4,000 cm^{-1}). The long wavelength output of these sources are limited to about 5 μm (2,000 cm^{-1}) by the absorption of the quartz envelope. Mercury discharge lamp with higher output is used for the far-IR region, especially at wavelengths beyond 50 μm (200 cm^{-1}).

(2) Detectors : Far-IR spectrometers used pyroelectric detectors that respond to changes in temperature as the intensity of IR radiation falling on them varies and in order to achieve the best sensitivity the time for the scan is typically a few seconds. There are also detectors an interferogram used to measure in as little as 10 milliseconds. For near-IR systems uncooled indium gallium arsenide photodiodes or DTGS are usually used.

(3) Beam splitter :The main function of beam-splitter is to transmit and reflect 50% of the incident radiation. However, as materials have a limited range of optical transmittance, several beam-splitters may be used interchangeably to cover a wide

spectral range. As for the mid-IR region, the beam splitter is generally made of KBr with a germanium-based coating that makes it semi-reflective where KBr absorbs strongly at wavelengths beyond 25 μm (400 cm^{-1}).

(4) Attenuated total reflectance :Attenuated total reflectance (ATR) is another part of FTIR spectrophotometer which is used to measure surface properties of solid or thin film samples rather than their bulk properties. Generally, ATR has a penetration depth of around 1 or 2 micrometers depending on sample conditions.

(5) Fourier transform :The interferogram in practice consists of a set of intensities measured for discrete values of retardation and difference between successive retardation values is constant. Thus, a discrete Fourier transform is needed. The fast Fourier transform (FFT) algorithm is used.

[5.2.2] Spectral range:

(1) Far-infrared : At first the FTIR spectrometers were developed for far-infrared range as it has good mechanical tolerance that is needed for good optical performance, which is dependent on the wavelength of the light used. For wavelengths which are relatively long of far-infrared range, a tolerances of ~10 μm is adequate, whereas for the rock-salt region tolerances need to be better than 1 μm.

(2) Mid-infrared :The development of FTIR spectrometers for the rock-salt region. The problems of manufacturing ultra-high precision optical and mechanical components had to be solved. A wide range of instruments are now available.

(3) Near-infrared : For the region of near-infrared the wavelength range lies between the rock-salt region till the start of the visible region at about 750 nm and overtones of fundamental vibrations can be observed in this region. It is used mainly in industrial applications such as process control and chemical imaging.

[5.2.3] Applications:

(1) Nano and biological materials : FTIR is used to investigate various nanomaterials and proteins bonds which is present with various organic and inorganic nanomaterials and their quantitative analysis information can be obtained with the help of FTIR.

(2) Microscopy and imaging : The microscope allows samples to be observed and measured from regions as small as 5 microns. This allows the distribution of different chemical species within the sample to be seen.

(3) Nanoscale and spectroscopy below the diffraction limit :The spatial resolution of FTIR can be improved below the micrometer scale by integrating it into scanning near-field optical microscopy platform. The corresponding technique is called nano-FTIR and allows for performing broadband spectroscopy on materials in ultra-small quantities and with 10 to 20 nm spatial resolution.

(4) FTIR as detector in chromatography : For the speed of FTIR, spectra is obtained from compounds as they are separated by a gas chromatograph. This technique is little used compared to GC-MS (gas chromatography-mass spectrometry) which is more sensitive. GC-IR method is used for identifying isomers, which by their nature have identical masses. Due to solvent liquid chromatography fractions are more difficult.

(5) Water content determination in plastics and composites : FTIR analysis can be used to understand and measure the water content which is present in thin plastic as well as composite parts. Such FTIR methods have been used for plastics, and then used for composite.

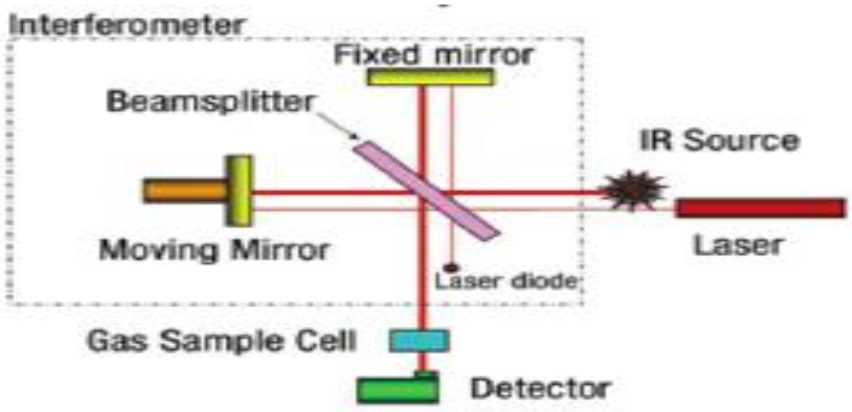

Figure 8: FTIR System

[5.2.4] Advantages:

There are advantages for an FT spectrometer compared to a scanning spectrometer :

(1) The information from all wavelengths is collected and results in a higher signal-to-noise ratio for a given scan-time for observations limited by a fixed detector noise contribution. It scan-time for a given resolution is short. Multiple scans are often

averaged, by increasing the signal-to-noise ratio and by the square root of the number of scans.

(2) FTIR spectrometers require an aperture to restrict the convergence of the collimated beam in the interferometer as convergent rays are modulated at different frequencies as the path difference is varied and the aperture is called a Jacquinot stop. For a given resolution and wavelength this circular aperture allows more light through than a slit, resulting in a higher signal-to-noise ratio.

(3) With the help of laser beam of known wavelength, the wavelength scale is calibrated which is then passed through the interferometer and becomes more stable as well as accurate in comparison to dispersive instruments, where the scale will depend on the mechanical movement of diffraction gratings.

(4) FTIR has less sensitivity to stray light, which means radiation of one wavelength appearing at another wavelength in the spectrum. In FT instruments there is no direct equivalent as the apparent wavelength is determined by the modulation frequency in the interferometer.

Figure 9: FTIR Machine

[5.3] Introduction to uv-vis near-infrared spectroscopy:

Uv-visible near-infrared (UV-Vis-NIR) In the ultraviolet-visible spectral region, a spectrophotometer measures optical transmittance, absorbance, and reflectance. Optical transmittance, absorbance, and reflectance in the ultraviolet-visible spectral range are measured using a Uv-vis near Infrared (UV-Vis-NIR) Spectrophotometer.

The percentage of the radiation absorbed, transmitted, or reflected at each wavelength is measured using UV-VIS absorption spectroscopy. Typically, this is achieved by scanning the wavelength range and measuring absorption. It is commonly used in organic chemistry to study the extent of multiple bonds or aromatic conjugation inside molecules. The technique can be extended to gases and solids, as well as beyond absorption to detect reflected light rather than transmitted light.

[5.3.1] Uv-vis spectroscopy analysis, absorption spectrum and absorbance units:

Uv-vis spectroscopy information is presented as a graph of absorbance or transmittance as a function of wavelength.

Light absorption can be described by two fundamental laws:

(1) **Lambert's Law** - The proportion of incident light which is absorbed by a transparent medium is independent of the intensity of the light provided that there is no other physical or chemical change in the medium.

Lambert's law can be expressed by:

$$\frac{\mathbf{I}}{\mathbf{I_0}} = \mathbf{T}$$

Where I is defined as the intensity of the transmitted light, I_0 is the intensity of the incident light, and T is the transmittance.

(2) **Beer's Law** - The absorption of light is directly proportional to the concentration of the absorbing medium and the thickness of the medium.

The combination of the two laws known as the Beer-Lambert Law defines the relationship between absorbance and transmittance.

$$\mathbf{A = \log\frac{I_0}{I} = \log\frac{100}{T} = \varepsilon cb}$$

Where absorbance has no unit of measurement, molar absorptivity

($dm^3mol^{-1}cm^{-1}$), molar concentration (mol dm^{-3}), and path length (cm).

[5.3.2] Tauc plot:

A Tauc plot is helps to determine optical bandgap. Typically, a Tauc plot shows that quantity hν (the photon energy) on the x-coordinate and the quantity (αhν)1/2 on the y-coordinate, where α is the absorption coefficient of the material. Thus, on extrapolating the linear region of x-coordinate we obtain the energy of the optical bandgap of the material.

