

**Synthesis and characterization of  $\text{MB}_x\text{O}_y\text{:Eu}$  ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ )  
phosphors and  $\text{TiO}_2$  semiconductor for application in  
luminescence and energy materials**

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**(B.Sc Hons)**

*A dissertation presented in fulfilment of the requirements for the  
degree*

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## **Dedication**

*This Thesis is dedicated to the memory of my late Mother*

***MAJAPI***

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## Abstract

MBxOy:Eu (M = Ca, Sr, Ba) phosphors with different Ca:B /Sr:B /Ba:B molar ratio and with constant Eu concentration have been synthesized by a solution combustion method at initial reaction temperature of 500<sup>0</sup>C for 15 minutes. The morphology, structure and luminescence properties of the synthesized nanostructures were investigated using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Photoluminescence (PL) spectroscopy. The XRD spectra of all the as prepared samples show monoclinic phase for Ca:B. The XRD spectra of variation of Strontium nitrate and europium nitrate shows no effect on the structure of the sample. The estimated average grain sizes calculated using the XRD spectra were found to be between 16 - 20 nm. The grain size was found to be significantly dependent on Sr: B mole ratios and concentration of Eu. XRD patterns analysis of samples with different Ba:B mole ratio when annealed at temperature above (700<sup>0</sup>C) confirms the existence of pure BaB8O13 phase (JCPDS: 74-0674). The variation of Eu concentrations content was found to have no effects on the crystal structure.

SEM micrograph show that the surface aspects are nanorod like for low Ca:B mole ratios but the grains become flake-like as the Ca:B molar ratio increased, giving rise to the increase in particle size resulting from agglomeration. SEM micrograph showed the presence of well-packed and randomly oriented platelet-like grains and the variation of Sr: B and Eu ion did not influence the surface aspect. SEM micrographs of the Ba:B phosphors at low magnification show agglomerates and high magnification depicts that particle with sizes in nano ranges are the primary sources of agglomerates.

The PL result also shows that the luminescence intensity of these emission spectra increased with increase in Ca: B molar ratios. The narrow emission lines between 590-688 nm are due to transitions Eu<sup>3+</sup>. The PL emission results showed that luminescence intensity was found to increase in both Sr: B and Eu ions with no effect on the luminescence band position. The excitation spectrum showed two broad bands in the range of 200–400 nm: one was the host lattice absorption with the maxima at 320 nm and the other was Ba-O absorption overlapped with the CT band of Eu<sup>3+</sup>, which indicated that the energy of the host lattice absorption could be efficiently transferred to the Eu<sup>2+</sup>.

Titanium dioxide (TiO<sub>2</sub>) powder was prepared by a sol-gel method. X-ray diffraction and Fourier transform infrared spectroscopy were used to determine film behaviour. The super-hydrophilicity was assessed by contact angle measurement. Photocatalytic properties of these

films were evaluated under UV irradiation. The XRD pattern of  $\text{TiO}_2$  powder samples confirmed the presence of polycrystalline anatase phase with a crystal size of 17 nm. The results indicated that UV light irradiation had significant effect band energy and photocatalytic properties of  $\text{TiO}_2$  nanopowders.

**Key words:** rare earths, solution combustion process, sol-gel, luminescence

## Declaration

I (Sithole Thokozane Moses) declare that the thesis hereby submitted by me for the Master's degree at the University of the Free State is my own independent work and has not previously been submitted by me at another university/faculty. I furthermore, cede copyright of the thesis in favour of the University of the Free State.

Signature:..... Date:.....

# Acronyms

**XRD—X-ray Diffraction**

**PL—Photoluminescence**

**SEM—Scanning Electron Microscopy**

**EDS—Energy Dispersive X-ray Spectroscopy**

**TiO<sub>2</sub>—Titanium Dioxide**

**FTIR— Fourier Transform-Infrared**

**TGA—Thermogravimetry Analysis**

**DSC—Differential Scanning Calorimetric**

**eV— Electron Volts**

**UV—Ultra Visible**

**JCPDS—Joint Committee on Powder Standards**

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# Chapter1

## Introduction

In recent days nanotechnology has induced great scientific advancement in the field of research and technology. Nanotechnology is the study and application of small object which can be used across all fields such as chemistry, biology, physics, material science and engineering.

### 1.1 Borates phosphor

Borate compounds are very good hosts for the development of luminescent materials [1]. A variety of borate host materials doped with rare earth and other ions have been reported as phosphor materials for a variety of applications [2–6]. In this connection, nanostructured materials show unique features that cannot be obtained from conventional macroscopic materials [7]. The specific properties of nanomaterials are arising from their increased surface to volume ratio and changed the electronic structure due to quantum confinement effect. The surface states can play a very important role on physical properties, especially the optical properties of the nanoparticles [8]. As the particles become smaller, the surface to volume ratio and the surface states increase and reduce the excited emissions via non-radiative surface recombination [9]. Current studies on various luminescent nanomaterials have revealed that they have potential applications in estimation of high doses of high energy ionizing radiations where the conventional microcrystalline phosphors have a limitation [10].

### 1.2 Europium

Europium is a ductile metal with hardness similar to that of lead. It crystallizes in a body-centered cubic lattice. Some properties of europium are strongly influenced by its half-filled electron shell. Europium has the second lowest melting point and the lowest density of all lanthanides [11]. Its chemical property is that europium is the most reactive rare earth element. It rapidly oxidizes in air, so that bulk oxidation of a centimeter-sized sample occurs within several days [12]. To obtain phosphors activated by  $\text{Eu}^{2+}$  ions, the reduction of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  must be realized since the raw material of the europium source is usually  $\text{Eu}_2\text{O}_3$ .

### 1.3 TiO<sub>2</sub> background

The quality of human life, economic prosperity, and global stability largely depends on a ready and reliable supply of energy. The global current rate of energy consumption is approximately  $4.1 \times 10^{20}$  J/yr, which is equivalent to 13 trillion watts. The World Bank predicts that the demand for energy will double (to 30 trillion watts) by 2050 with an increase of the world's population to 9 billion people accompanied by a rapid technological development and economic growth [13]. Provision of sustainable energy is essential for the global economic development and human well-being. More than 80% of our current energy production comes from carbon based fossil fuels such as coal, oil, and natural gas [14]. We utilize energy mainly in the form of electricity and liquid fuels, which are used for domestic, commercial, industrial, and transportation sectors. Although these carbon-based fuels can supply energy for another century or may be several hundred years [15], continuous reliance on them will cause severe problems to our economy and environment. Economic problems are predicted to arise from a steady increase of oil prices because of continuous demand but restricted supply. Environmental problems, such as global warming, are mainly caused by increase in man-made (anthropogenic) carbon dioxide in the atmosphere originating from burning of fossil fuels. The utilization of the green energy and hence solar energy has become the on-going topics and solution for both governments and scientific communities. The most cost-effective and the improvement of both power conversion efficiency and stability of fabricating solar cells is the solution to this current energy crisis predicament. The substantial investments from both the scientific community and human race to this research field will certainly boost the usage, purchasing and manufacturing of energy materials as an alternative form of renewable energy [9].