A similar type of procedure is adopted to determine the optical bandgap of crystalline semiconductors. If the ordinate is given by (α)1/r, in which the exponent 1/r denotes the nature of the transition:

r = 1/2 for direct allowed transitions

r = 3/2 for direct forbidden transitions.

r = 2 for indirect allowed transitions

r = 3 for indirect forbidden transitions

[5.3.3] Measurement setup:

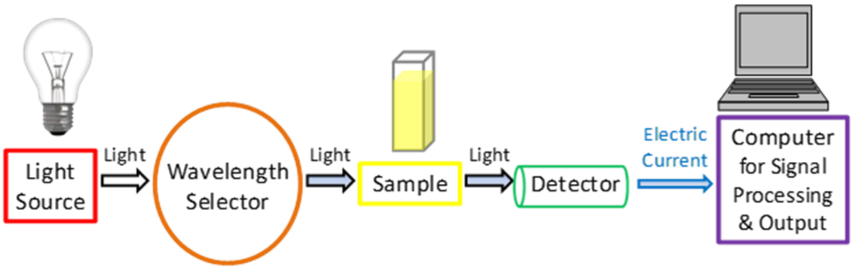

Figure 10: UV-vis system

(1) Light source : A single xenon lamp is commonly used as high intensity source of light for both UV and visible ranges. Xenon lamps have higher costs and are less stable in comparison to tungsten and halogen lamps.For instruments a tungsten or halogen lamp is commonly used for visible light and a deuterium lamp is used as a source of UV light. Different light sources are used to scan both the UV and visible wavelengths and during the measurement the light source will switch to

measure all wavelengths. Practically the switchover will occur during the scan between 300 and 350 nm where the light emission is similar to both light sources and the transition can be made more smoothly.

(2) Wavelength selection :

(a) Monochromators : Monochromator separates light into narrow band of wavelength. It is based on diffraction gratings that can be rotated to choose the incoming and reflected angles to get the desired wavelength of light. The diffraction grating's groove frequency is measured as the number of grooves per mm. Better optical resolution provided by higher groove frequency but a narrower usable wavelength range. Larger usable wavelength range is given by lower groove frequency but a worse optical resolution is obtained. 300 to 2000 grooves per mm are generally used for UV-Vis spectroscopy. The spectroscopic measurements are primarily dependent on physical imperfections in the diffraction grating and in the optical setup. Ruled diffraction gratings have more defects than blazed holographic diffraction gratings. Blazed holographic diffraction gratings provide better quality measurements.

(b) Absorption filters : Absorption filters are generally made of colored glass or plastic designed to absorb particular wavelengths of light.

(c) Interference filters or dichroic filters : Commonly are made of many layers of dielectric material where interference occurs between the thin layers of materials. These filters are used to eliminate undesirable wavelengths by destructive interference and thus acting as a wavelength selector.

(d) Cutoff filters : Cutoff filters allow to pass light either below or above a certain wavelength. These are commonly implemented using interference filters.

(e) Bandpass filters : Bandpass filters allow a wide range of wavelengths to pass through that can be implemented by combining short pass and long pass filters together. Monochromators are generally used for bandpass filters for their versatility and precise measurements and to improve the signal-to-noise ratio.

(3) Sample analysis : First the light will pass through a sample which is known as "blank sample", here the cuvette is filled with a similar solvent which is used to prepare the sample. The reference sample signal is later used by the instrument to obtain the true absorbance values of the analytes.

(4) Detection : Detectors are used to convert the light into an electronic signal which is readable after the light passes through the sample. Detectors have photoelectric coatings or semiconductor material on its surface which ejects negatively charged electrons when exposed to light. These electrons which are ejected produce an electric current proportional to the light intensity is generated. As for semiconductors when exposed to light, an electric current proportional to the light intensity can pass through. These electric current that is generated from the detector which is used generate signal that is used to recognize and helps to get an output on computer screen.

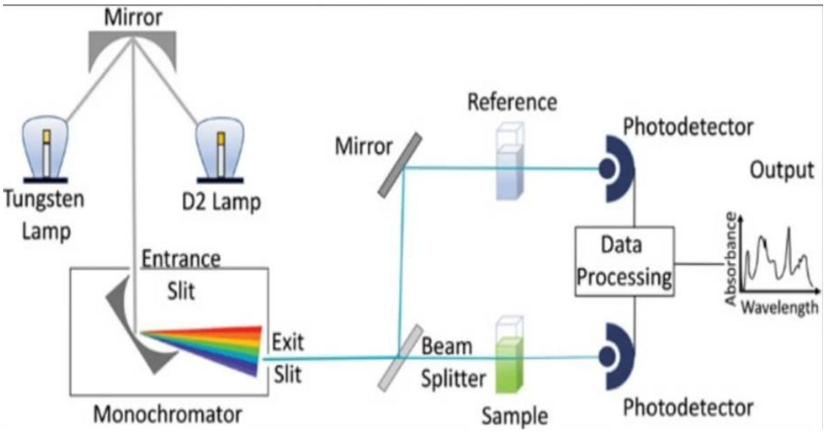

Figure 11: Uv-vis Spectroscopy generation

[5.3.4] Strengths and limitations of uv-vis spectroscopy:

The technique is non-destructive, allowing the sample to be reused or proceed to further processing or analyses :

(1) Measurements can be made quickly, allowing easy integration into experimental protocols.
(2) Instruments are easy to use and requires little training before using the instrument.
(3) Data analysis generally requires minimal processing, again meaning little user training is required.
(4) The instrument is not much expensive as a result it is easy to acquire and operate thus making it accessible for many laboratories.

Although there are many strengths but there are also certain weaknesses :

(1) Stray light : In a real instrument, wavelength selectors are not perfect and a small amount of light from a wide wavelength range may still be transmitted from the light source.

(2) Light scattering : Light scattering is generally caused by suspended solids in liquid samples, which can also cause serious measurement errors. If bubbles are present in the cuvette or by any change sample scatter light, then the results will be irreproducible.

(3) Interference from multiple absorbing species : For a proper quantitative analysis, each chemical species should be separated from the sample and examined individually.

(4) Geometrical considerations : If the instrument components are not properly aligned especially the cuvette which is holding the sample, will give results which are inaccurate and not producible.

Figure 12: UV machine

[5.4] Introduction to photoluminescence spectroscopy:

Photoluminescence(PL) spectroscopy can determine impurity level, fluorescence property , defect detection , surface structure and excited states. PL is performed in a non-contact mode. It is used to understand material electronic structure with light and matter.

[5.4.1] Basic principle:

When light energy strikes a sample the excess energy gets absorbed by the material and the phenomenon is known as photo excitation. One method by which sample dissipates this excess energy is none other than light emission known as luminescence. Luminescence caused by photo excitation is called as photoluminescence. When a material gets excited the electron of the material occupy the excited states. To come back to their stable or ground state this excited electrons dissipate the excess energy in form of light. The difference in energy between the electronic states that is between excited and equilibrium states is proportional to the emitted energy. The proportion of radiative process determines the amount of light emitted.

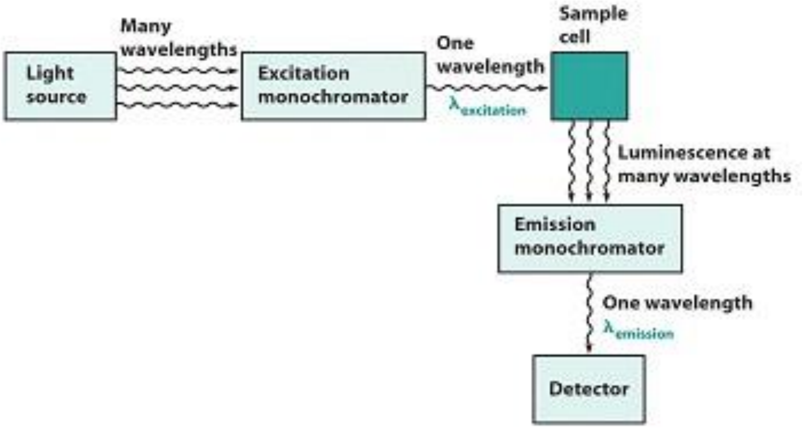

Figure 13: Photoluminescence

[5.4.2] Different modes of photoluminescence:

(1) Fluorescence : When the internal energy transition is initiated by emitting photons, before getting restored to the ground state, a certain joule of this absorbed energy is liberated resulted in the emitted light which have less energy than that was absorbed. The lifetime of 10^{-8} to 10^{-4} s is fluorescence.

(2) Resonant radiation : Photon of specific wavelength is absorbed accompanied by instantaneous emission of an equivalent photon. In this process there is no energy

transition between absorption and emission and the time scale is of the order of 10 nanoseconds.

(3) Phosphorescence : Here transition is radiation based in which the absorbed energy has to undergo electronic transitions with multiple spin states. The life span is 10^{-4} to 10^{-2} s and thus longer life span than Fluorescence. Thus, phosphorescence occurs less frequently than fluorescence because at this state inter system crossing to lower energy state occurs more prior the occurrence of phosphorescence.

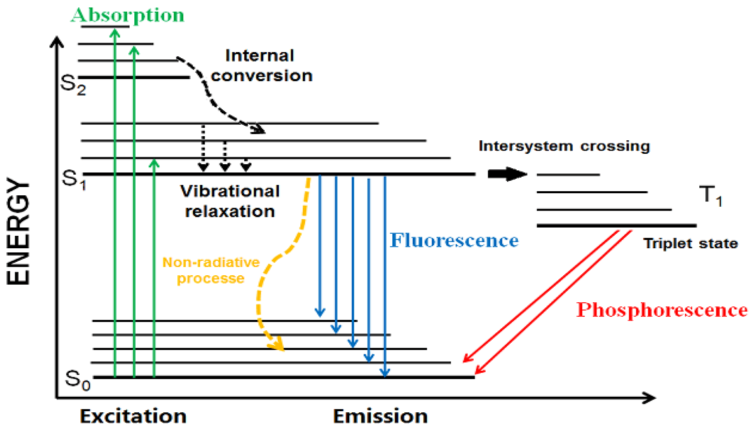

Figure 14: Different modes of photoluminescence

[5.4.3] Spectroscopy:

Light when focused on the material electrons can migrate into excited states. On return to their equilibrium state the electrons release excess energy which may or may not involve emission of light. The energy of the light produced is determined by the difference in energy levels between electron states which involved the transition between the excited state and equilibrium state. The amount of light emitted is proportional to contribution of radiative process. For most cases the released light has longer wavelength than the absorbed radiation and contains less energy.

In strong absorbed electromagnetic radiation , two photons can be absorbed by one electron which results in emission of light of shorter wavelength than absorbed energy. If the wavelength is same for released radiation and absorbed light then fluorescence occurs. Photoluminescence happens when radiation is absorbed in ultraviolet region and when released it is in the visible range.

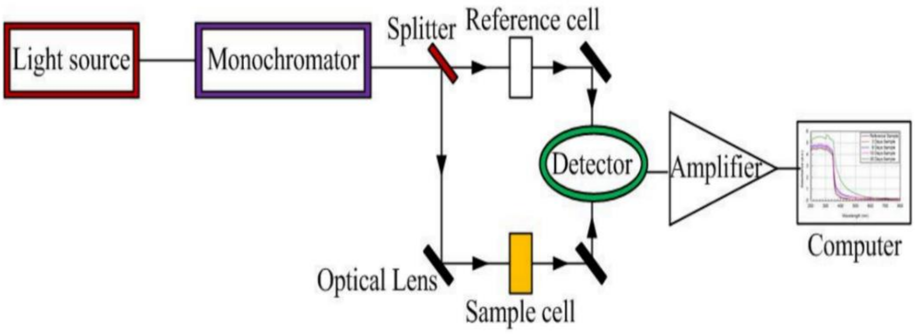

Figure 15: Spectroscopy

[5.4.4] Relation between absorption and emission spectrum:

In the given diagram S_o is the ground state and S_1 is the excited state. At lower energies than absorption Fluorescence and Phosphorescence occur. The wavelength λ_o is denoted by the transition from S_o to S_1 when molecules are excited at S_1 vibrationally they will move to lower energy before radiation. For both emission and absorption spectra if spacing of vibrational levels are nor or less equivalent the probability of transition will be similar.

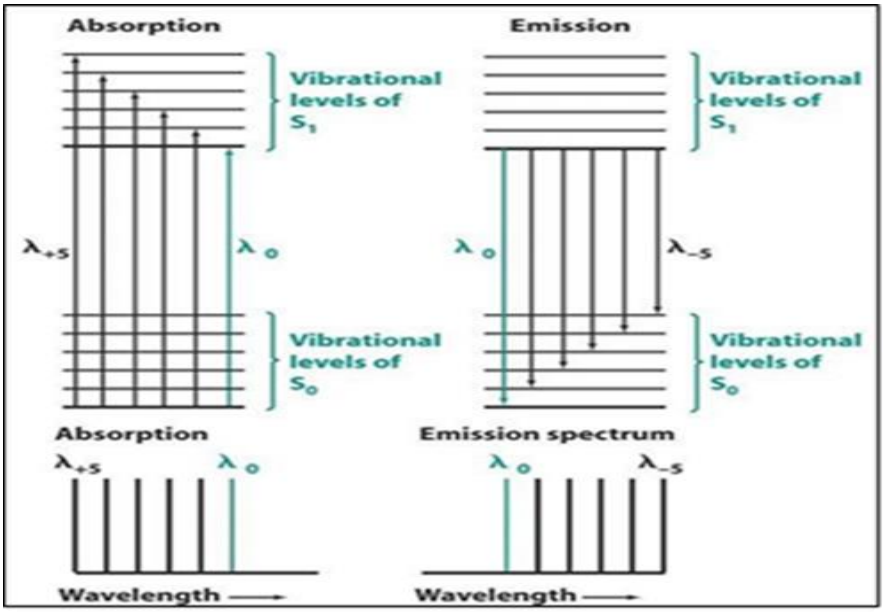

Figure 16: Absorption and emission

[5.4.5] Instrument of photoluminescence:

The fluorescence of the given sample is measured by analytical equipment. Both wavelengths are scanned to record all the phenomena's like emission, excitation, fluorescence and also time, temperature, concentration can be measured. Spectrometer use laser source, monochromators, detectors and spectrums.

(1) Source of Illumination: 150W ozone -free xenon arc lamp, a continuous type is used as light source. The lamp light is collected by a diamond which is turned into elliptical shaped mirror and then directed to the entry slit of the excitation monochromator from the lamps housing which helps to vent out heat of the device and protects against lamps failure. The ability to resolve the entire spectrum stretches and decreases aberrations and re- diffraction.

(1) Monochromators : There are two types of monochromators are excitation and another emitter. To maintain high resolution across the spectrum it employs whole reflective optics while also reducing aberrations(spherical) and re- diffraction.

(2) Gratings : Grating an important component of monochromator, and the aim is to scatter striking light through the grooves which are vertically positioned. Spectra is obtained by rotating gratings with 1200 grooves per mm and blazed at 330 nm(excitation) and 500 nm (emission). The grating has a coating of MgF_2 for oxidation prevention.

(3) Slits : They exists at entrance and exit sites and are very flexible. The width of the excitation monochromator slit defines the incident lights bandpass and the emission monochromator controls the fluorescence intensity signal. The slit width is determined by the signal strength and spectral resolution. Greater slit width results in decrease of resolution as more light falls on the sample and detector and in case of narrower slits there is increase in resolution but at the expense of signal.

(4) Shutter : Excitation shutter is installed under exit slit in excitation monochromator to protect the sample from photobleaching or photodegradation caused by prolonged exposure to light. The detector is shield by emission shutter which is located before the entry of emission monochromator.

(5) Sample compartment : Fiber optic bundles and different attachments are present in sample compartment for the transportation of excitation beam to the remote sample and return the emission beam to the emission monochromator.

(6) Detectors : Two type of detectors are present signal and reference detectors. The signal detector directs the signal to a photon counting module. The reference detector is used to monitor the xenon lamp for wavelength and time-dependent output adjustment. The detector is UV based and increases with the silicon photodiode, situated before the compartment.

[5.4.6] Applications:

(1) Identification of level of impurity as well as defect- In case of radiative transition localized defect levels are induced. PL energy can identify specific flaws where PL quantity can determine their concentration.PL spectra of the sample at low temperature display spectrum peaks which are associated with impurities existing inside the host material. Highly sensitive Fourier transform has the potential to detect very minute amount of planned and unexpected impurities and which can have a significant impact on material quality and device.

(2) Recombination phenomenon- Both radiation and non-radiation processes involve recombination. The amount of PL material emitted is directly related to recombination mechanism. So PL analysis includes tracking changes in quality of material as a function of variables such as growth and processing which helps in understanding the fundamental physics of recombination.

(3) Surface structure and excited states- Some most utilized conventional methods such as XRD, IR, and Raman spectroscopy are frequently insensitive to oxide – supported catalysts with low metal oxide concentrations. PL is largely sensitive to surface effects or semiconductor – based particle absorbed species it can be used as a probe of electron- hole surface processes.

[5.4.7] PL spectroscopy limitations:

It can be used to find of concentrations optical centers and at some centers large number of excited states that are not occupied at low temperature are present. PL have disappearance of luminous signal.