### 1.4 Statement of the problem

The entire world is seriously experiencing the energy crisis and the somewhat incompetence of the current energy production methods which are not meeting the energy demands of our current lifestyles. Among the forms of green energies (e.g. hydropower, wind power, geothermal power and biomass) solar power is one of the most sustainable energy due to its abundance and renewability. Using the photovoltaic (PV) effect, sunlight can be converted directly into electricity [9]. However, the classical efficiency limit of silicon-based solar cells

is currently estimated to be 29%, and detailed-balance calculations show that this number could be improved up to approximately 37% using spectral modification [9]. There are three spectral modification methods in place to be used namely downconversion (DC), photoluminescence (PL) and upconversion (UC). It is known that light with energy lower than the threshold of  $\sim 1.25$  eV would be suited for upconversion (UC), whereas light with energy higher than the threshold of  $\sim 1.25$  eV would be better suited for downconversion (DC) applications for an ideal semiconductor with a threshold of  $\sim 1.35$  eV. South Africa is known as a key international source and producer in the consumer and industry arenas of metals, alloys, and semiconductor products and a leading country in nanotechnology [9].

## 1.5 Research objectives

To investigate:

- The effect of different rare earth ions concentration and Ca/B on the structural and luminescent properties of  $\text{CaB}_4\text{O}_7:\text{Eu}^{3+}$  nano-phosphors prepared using solution - combustion method.
- The effect of different rare earth ions concentration and Sr/B on the structural and luminescent properties of  $\text{SrB}_6\text{O}_{10}:\text{Eu}^{2+}$  nano-phosphors prepared using solution - combustion method.
- The effect of different rare earth ions concentration and Ba/B on the structural and luminescent properties of  $\text{BaB}_8\text{BO}_{13}:\text{Eu}^{2+}$  nano-phosphors prepared using solution - combustion method.
- Effect of Temperature on the synthesis and Characterization of Titanium dioxide powder prepared by a sol-gel method for solar energy applications.
- Effect of  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  concentration as a precursor via sol-gel method.

## 1.5Thesis Layout

Chapter 2: literature survey and background information is presented on the relevant theoretical aspects of present research on synthesis and characterization of  $\text{MBxOy}:\text{Eu}$  ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ ) nanophosphors and  $\text{TiO}_2$  nanomaterial. The experimental procedures followed during the preparation of  $\text{MBxOy}:\text{Eu}$  ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ ) nanophosphors and  $\text{TiO}_2$

nanomaterial with techniques used are discussed in detail in chapter 3. A large number of structural, morphological and optical characterization techniques were used in this study, and these are thus discussed in this chapter. Chapter 5, 6, 7: This chapters presents luminescent properties of  $MBxOy:Eu$  ( $M = Ca, Sr, Ba$ ) phosphor prepared by Combustion method. Chapter 8, 9: This chapter presents the structural, morphological and optical properties of  $TiO_2$  prepared via sol-gel. Chapter 10: A summary of the thesis, concluding remarks and suggestion for possible future studies are presented.

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# Chapter 2

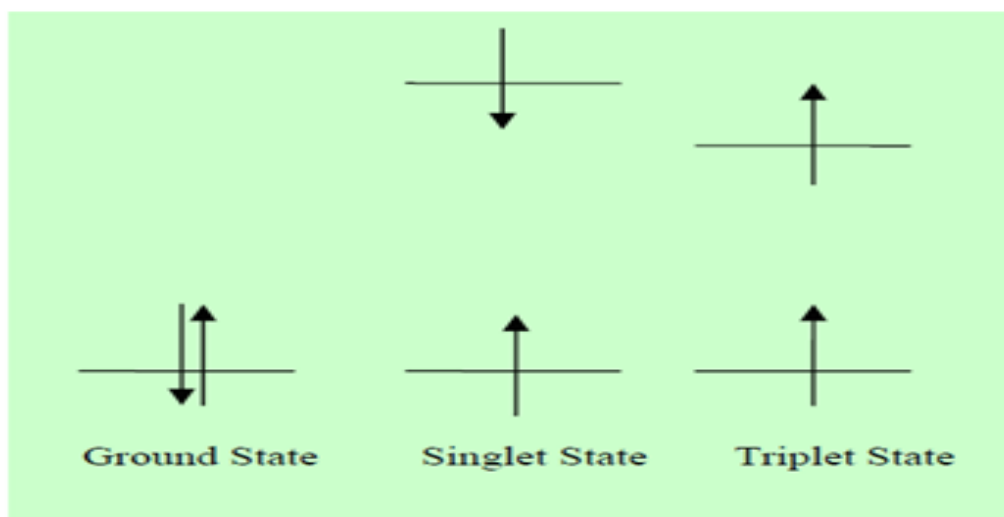
## Literature Review

### 2.1 Background of phosphor

A material can emit light either through incandescence, where all atoms radiate, or by luminescence, where only a small fraction of atoms, called emission centre's or luminescence center's, emit light. In inorganic phosphors, these in homogeneities in the crystal structure are created usually by addition of a trace amount of dopants, impurities called activators. The wavelength emitted by the emission centre is dependent on the atom itself, and on the surrounding crystal structure. An activator is an impurity ion which is added intentionally into the host material to give rise to a centre that can be excited to luminescence. The impurity concentrations in general are relatively low because of the fact that at higher concentrations the efficiency of the luminescence process usually decreases due to concentration quenching effects. Most phosphors have a white body colour, which is an essential feature that prevents absorption of visible light by the phosphors [1]. Light emission from a phosphor is referred to as either fluorescence or phosphorescence. Light emission during the time when a substance is exposed to the exciting radiation is called fluorescence, while the after-glow if detectable by the human eye after the cessation of excitation is referred to as phosphorescence. However, in organic molecules, the two terms are distinguished by whether the transition to emit light is allowed or forbidden by spin selection rules. Light emission due to an allowed transition is called fluorescence, while that due to a forbidden transition is called phosphorescence [2].

Photoluminescence can be defined as the emission of light which is caused by the irradiation of a substance with other light. The term embraces both fluorescence and phosphorescence, which differ in the time after irradiating over with the luminescence occurs [3]. Fluorescence is a kind of luminescence, excited by irradiation of a substance with light. The light hitting a sample puts atoms, ions or molecules in the sample into excited states, from where they decay into lower-lying states which is their ground states, through spontaneous emission of fluorescence photons [4]. Phosphorescence is a kind of photoluminescence which lasts

relatively long after excitation of the medium. The excitation energy is stored in metastable electronic states (often triplet states), exhibiting only forbidden transitions to lower states. The stored energy can be released only through relatively slow processes, which are often thermally activated.



**Figure 2.1** Electronic transitions, paired electrons in ground and singlet state.

## 2.2 Singlet and Triplet States

Electrons in molecular orbitals are paired, according to Pauli Exclusion Principle. When an electron absorbs enough energy it will be excited to a higher energy state; but will keep the orientation of its spin. The molecular electronic state in which electrons are paired is called a singlet transition. On the other hand, the molecular electronic state in which the two electrons are unpaired is called a triplet state. The triplet state is achieved when an electron is transferred from a singlet energy level into a triplet energy level, by a process called intersystem crossing; accompanied by a flip in spin.

In a singlet state, the spins of the two electrons are paired and thus exhibit no magnetic field and called diamagnetic. Diamagnetic molecules, containing paired electron, are neither attracted nor repelled by a magnetic field. On the other hand, molecules in the triplet state have unpaired electrons and are thus paramagnetic which means that they are either repelled or attracted to magnetic fields. The terms singlet and triplet stems from the definition of multiplicity where:

$$\text{Multiplicity} = 2S + 1 \quad 2.1$$

Where, S is the total spin. The total spin for a singlet state is zero (-1/2, +1/2) since electrons are paired which gives a multiplicity of one (the term singlet state).

$$\text{Multiplicity} = (2 * 0) + 1 = 1 \quad 2.2$$

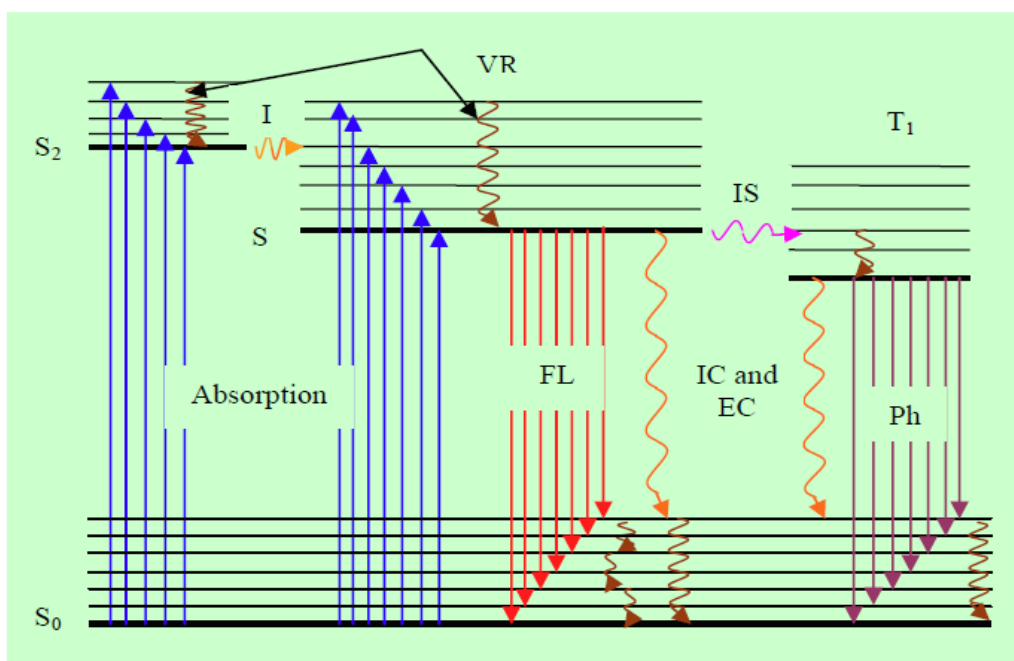
In a triplet state, the total spin is one (the two electrons are unpaired) and the multiplicity is three:

$$\text{Multiplicity} = (2 * 1) + 1 = 3 \quad 2.3$$

It should also be indicated that the probability of a singlet to triplet transition is much lower than a singlet to singlet transition. Therefore, the intensity of the emission from a triplet state to a singlet state is much lower than emission intensities from a singlet to a singlet state

### *Energy Level Diagram for Photoluminescent Molecules*

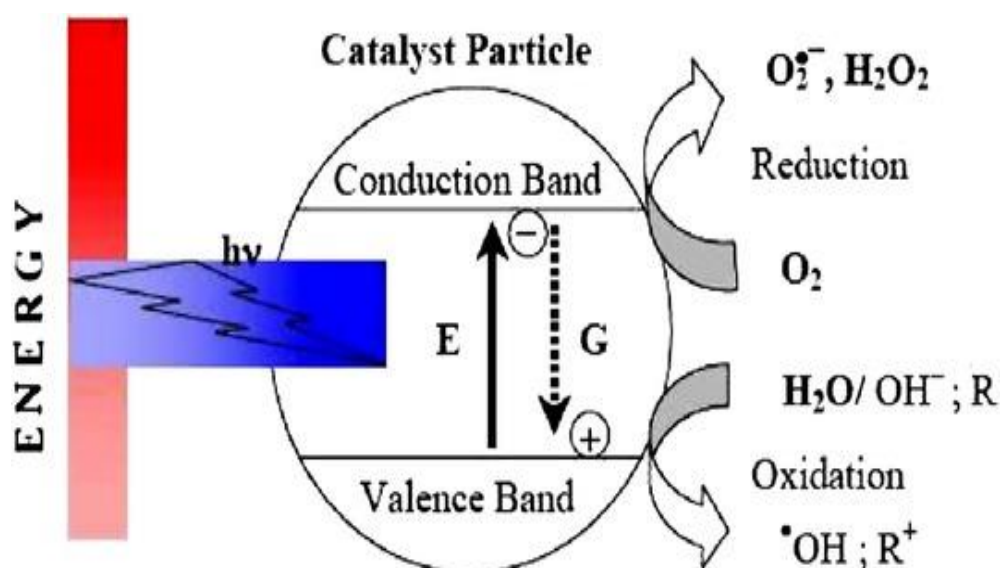
The following diagram represents the main processes taking place in a photoluminescent molecule when it absorbs and emits energy.



**Figure 2.2** Schematic representation of different processes in luminescence transitions.

## 2.3 Titanium dioxide (TiO<sub>2</sub>)

Recently, considerable effort has been devoted to synthesizing inorganic nanomaterials given their unique physical properties compared to their bulk counterparts [5, 6]. The favourable properties of the nanomaterial make them very attractive in various applications including catalysis, high efficiency solar cells, coatings, and sensors [7-8]. Figure 1.1 shows the basic principle of which solar energy removes organics from polluted water or produces fuel. When TiO<sub>2</sub> (a semiconductor) absorbs ultraviolet radiation from sunlight, it produces pairs of electrons and holes. The excess energy of this excited electron promotes the electron to the conduction band thereby creating electron (e<sup>-</sup>) and hole (h<sup>+</sup>) pairs. The positive-hole of TiO<sub>2</sub> breaks apart the water molecule to form hydrogen gas and a hydroxyl radical, which rapidly destroys the chemical bonds of the contaminant. The negative-electron reacts with an oxygen molecule to form a super oxide anion. This cycle continues as long as light is available [9].



**Figure 2.3** Mechanism of semiconductor photocatalysis [10].

Upon absorption of photons with energies larger than the band gap of TiO<sub>2</sub>, electrons are excited from the valence band to the conduction band, creating electron-hole pairs [11]. These photo-generated charge carriers undergo recombination, become trapped in metastable states, or migrate to the surface of the TiO<sub>2</sub>, where they can react with adsorbed molecules

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# Chapter 3

## Synthesis and Techniques

### 3.1 Introduction

The method used to synthesize phosphor powders and experimental techniques will be discussed in this Chapter. The combustion method was used to synthesize the Borate phosphors. Synthesized powders that were investigated in this study were characterized using x-ray diffraction (XRD) with  $\text{Cu K}\alpha = 1.5406 \text{ \AA}$ , which was operated at 40 kV voltage and 40 mA anode current. Data were collected in  $2\theta$  values from  $20^\circ$  to  $80^\circ$  to investigate the crystal structure and morphologies and sizes of the particles were examined using a PHI 700 Nano Scanning Auger Microprobe (Nano SAM) and a Shimadzu model ZU SSX-550 Superscan scanning electron microscope (SEM). Photoluminescence (PL) measurements were performed at room temperature on a Cary Eclipse fluorescence spectrophotometer (Model: LS 55) with a built-in 150 W xenon lamp as the excitation source and a grating to select a suitable wavelength for excitation.