Figure 17: PL Machine

Experiment-6

RESULTS & DISCUSSIONS

[6.1] Xrd:

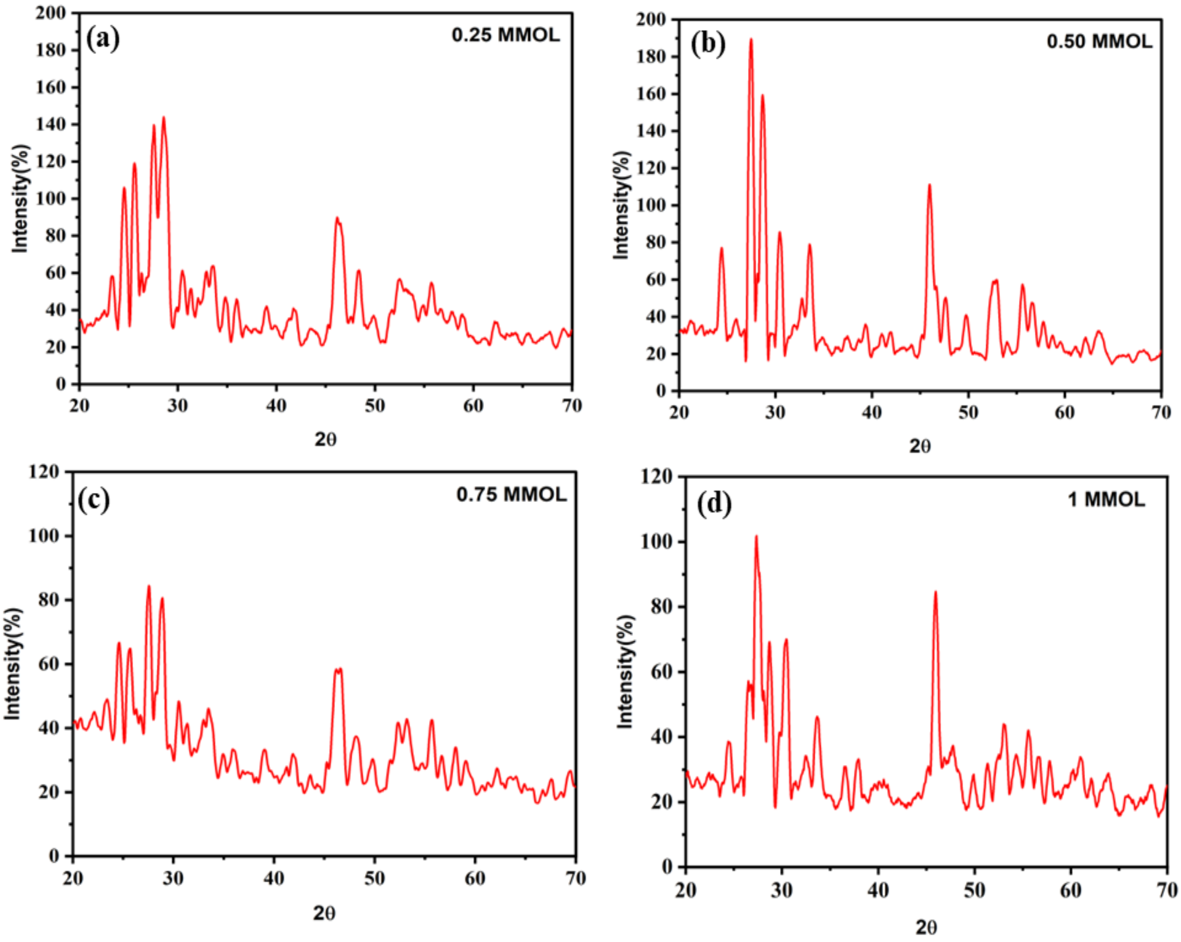

Figure 18 : XRD pattern of (a)NCWO$_{0.25}$, (b)NCWO$_{0.50}$, (c)NCWO$_{0.75}$ and (d)NCWO$_{1.00}$.

In the following table the hkl co-ordinates of the xrd peaks are given-

(a)NCWO$_{0.25}$

2θ	**JCPDS**	**h**	**k**	**l**
23.27	23.12	1	0	1
24.60	24.441	-1	1	0
25.60	25.138	-1	-1	2
27.59	27.467	0	2	0
28.54	28.64	0	0	2
30.47	29.925	-2	-2	2
33.56	33.324	1	2	1

34.86	34.72	0	1	2
38.98	38.89	1	-2	1
41.79	41.72	0	3	0
46.18	46.18	-2	0	3
48.37	48.38	3	1	1
52.48	52.68	2	-2	1
55.71	55.90	-4	-4	1
62.23	62.105	-5	-3	2

(b) NCWO$_{0.50}$

2 θ	JCPDS	h	k	l
24.36	24.441	-1	1	0
25.88	26.152	-2	-2	1
27.45	27.46	0	2	0
28.68	28.64	0	0	2
30.40	29.925	-2	-2	1
33.55	33.324	1	2	1
39.322	39.11	2	2	1
40.90	40.794	0	-3	1
45.98	45.891	-1	-3	3
47.62	47.588	0	3	1
49.75	49.72	-4	-2	1
52.76	52.77	-4	-1	1
55.579	55.484	-2	1	3
56.60	56.278	1	-2	3
57.76	57.6923	-3	-5	2
58.73	58.72	-3	-4	4
63.46	63.309	2	-1	3

(c) $NCWO_{0.75}$

2 θ	**JCPDS**	**h**	**k**	**l**
22.10	22.48	-1	-2	1
23.34	23.12	1	0	1
24.57	24.44	-1	1	0
25.677	25.138	-1	-1	2
27.52	27.467	0	2	0
28.89	28.72	0	-1	2
30.54	29.925	-2	-2	2
33.49	33.324	1	2	1
34.93	34.923	0	-2	2
36.02	36.378	-3	-2	1
38.98	38.89	1	-2	1
41.86	41.72	0	3	0
43.64	43.80	-3	0	1
46.47	46.17	-2	0	3
48.16	48.38	3	1	1
49.822	49.723	-4	-2	1
52.28	52.68	2	-2	1
53.173	53.125	1	1	3
55.71	55.99	-4	-4	3
69.43	69.983	2	4	2

(d) $NCWO_{1.00}$

2 θ	**JCPDS**	**h**	**k**	**l**
24.43	24.44	-1	1	0
26.70	26.399	2	1	0
27.38	27.46	0	2	0
28.68	28.64	0	0	2
30.47	29.925	-2	-2	2
33.63	33.99	0	2	1

36.5	36.5	2	0	1
37.87	37.73	-1	-3	2
45.91	45.89	-1	-3	3
47.75	47.97	-1	-4	1
49.89	49.72	-4	-2	1
51.39	51.59	3	0	1
53.10	53.12	1	1	3
55.49	55.48	-2	1	3
63.49	63.96	0	-4	3

From XRD analysis it can be found that all the four samples are anorthic in nature.

[6.2] Ftir:

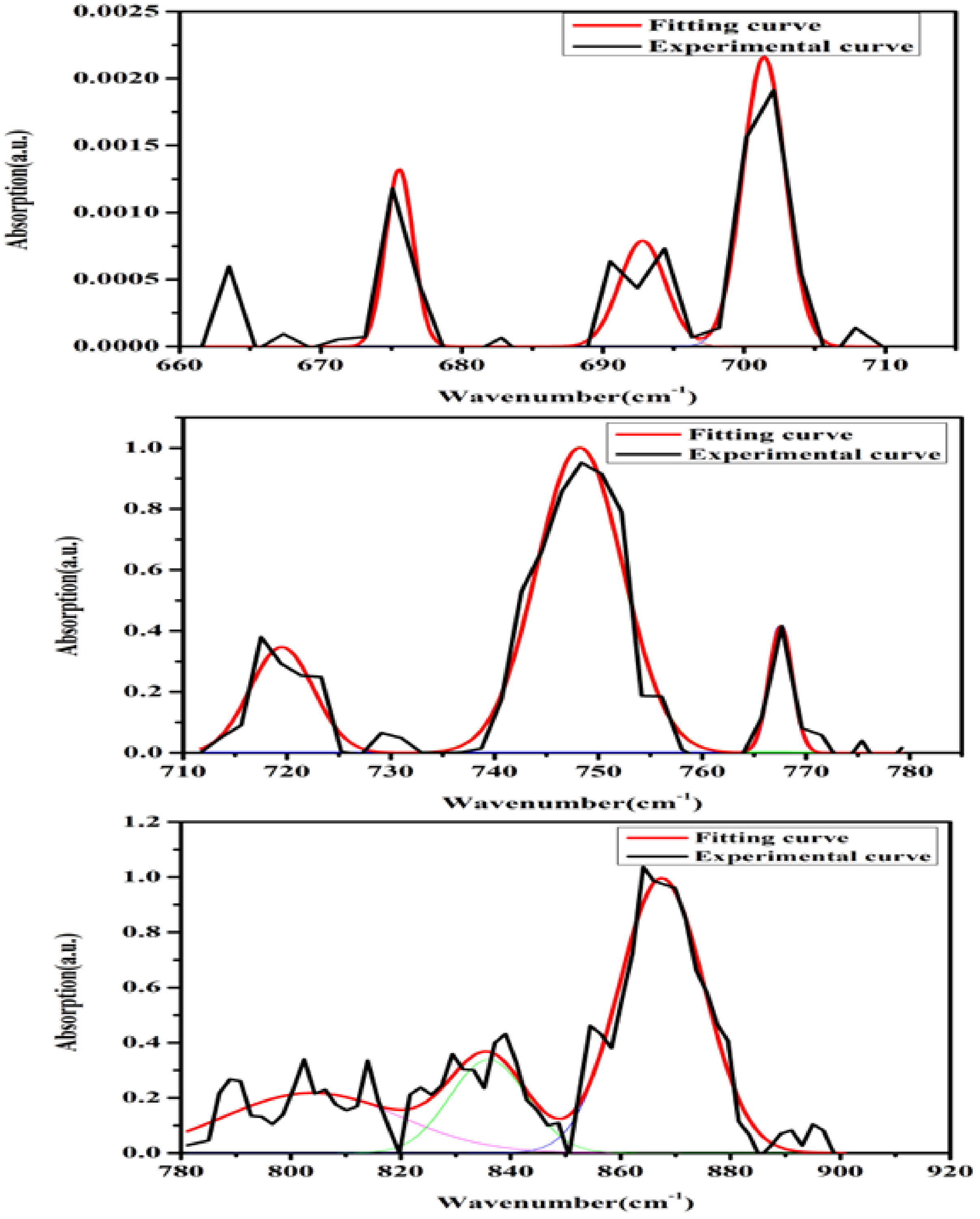

Figure 19(a): FTIR Graph of $NCWO_{0.25}$

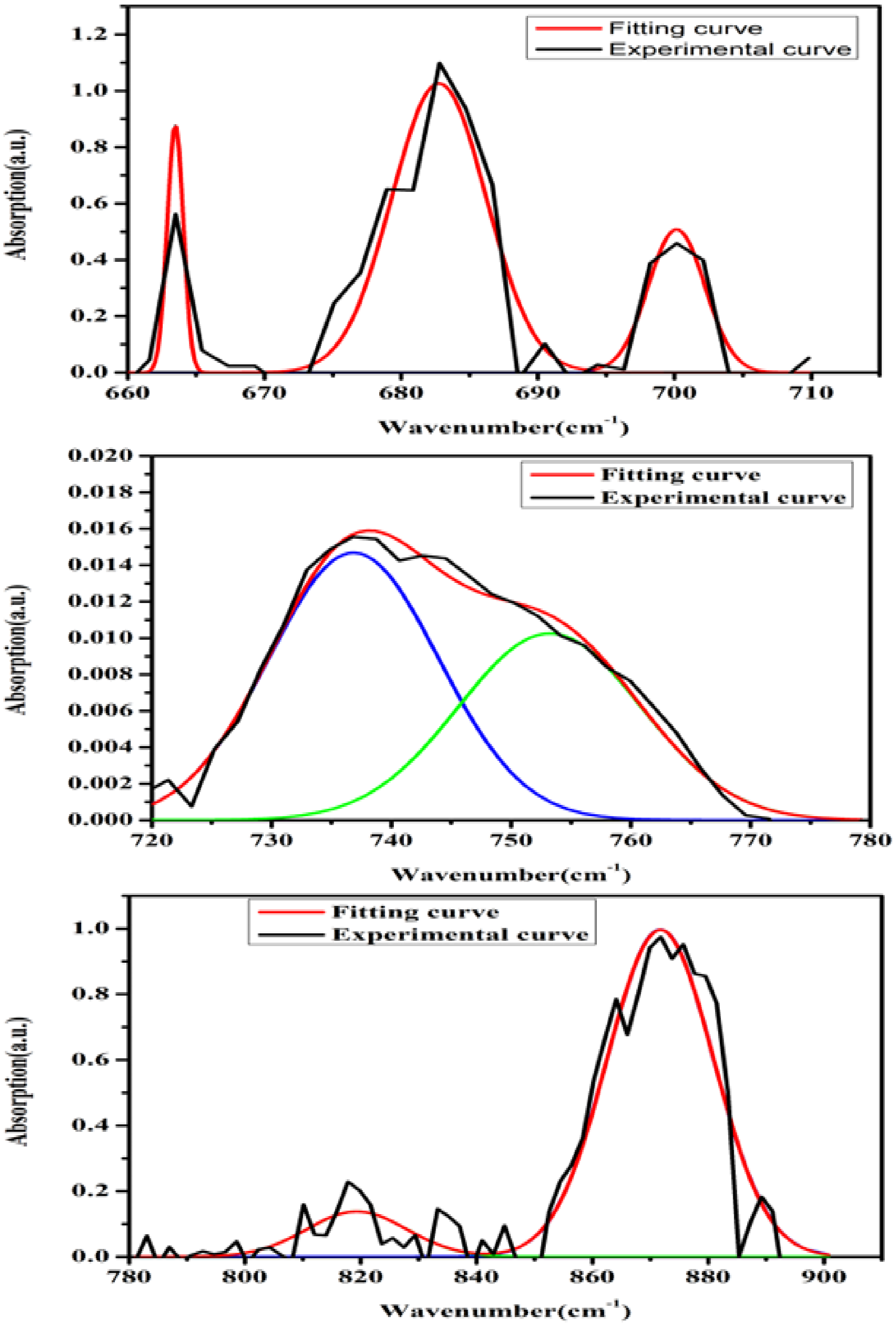

Figure 19(b): FTIR Graph of $NCWO_{0.5}$

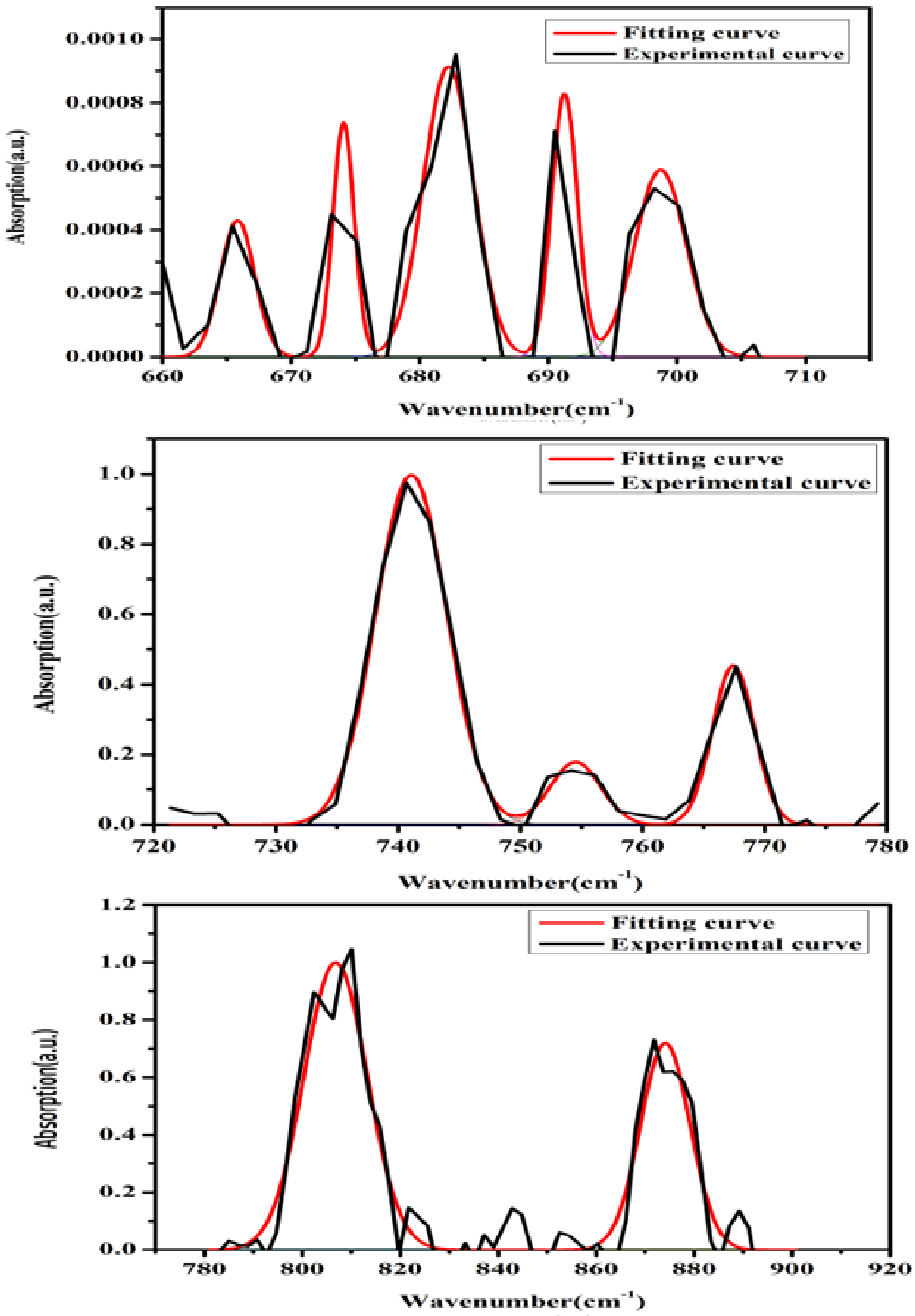

Figure 19(c): FTIR Graph of $NCWO_{0.75}$

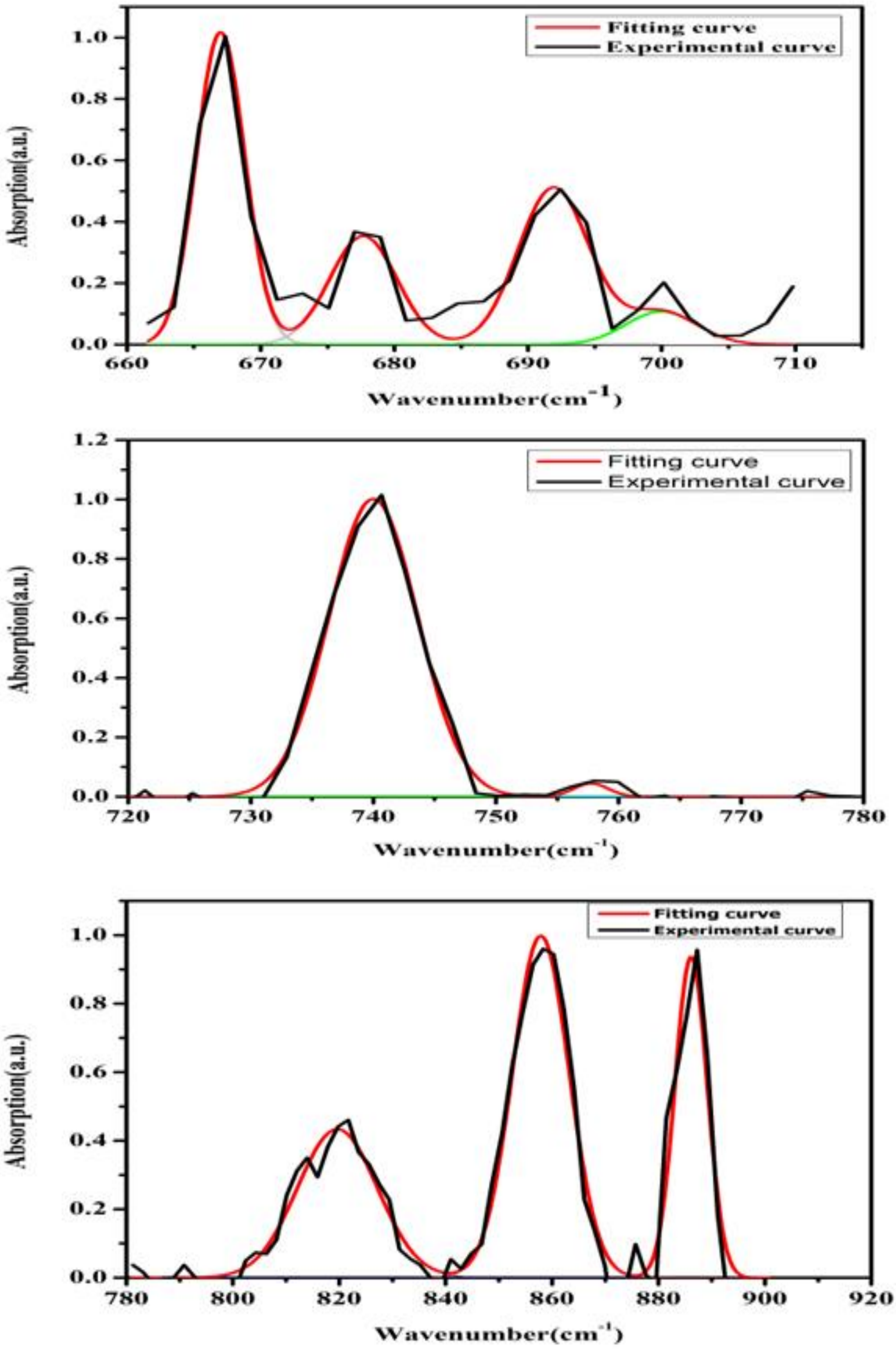

Figure 19(d): FTIR Graph of $NCWO_{1.00}$

(1) In FTIR 0.25 mmol 675,691,766 for (W-O) bond[63- 65] and 718,801,832,864 for (O-W-O) bond [66-69]and 746 for (W-O-W) bond [70] and 766 for (W-O) bond and stretching vibration (O-W-O) [71].

(2) In FTIR 0.50 mmol 663 for (O-W-O) group [72],681 for (W-O) bond [73], 699 and 734 for (W-O) group[74-75],750 for (WO_6) formation[76], 820 for (W_2O_8) formation[77] and 868 is due to the stretching modes of (W–O) bonds and (WO_6) octahedra forming the structure elements[78].

(3) In FTIR 0.75 mmol 665 for (O-W-O) group[79], 674 for broad (W-O-W)band [80],681 for (W-O) bond[71],690 for (W-O) bond [81],697 and 739 for formation of (WO_3) group[82-83]. The peaks 752 for (W-O-W) band [67],766 for (W-O) band [65]. Peak 803 is for (W-O) band [84] and peak 871 for antisymmetric stretching[85].

(4) In FTIR 1.00 mmol peaks 666[86],738[71],855[91] and 883[65] is responsible for (W-O) bond formation and peak at 676 for stretching of (W-O) band [87]. For peak 690 for (W-O) bond [88]and peak 755 for (WO_3) group[89].Peak 814 for (W-O-W) band formation[90].

[6.3] Uv Spectroscopy:

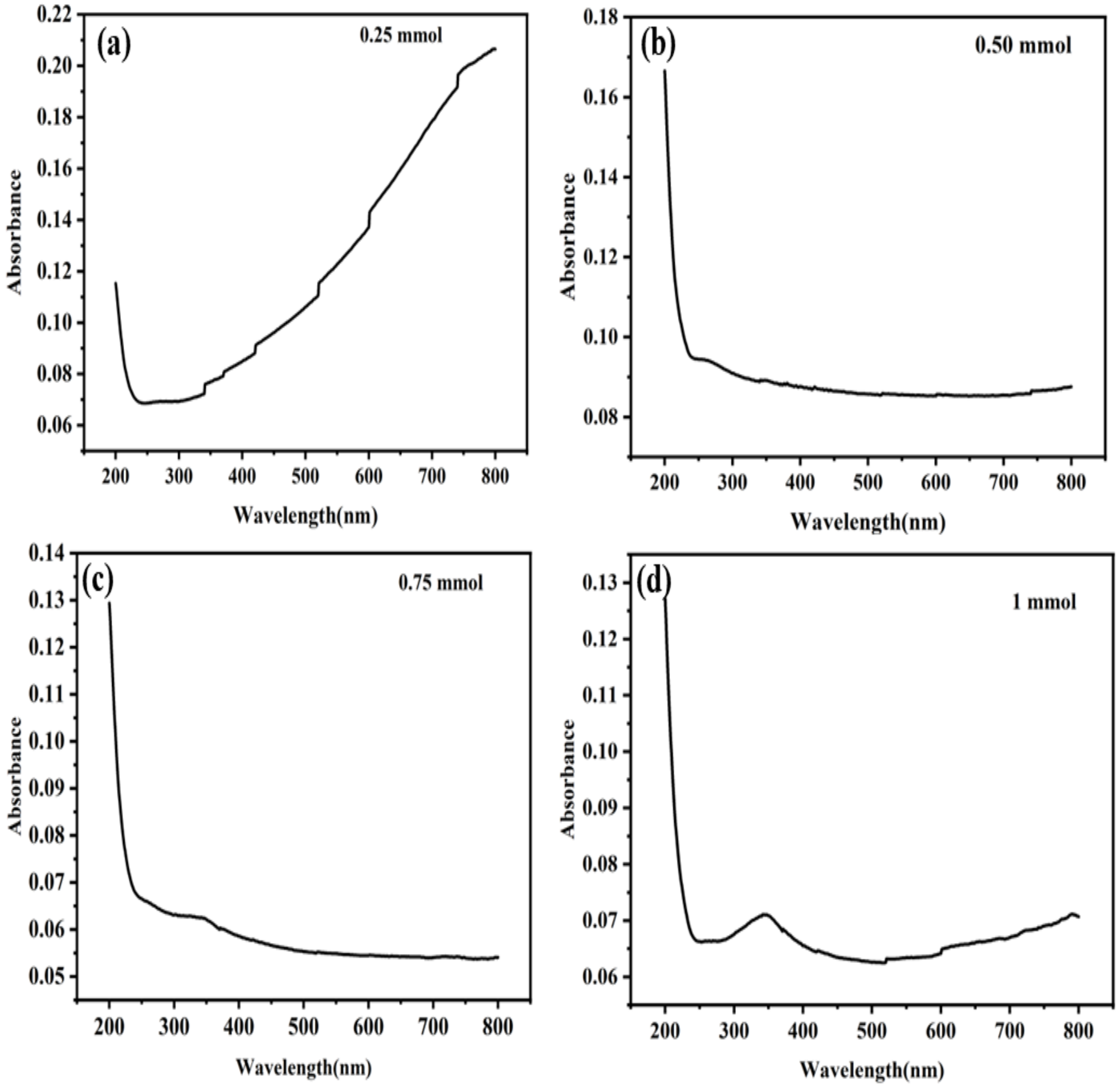

Figure 20 : UV-vis graph of (a)$NCWO_{0.25}$, (b)$NCWO_{0.50}$, (c)$NCWO_{0.75}$ and (d)$NCWO_{1.00}$.

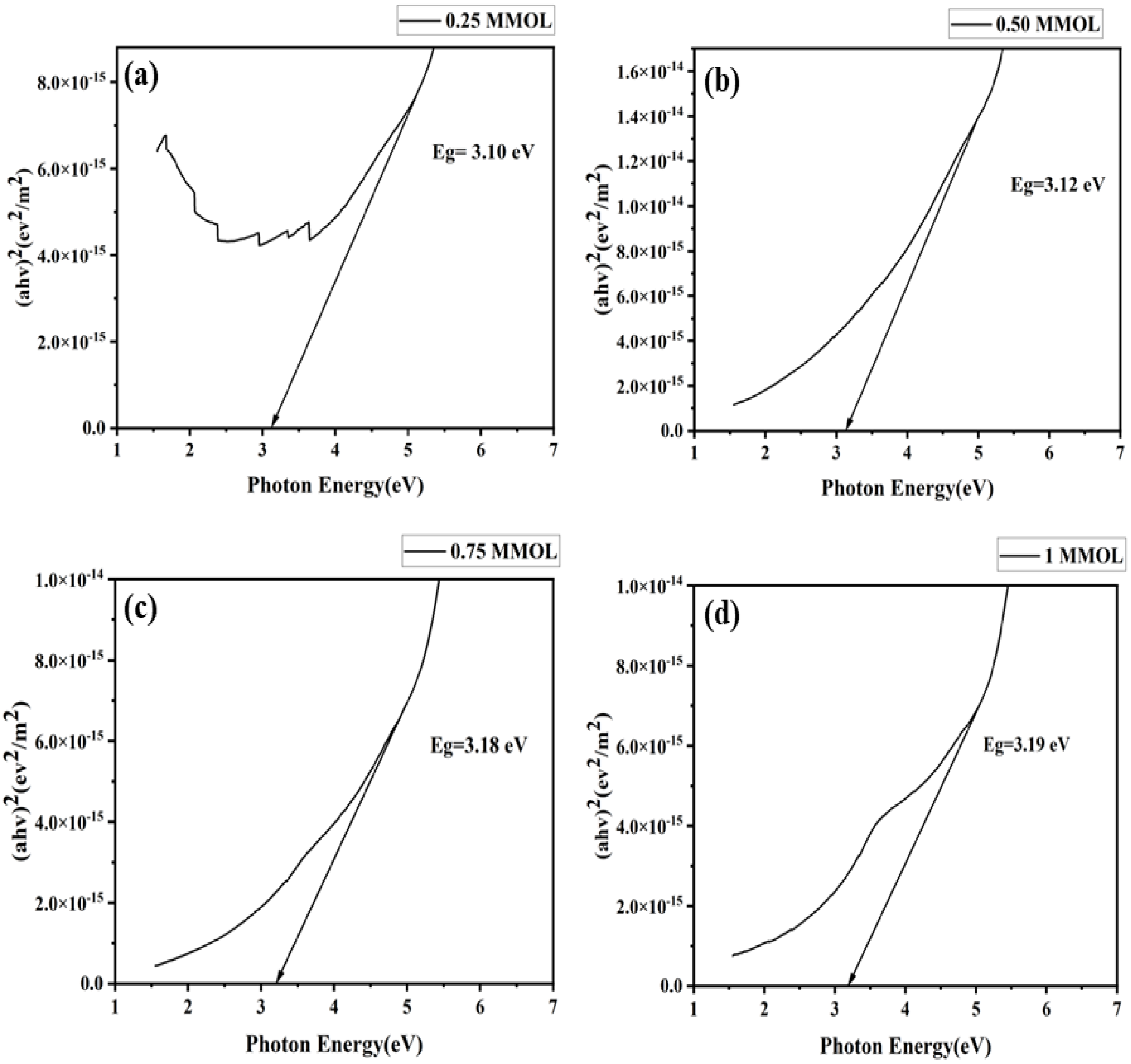

Figure 21: The band gap from UV-Vis bandgap graph of (a)$NCWO_{0.25}$ is 3.10 eV, (b)$NCWO_{0.50}$ is 3.12 eV , (c)$NCWO_{0.75}$ is 3.18eV and (d)$NCWO_{1.00}$ is 3.19 eV.

From the above graph it can be found out that the band gap decreases with decrease in molar concentration of trisodium citrate.

[6.4] Photoluminesce spectroscopy:

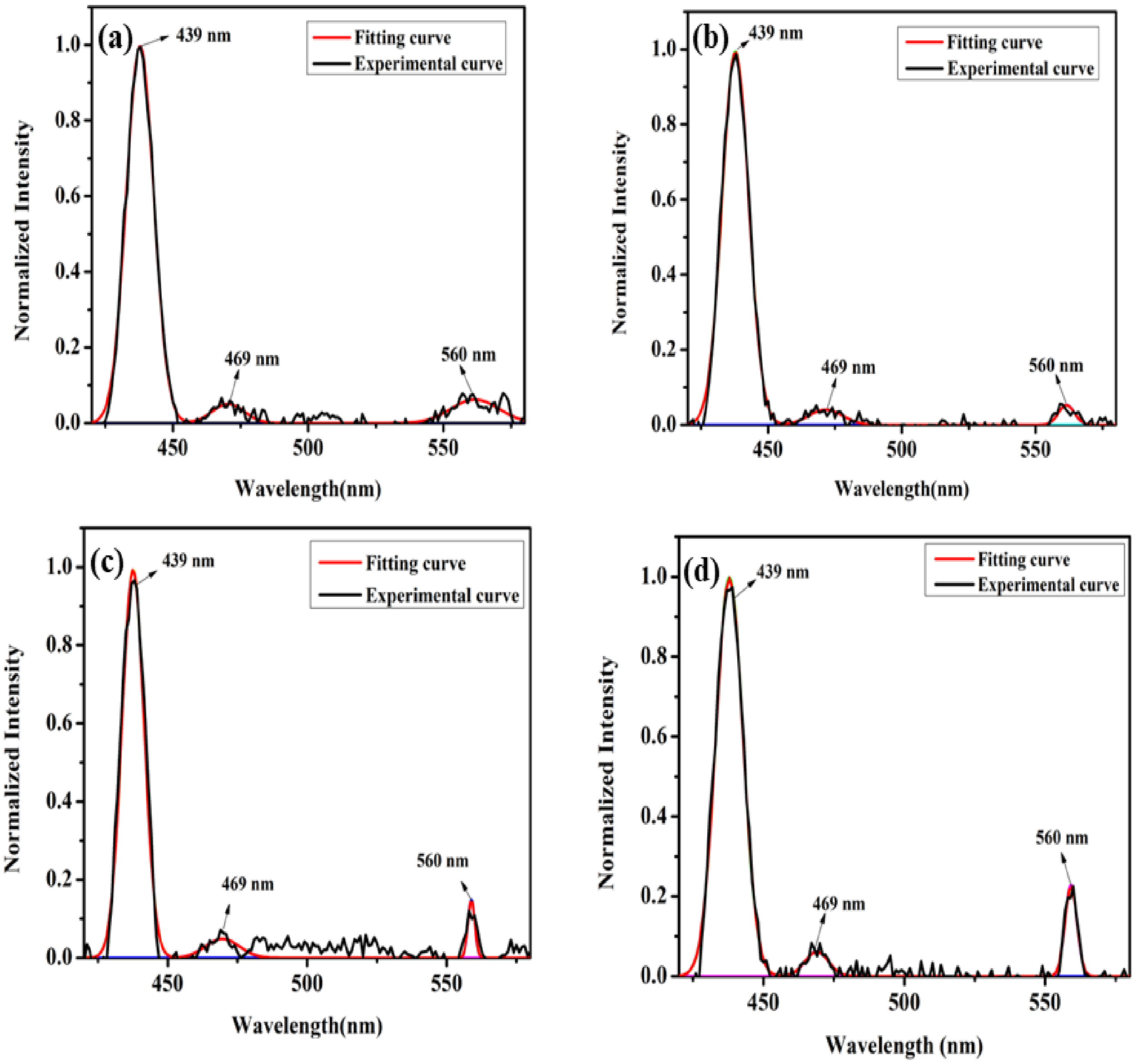

Figure 22: Photoluminescence Graph (a)NCWO$_{0.25}$, (b)NCWO$_{0.50}$, (c)NCWO$_{0.75}$ and (d)NCWO$_{1.00}$.

A strong peak at 439 nm (blue I) and a blue peak at 469 (blue II) and green emission occurred at 560 nm have been noticed in the visible region. From earlier studies it is found that emissions from scheelite materials are mostly from 5d to 4f transitions within lanthanides, although proper understanding is still under debate.

Previously it was found that LiCe(WO$_4$)$_2$, have two emission peaks at 390 and 412 nm, were ascribed to $^5D_0$ - $^2F_{5/2}$ and $^5D_0$ - $^2F_{7/2}$ transitions within Ce^{3+}, while Dorenbos et al. had calculated them at 451 and 485 nm. The equation which is provided by van Uitert et al.

$$\frac{1}{\lambda} = \frac{Q}{hc}[1 - \left(\frac{V}{4}\right)^{\frac{1}{v}} 10^{-\frac{nrEa}{80}}]$$

helps to understand the emission wavelength (λ) from NCWO, where 5d – 4f transition occurs within Ce^{3+} within the regular CeO_8 dodecahedron.

Here Q = the energy of 5d band edge of free Ce^{3+} ion(= 200 nm) , V= valance of the Ce^{3+}, 'n'= number of anions in the immediate shell around Ce^{3+}, and E_a= electron affinity of the atoms forming anions, and 'r'= is the radius of the host cation replaced by the Ce^{3+} ion. From the equation we have calculated λ = 435 nm is well correlated with 439 nm experimental blue I emission.

[6.5] Cie plot:

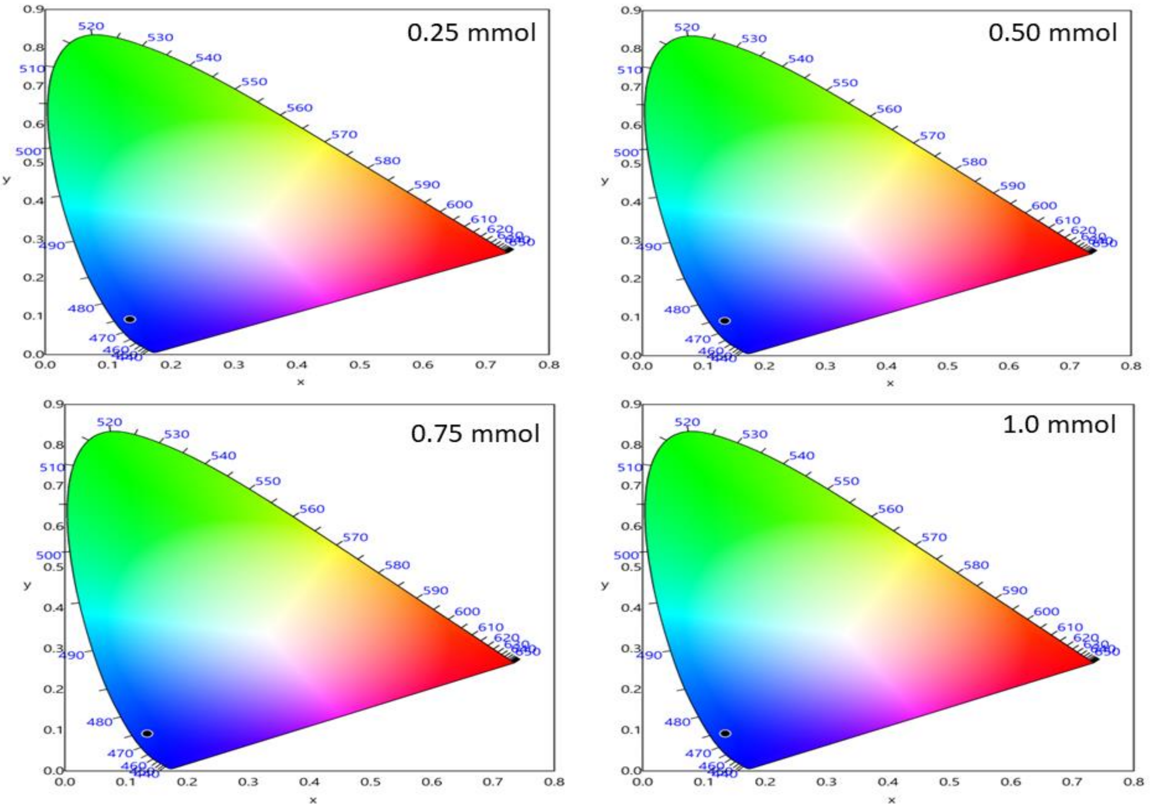

Figure 23: CIE Graph of (a)$NCWO_{0.25}$, (b)$NCWO_{0.50}$, (c)$NCWO_{0.75}$ and (d)$NCWO_{1.00}$.

Commission International De I'Eclairage (CIE) coordinates (shown in Figure 26) are calculated to be (0.1425, 0.0925),(0.1405, 0.0925),(0.1392,0.0925) and (0.1390,0.0925) . The $NCWO_{0.25}$, $NCWO_{0.50}$,$NCWO_{0.75}$,$NCWO_{1.0}$ coordinates gives blue emission from synthesized samples, while variation in the coordinates are ascribed to different contribution from blue II and III. Color purity ~ 80% has been estimated for both samples from equation.

Color purity = $\frac{\sqrt{(x-x_i)^2+(y-y_i)^2}}{\sqrt{(x_d-x_i)^2+(y_d-y_i)^2}} \times 100\%$

where (x, y) represents the color coordinates of the phosphor; (xi, yi) is the illuminant point of the 1931 CIE Standard Source with the color coordinates of (0.3101, 0.3162); (xd, yd) refers to color coordinates of the dominant wavelength and the correlated color temperatures (CCTs) ~ 7340 and 7715 K for and have been calculated from McCamy’s relation as given where n = $\frac{(x-0.3320)}{(0.1858-y)}$ and (x, y) represents the chromaticity co-ordinates stated NCWO can be a potential material for cold blue lighting applications.

CHAPTER-7

CONCLUSION

[7.1] Conclusion:

In this work hydrothermal method have been used by which four different type of sample have been prepared based on the concentration variation of one of the key materials. Through the different types of characterization methods namely XRD,FTIR,UV-vis and PL spectroscopy the type of crystal structure, formation of different groups, the variation in band gap and optical properties are discovered. The PL spectra gives broad blue emission due to the effect of both Ce^{3+} and WO_4^{2-}.Through the CIE diagram the color purity is obtained also confirm blue emission.

[7.2] Future scope:

Some of the possible applications are mentioned below-

(1)The nanoparticles can be used for solid state lightning like blue light emitting diodes.

(2) It can be used in other optoelectronic devices.

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