### 3.2 Combustion

The solution combustion synthesis is a versatile, simple, and rapid synthesis method for nanomaterials (eg, phosphor) using self-sustained reaction in homogenous solutions of various oxidizers. It has generated more interest in the field of nano-luminescence materials. Combustion synthesis (CS) or self-propagating high-temperature synthesis (SHS) is an effective, low-cost method for production of various industrially useful materials. Today CS has become a very popular approach for preparation of nanomaterials and is practised in 65 countries. Recently, a number of important breakthroughs in this field have been made, notably for development of new catalysts and nanocarriers with properties better than those for similar traditional materials. The extensive research carried out in last five years emphasized the SHS capabilities for materials improvement, energy saving and

environmental protection. The importance of industrialization of the SHS process is also realized [1].

MBxOy:Eu (M = Ca, Sr, Ba) phosphor powders were prepared by a solutions combustion method. All the reagents were of analytical purity, and were used without further purification. In a typical procedure solution 1, three glass beaker were used with the same constant of Eu(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, (H<sub>3</sub>BO<sub>3</sub>), NH<sub>3</sub>(ON)H<sub>2</sub>, NH<sub>4</sub>NO<sub>3</sub> were mixed and different amount of Ca(NO<sub>3</sub>)<sub>2</sub>, Sr(NO<sub>3</sub>)<sub>2</sub>, Ba(NO<sub>3</sub>)<sub>2</sub> were added. Solution 2: Eu(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O were varied while (H<sub>3</sub>BO<sub>3</sub>), NH<sub>3</sub>(ON)H<sub>2</sub>, NH<sub>4</sub>NO<sub>3</sub> were mixed in constant amount of Ca(NO<sub>3</sub>)<sub>2</sub>, Sr(NO<sub>3</sub>)<sub>2</sub>, Ba(NO<sub>3</sub>)<sub>2</sub>. In each glass beaker 15 ml of deionized water was added and the above solutions were stirred for 20 minutes in a 250 ml beaker at room temperature vigorous until everything has dissolved. The solution was later transferred into a crucible, and then the crucible was introduced into a furnace maintained at 500 °C. The solution under-went dehydration followed by decomposition with the evolution of large amounts of gases. The mixture then froths and swells forming foam, which ruptures with a flame and glows to incandescence. During the incandescence the foam further swells to the capacity of the container. The entire combustion process was over in less than 15 min. For this stoichiometric compositions of the analytical reagent grade metal nitrates, oxidizers and urea (fuel) were calculated using the total oxidizing and reducing valences of the components, which serve as a numerical coefficient so that the equivalence ratio is unity [2].

It has generated more interest in the field of nano-luminescence materials. The solution combustion method has been carried out using urea (CH<sub>4</sub>N<sub>2</sub>O), glycine (C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>) and carbon hydrazides (CH<sub>6</sub>N<sub>4</sub>O) as fuel. It is an exothermic process that occurs with the evolution of heat. The energy needed for the combustion reaction to take place is supplied from the reaction itself hence it is called a self-propagating high-temperature synthesis [3, 4]. The characteristics of solution combustion reaction, to reduce power and generate gas and can be controlled by the selection of the fuel such as (CH<sub>4</sub>N<sub>2</sub>O), (C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>) and (CH<sub>6</sub>N<sub>4</sub>O). Compared to other conventional ceramic process technique solution combustion method has shown advantages of taking few seconds to complete the reaction and the equipment processing are inexpensive [5]. During the combustion process, large volume of gases will evolve which prevent the agglomeration and lead to the formation of fine powders with nano structures [6]. Release of heat during the combustion reaction depends on the fuel-oxidant stoichiometry in the precursor composition [7]. For the combustion synthesis of oxides, metal

nitrate is used as oxidizer, and fuels used are hydrazine-based compounds, citric acid, or urea.

In recent years, with the development of the synthesis technologies on materials, several chemical methods have been applied to prepare luminescence powders [8], of which combustion synthesis is the most important one. There are many merits of the combustion synthesis. First, the process is conducted in the liquid state, so that each component can be accurately controlled and uniformly mixed. Second, the process, which has been extensively applied to preparation of various nano-scale materials, takes only a few minutes [9]. Third, it involves inexpensive processing equipment. Fourth, the final product is obtained in only one step using the chemical energy of the reactants and finally the final products are of high purity due to liberation of volatile impurities [10].

### **3.3 Sol-Gel Process**

#### **3.3.1. Materials**

Starting material used where Tetra-n- butyl-orthotitanate ( $C_{16}H_{38}O_4Ti$ ) as a source of  $TiO_2$ , Ethylenediamine ( $C_2H_4(NH_2)_2$ ), Absolute Ethanol ( $C_2H_5OH$ ), De-ionized ( $H_2O$ ). These materials were purchased from Sigma Aldrich. Titanium Dioxide was prepared by adding different concentrations of ( $C_{16}H_{38}O_4Ti$ ) dropwise into a mixture of ( $C_2H_4(NH_2)_2$ ) and ( $C_2H_5OH$ ) under vigorous stirring with magnetic stirrer for 2 hours, then addition of de-ionized water and absolute ethanol solution to form a transparent sol. The solution was then placed in the fume-hood to chill for about 3-4 days, and then a milky gel was obtained. A gel were annealed at different annealing temperatures from 500 °C - 900 °C for 2 hours in a furnace to eliminate impurities, while various gases evaporates, then a gel crystallised to  $TiO_2$  powders. Finally the  $TiO_2$  powders were crushed into fine powders.

#### **3.3.2. Synthesis of titanium dioxide nanoparticles**

Sol-gel is a wet chemical process in which a solution of metal-organic compounds is subjected to hydrolysis and condensation reactions leading to a  $M-O-M$  gel structure (M=metal, O=oxygen). If the chemical reactions are controlled properly, the solution will become a structured liquid containing a matrix of metal-organic chains. When this solution is

coated onto a surface, the evaporation of solvents leads to an amorphous structure called a gel, which is formed by the cross-linking of metal-organic groups altogether [11]. In order to eliminate the organic species, the film is heated between 300-500°C to evaporate and decompose the organic ligands and redundant solvents. This step is often referred as the drying stage. The as-dried film still remains in amorphous state so it is sintered at higher temperature to convert the amorphous layer into a nano-crystalline metal oxide structure. The sintering temperature may vary between 500-900°C depending on the nature of metal ions, the desired phase, porosity and particle size.

In the present study, the most convenient ways of synthesizing various nanomaterials have preferable due to low cost, ease fabrication and low temperature. The sol-gel method has the advantage of easy control of chemical composition of thin layers [11-12]. This method has various advantages over other method, such as co-precipitation or allowing impregnation, which can be achieved by introducing dopant, molecular scale mixing, high purity of the precursors and homogeneity of sol-gel products with high purity physical, morphological and chemical properties of nanomaterial. Therefore, that was the reason why sol gel synthesis method is preferred as the method of titanium dioxide nanomaterials synthesis. Titanium dioxide layers prepared by sol-gel method have been used for production of architectural windows [13-14], as working electrodes in electro chromic devices (ECD) [15-28] and also for solar cell applications [29-35]. In the last decade, titanium oxide layers have been applied in nanocell photovoltaic systems [23-25] and as photocatalyst to remove organic pollutants from industrial air and water. Also, gas sensors, ultra-filtration membranes, and semiconductor devices can be based on sol-gel titania coatings [26-32]. The terms “sol” and “gel” are being defined as a “sol” is a stable suspension of colloidal solid particles or polymers in a liquid. The particles can be amorphous or crystalline. A “gel” consists of a porous, three-dimensionally continuous solid network surrounding and supporting a continuous liquid phase (“wet gel”). In “colloidal” (“particulate”) gels, the network is made by agglomeration of dense colloidal particles, whereas in “polymeric” gels the particles have a polymeric sub-structure made by aggregation of sub-colloidal chemical units.

### 3.4. Characterization techniques

#### 3.4.1. X-ray Diffraction



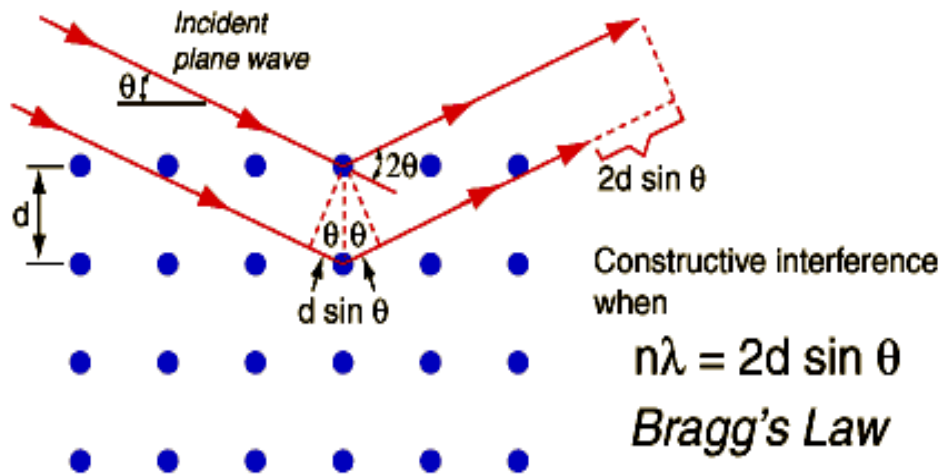
**Figure 3.1** The D8 Advanced AXS GmbH X-ray diffractometer used in this study is shown in the figure.

XRD is an efficient analytical technique used for identification of structural properties of crystalline materials. It is also used for identification of phases, determination of crystallite size, lattice constants, and degree of crystallinity in a mixture of amorphous and crystalline materials. X-ray diffractometer consists of three basic elements: an X-ray tube, a sample holder, and an X-ray detector [33]. It can provide valuable information about the crystalline phase and average crystallite size. The crystal size measured by this technique is smaller than the measurement limit of the optical or electronic microscope. In a crystalline material, the

incident X-ray beam that diffracts from the various planes of atoms at a certain angle ( $2\theta$ ) can interfere constructively resulting in increased intensity of the reflected beam. This intensity is displayed by a peak in the XRD plot, which is associated with d-spacing values of the corresponding structure. The X-rays are generated in a cathode ray tube by heating a filament to produce electrons, which are then accelerated towards a target by applying a voltage. When the electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. The interaction of incident rays with the sample produces constructive interference when the conditions satisfy Bragg's Law:

$$n\lambda = 2d\sin\theta \quad (3.1)$$

where  $\lambda$  the wavelength of the incident light rays,  $d$  is the distance between lattice planes,  $\theta$  is the angle of incidence with lattice plane. This law relates the wavelength of electromagnetic radiation to the diffraction angle and lattice spacing in a crystalline sample as shown in figure 3.2. The figure shows the x-rays waves incident on the parallel planes of atoms in the crystal, with each plane reflecting at a very small fraction in the radiation. The diffracted beams are formed when the reflections from the parallel planes of atoms interfere constructively [34].



**Figure 3.2** Schematic of the reflection of x-rays by crystal planes [35].

By scanning the sample through a range of  $2\theta$  angles when the detector is rotated at double angular velocity, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. The recorded spectra consists of several components, the most common being  $K_\alpha$  and  $K_\beta$ . The specific wavelengths are characteristics of the target material such as copper (Cu), iron (Fe), molybdenum (Mo), and chromium (Cr).

Copper is the most common target material for single-crystal and powder diffraction, with  $\text{CuK}_\alpha$  radiation =  $1.5418\text{\AA}$  [36]. The X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. The crystalline phases are determined from the diffraction patterns. The width of the diffraction lines correlates with the sizes of crystallites. As the crystallite sizes decrease, the line width is broadened due to loss of range order relative to the bulk. The average crystallite size,  $D$ , can be estimated from the broadened peaks by using Debye-Scherrer equation

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (3.2)$$

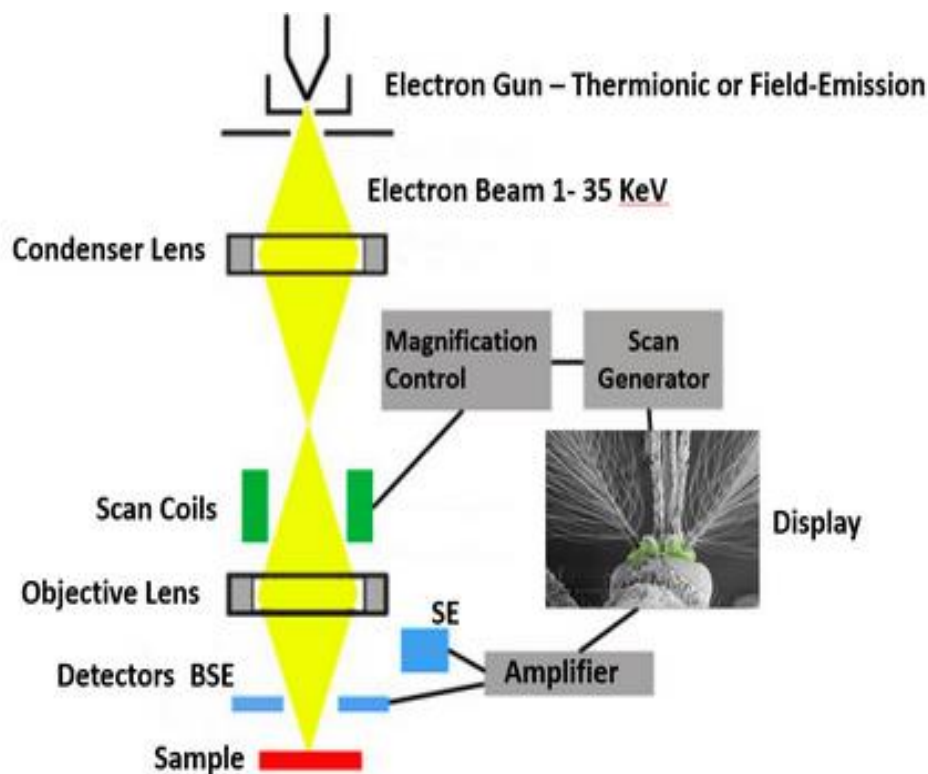
where  $\beta$  is the full width at half maximum of a diffraction line located at an angle  $\theta$ , and while  $\lambda$  is the X-ray Diffraction wavelength.



**Figure 3.3** XRD samples and holders.

### 3.5. Scanning Electron Microscope (SEM)

SEM is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons [36]. The microscope operates at a high vacuum. The SEM generates a beam of incident electrons in a column above the sample chamber. The electrons are produced by a thermal emission source, such as a heated tungsten filament, or by a field emission cathode [37]. The electrons are focused into a small beam by a series of electromagnetic lenses in the SEM column. Scanning coils direct and position the focused beam onto the sample surface. The electron beam is scanned in a raster pattern over the surface for imaging. The emitted electrons are detected for each position in the scanned area by an electron detector. Figure 3.4 shows the basic construction of a SEM. Electrons from the electron gun located at the top of the column flow into the metal plate as acting as the anode by applying a positive voltage. From the anode they pass through the lens to the specimen stage. When the beam hits the sample, electrons are ejected from the sample. The secondary electron detector or backscattered electron detector are used to detect the electrons emitted from the specimen. The output of the secondary electron detector is transferred to display unit. The specimen is observed at high magnification.



**Figure 3.4** Schematic presentation of scanning electron microscopy [38].

High energy electrons that are rejected by an elastic collision of an incident electron are referred to as backscattered electrons. Backscattered provide high resolution imaging of the elemental composition, and surface topography. Elastic interaction between the sample and the incident electron beam produce backscattered electrons. Emitted low energy electrons resulting from inelastic scattering are secondary electrons [38]. Secondary electron provides high resolution imaging of fine surface morphology. Inelastic electron scattering is caused by the interaction between the sample's electron and the incident electrons that result in the emission of low-energy electrons from near the sample's surface. The intensity of the emitted electron signal is displayed on a cathode ray tube (CRT). By synchronizing the CRT scan to that of the scan of the incident beam, the CRT display represents the morphology of the sample surface area scanned by the beam. If the screen is 500 mm across and the scanned area on the specimen is 5 mm across, the magnification is  $\times 100$ . To go to a higher magnification, a relatively small area must be scanned, for example, the scanned area is 0.5 mm across, the magnification is  $\times 1000$ , and so on [38]. Magnification is controlled by the current supplied to the scanning coils, or voltage supplied to the deflector plates, and not by the power of the objective lens. Figure 3.5 shows Superscan SSX-550 SEM-EDX technique used during the measurements.

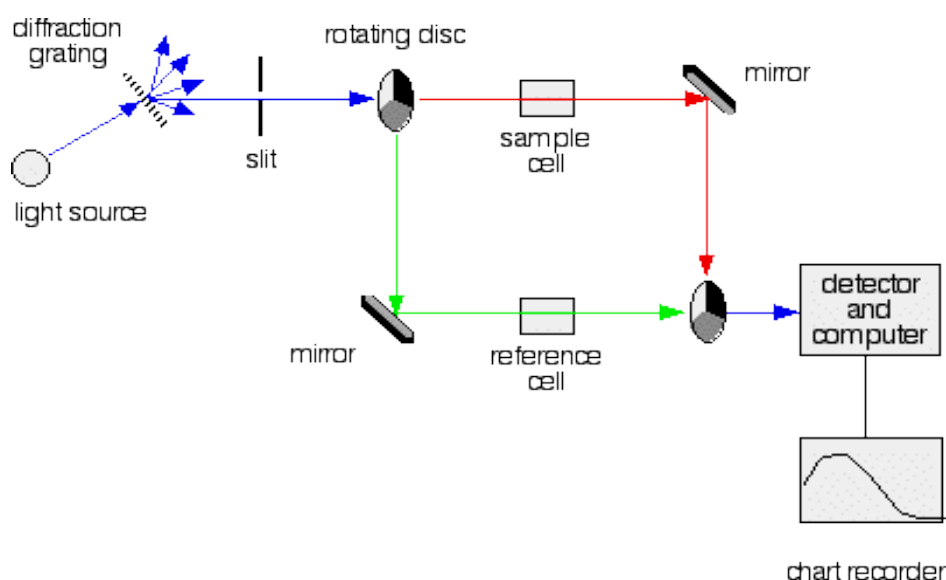


**Figure 3.5** Superscan SSX-550 SEM-EDX techniques.

### 3.6 UV-VIS Spectrometer (UV)

UV-Vis spectrophotometry is a technique that involves absorption and/or reflectance of light (radiation) in the ultraviolet-visible spectral region. It measures the intensity ( $I$ ) of light passing through a sample, and compares it to the original intensity ( $I_0$ ) of light before it passes through the sample. The ratio  $I/I_0$  are called the transmittance, and are expressed as a percentage (%T). The absorbance ( $A$ ) is related to the transmittance by the following equation:

$$A = -\log\left(\frac{\%T}{100}\right) \quad 3.3$$



**Figure 3.6** Schematic of the UV-Visible spectrophotometer [39].

In UV-Vis spectrophotometry the light beam provided by the light source passes through the diffraction grating and the slits [40]. The radiation is separated according to its frequency wavelength by a diffraction grating followed by a narrow slit. The slit ensures that the radiation is of a narrow waveband that is monochromatic. Detection of the radiation passing through the sample or reference cell can be achieved by either a photomultiplier or a photodiode. Single photodiode detectors and photomultiplier tubes are used with scanning

monochromator, which filter the light so that only the light of a single wavelength reaches the detector at one time. The scanning monochromator moves the diffraction grating to step-through each wavelength so that its intensity may be measured as a function of wavelength.

The UV/Visible spectroscopy representation observed in figure 7 is equipped with two source lamps: Deuterium (from about 10 nm to 330 nm) and Tungsten lamps (300 nm to wavelength greater than 3000 nm). The lamps are used to irradiate the sample, with the Deuterium used from 200 nm up to 319 and then shift to Tungsten up to 1000 nm. Upon irradiating of the sample, the source beam is split into two beams. One beam is directed to the sample and the other is sent to the detector as a reference [40].

The sample is positioned inside an integrating sphere that collects the diffusely scattered light by the sample. Some of the incident light is absorbed by the sample. The collected light eventually falls onto the detector, which subtracts the collected light from the source light to determine the amount that has been absorbed. The detectors used in this system are the PbS and PMT measuring the near infrared region, and Ultraviolet and visible region, respectively. This technique allows determination of the absorbance characteristics of materials.

The absorption data from the UV-Vis spectrophotometer in this context was used to determine the band gap energy ( $E_g$ ) of the material. The band gap energy is determined by using Tauc's relation. The band gap indicates the difference in energy between the top of the valence band filled with electrons and the bottom of the conduction band devoid of electrons. The following relational expression proposed by Tauc, Davis, and Mott is used.

$$(h\nu\alpha) = A(h\nu - E_g)^{\frac{1}{n}} \quad 3.4$$

where  $h$ : Planck's constant,  $\nu$ : frequency of vibration,  $\alpha$ : absorption coefficient,  $A$ : proportional constant, and  $E_g$  band gap energy. The value of the exponent  $n$  denotes the nature of the sample transition.

For direct allowed transition  $n = \frac{1}{2}$

For direct forbidden transition  $n = \frac{3}{2}$

For indirect allowed transition  $n = 2$

For indirect forbidden transition  $n = 3$

Since the materials analyzed in this study have an indirect allowed transition,  $n=2$  was used.

When  $(h\nu\alpha)^{\frac{1}{n}} = 0$ , this means that

$$E_g = h\nu \quad (3.5)$$

$E_g$  is estimated by extrapolating a tangent line through the plot of  $(h\nu\alpha)^{\frac{1}{n}}$  against  $h\nu$ . Figure 8 below shows the Perkin Elmer Lambda 950 UV-VIS spectrometer used during the absorption measurements.



**Figure 3.7** Perkin Elmer Lamb 950 UV-VIS Spectrometer at the University of the Free Physics department.

### 3.4.1 Photoluminescence spectroscopy



**Figure 3.8** The Varian Cary Eclipse Spectrometer used in this study.

Photoluminescence spectroscopy is a technique used to analyse the luminescence of a material. Light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process is called photo-excitation [41, 42]. One way this excess energy can be dissipated by the sample is through the emission of light or luminescence. The excitation source which produces photons used in this context was (CW Xenon lamp) and supplies excitation energy to the sample, emitted luminescence is dispersed in a spectral device, a detector converts the optical signal into electric signal that is then processed by the electronic devices and finally by a control computer [41]. The photons pass through the monochromator that only select the certain wavelength to pass through to the sample cell. Luminescence given off is detected by and processed by the computer's software.

### 3.4.2 Photoluminescence

Photoluminescence can be further described as an excitation of valence band electrons to a higher energy state which is the conduction band and then a return to lower energy state valence band accompanied by the emission of a photon [42]. The period between absorption

and emission is typically extremely short, in order of 10 nanoseconds. The optical emission associated with photoluminescence is generally divided into two types: intrinsic and extrinsic.

The shape of the emission spectrum is affected by the thermal distribution of the electrons and holes within their bands [43]. The photoluminescence emission in materials, i.e. in inorganic insulators and semiconductors is classified in terms of the nature of the electronic transitions producing it is either intrinsic or extrinsic photoluminescence. In this study the classification of the electronic transitions in photoluminescence are due to intrinsic luminescence effects the nature of this effect is discussed in the below sections [43].

### ***3.4.3. Intrinsic photoluminescence***

Intrinsic photoluminescence is a kind of luminescence that may arise due to the presence of a variety of defects in a crystal structure. This type of luminescence does not involve impurity atoms. There are three kinds of intrinsic photoluminescence namely: band to band, excitons and cross luminescence. In general there are several factors that may influence intrinsic photoluminescence such as: Non stoichiometry - a state of a material (semiconductor) not having exactly the correct elemental proportion. Structural imperfections – owing to poor ordering, radiation damage, or shock damage [43].

## **3.8 Differential scanning calorimetry (DSC)**

Differential scanning calorimetry or DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at very nearly the same temperature throughout the experiment.

Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned.

The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more (or less) heat will need to flow to it than the reference to maintain both at the same temperature.

Whether more or less heat must flow to the sample depends on whether the process is exothermic or endothermic. For example, as a solid sample melts to a liquid it will require more heat flowing to the sample to increase its temperature at the same rate as the reference.

This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Likewise, as the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions.

DSC may also be used to observe more subtle phase changes, such as glass transitions. DSC is widely used in industrial settings as a quality control instrument due to its applicability in evaluating sample purity and for studying polymer curing. The result of a DSC experiment is a heating or cooling curve.



**Figure 3.9** The Perkin-Elmer DSC7 thermal analyzer.

### 3.9 Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) is a thermal analysis technique used to measure changes in the weight (mass) of a sample as function of temperature and or time. Its principal uses include measurement of a material's thermal stability, absorbed moisture content and

composition. It is useful to determine the amount of material lost as the sample is heated [44]. In TGA, a sample is placed into a tared TGA sample pan which is attached to a sensitive microbalance assembly, as shown in figure. 3.10. The sample holder portion of the TGA balance assembly is subsequently placed into a high temperature furnace. The balance assembly measures the initial sample weight at room temperature and then continuously as the temperature increases the material loses weight as species decompose or evaporate from the sample. These changes are detected by the analytical balance from which the sample is suspended. A plot of TGA data is typically weight percent on the y-axis and temperature on the x-axis. The data would be plotted with weight percent as the y-axis and time as the x-axis. The doped and undoped xerogels were used as a precursor for TGA. In order to determine the thermal stability of the various xerogels, thermogravimetric analyses were performed in a Perkin-Elmer TGA7 thermal analyzer in the flowing nitrogen atmosphere under the constant flow rate  $20 \text{ ml min}^{-1}$ , as shown in figure. 3.11. The xerogels were also annealed at  $600 \text{ }^{\circ}\text{C}$  and the resulting powders were used as precursor for other techniques. The samples approximately weighting 5-10 mg each were then heated from  $25$  to  $600 \text{ }^{\circ}\text{C}$  at a heating rate of  $10 \text{ }^{\circ}\text{C min}^{-1}$ . The instrument was computer controlled and calculations were done using Pyris Software.



**Figure 3.10 Photo of TGA apparatus.**

### 3.10 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is the useful technique to identify the types of chemical bonds. It can be utilized to quantitate some of the unknown components in a mixture [45]. FTIR is like molecular fingerprint. A schematic diagram is shown in figure 3.11.

The beam emitted from the source is passing through an aperture and control the amount of energy on the sample. The beam then enters the interferometer, which produces a signal that has spectral encoding into it. The beam is split into 2 by the beam splitter upon entering the interferometer. One beam reflects off a flat mirror which is fixed in place while the other beam reflects off a flat mirror which allows this mirror to move very short distance away from the beamsplitter. These two beams later recombine to form an interferogram. The laser beam incident to the interferometer is used for wave calibration, mirror position control and to collect data of the spectrometer. The beam enters the sample the sample where it is transmitted through the sample surface. Then the detector detects the beam for measurement [45]. In this study the Bruker TENSOR 27 Series.

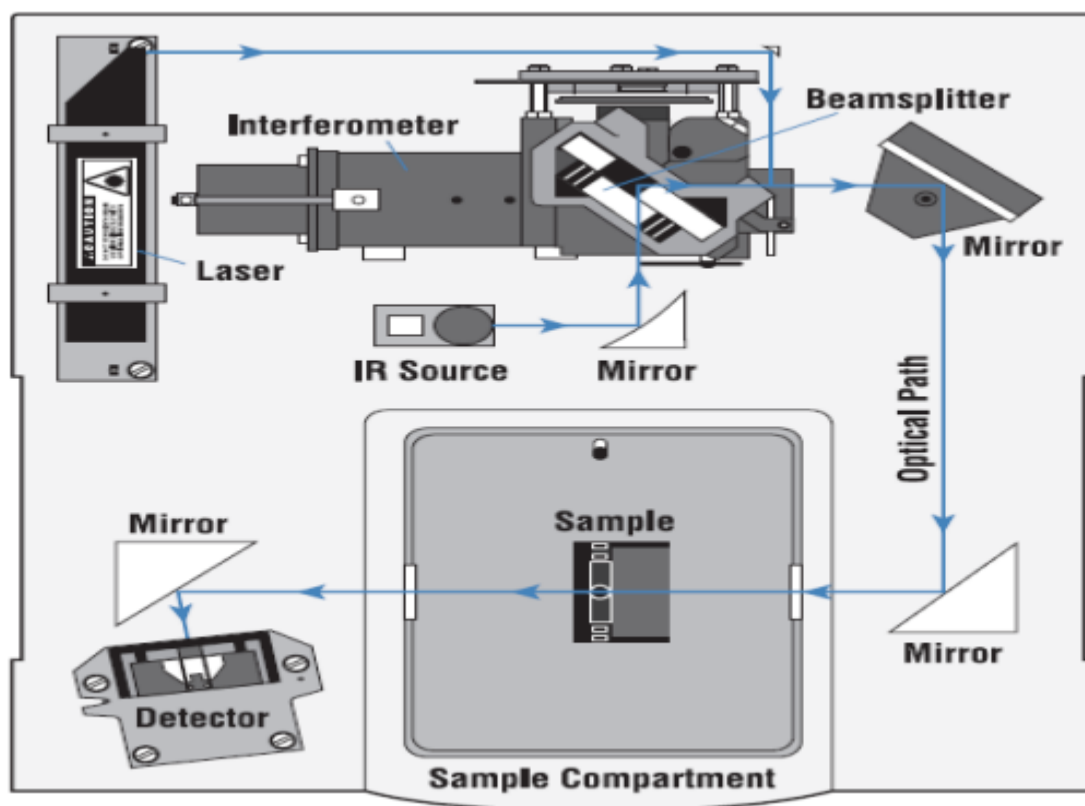


Figure 3.11 A simplified layout FTIR spectrometer.



**Figure 3.12 Bruker TENSOR 27 Series FTIR spectroscopy**

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# Chapter 4

## Synthesis and characterization of $\text{CaB}_4\text{O}_7:\text{Eu}^{3+}$ nano-phosphors prepared using solution - combustion method

### 4.1 Introduction

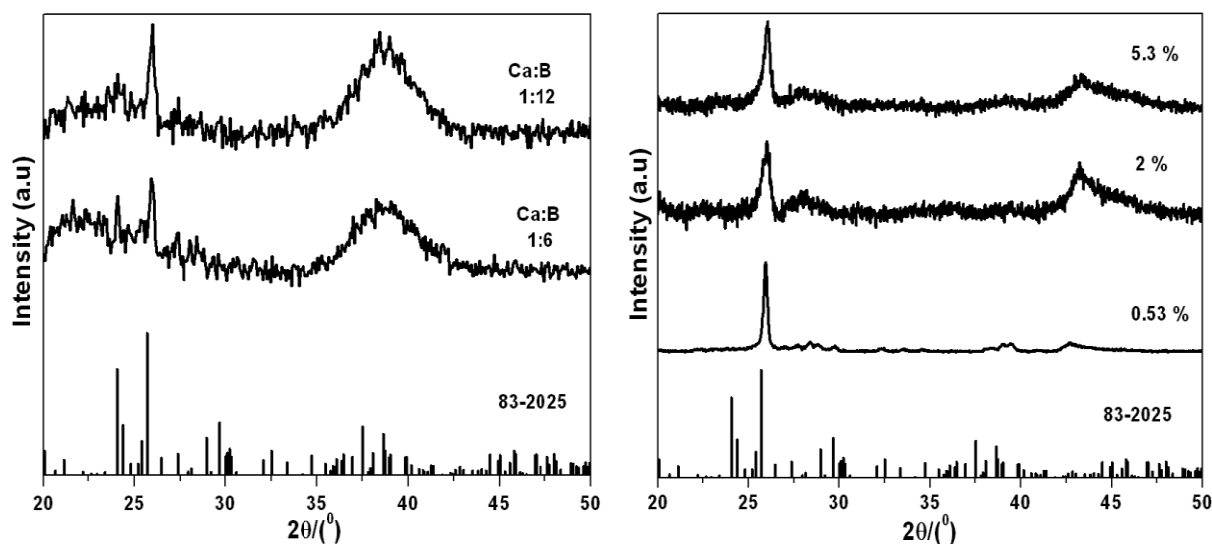
In the last two decades, a burst of research activities has been devoted to nanomaterials. It has attracted many works in various fields from material science to biotechnologies and genetics [1–3]. Borates with non-centrosymmetric crystal structure are among the most frequently used nonlinear optical materials [4]. Phosphor nanocrystals are exceptionally promising materials in many fields of technology including photonics, luminescent displays, fluorescent lamps, lasers, cathodoluminescence, and biotechnology [5]. Europium ion ( $\text{Eu}^{3+}$ ) is widely used as a luminescent center in a number of phosphors for the exhibited characteristic red emission mainly corresponding to its  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition [6, 7]. In the luminescence study of  $\text{CaB}_4\text{O}_7:\text{Eu}^{3+}$  nano-phosphors, the  $\text{Eu}^{3+}$  ion plays an important role as a luminescent probe. Borates doped with trivalent europium ions have excellent efficiencies and appropriate absorption Bands [6]. A great deal of work has been done on  $\text{Eu}^{3+}$  activation of these hosts [8]. Solution combustion is a well-known method for synthesis of rare earth activated insulating materials at low temperatures (350-500 °C) and very short times (<10 minutes). Wet chemical methods such as sol-gel [9, 10] and polymerized-complex [11] have been used to synthesis  $\text{CaB}_3\text{O}_7:\text{Eu}$  red phosphor. Although these methods have more control on size, structure and morphology, conventional solid reaction shows higher luminescence intensity [12]. Combustion synthesis offers many potential advantages over conventional techniques of synthesis, including relatively simple equipment, shorter processing time, lower energy requirement and higher purity [13]. The initial combustion process used the conventional furnace as heating system. This method was accidentally discovered in 1988 in Prof. Patil's lab in India [14]. In this paper, red phosphor  $\text{CaB}_4\text{O}_7:\text{Eu}^{3+}$  have been successfully synthesized at

500 °C by combustion reaction. The effects of urea, boric acid and europium concentration on structural, morphology and Luminescence of  $\text{CaB}_4\text{O}_7:\text{Eu}^{3+}$  were studied in detail.

## 4.2 Results and Discussion

### 4.2.1 Structure and morphology

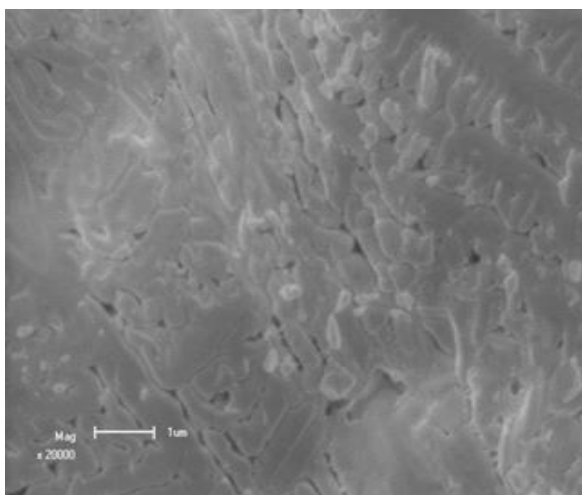
Figure 4.1 shows XRD patterns of  $\text{CaB}_4\text{O}_7:\text{Eu}^{3+}$  samples synthesized with different Ca:B molar ratio and Eu ions concentrations. Fig. 1(a) the XRD patterns of the samples are in good agreement with the reference database JCPDS card 83-2025, confirming the composition of the sample to be  $\text{CaB}_4\text{O}_7$ . The obtained product has a monoclinic lattice with the lattice parameters  $a = 12.34$ ,  $b = 9.50$ ,  $c = 7.850$ . Figure 4.1(b) it also shows the monoclinic structure with the single phase. The results also showed that varying the Eu % does not affect the crystal structure of the phosphor. Moreover, the increase of the Eu concentration promotes urea decomposition and causes the more rapid ignition of the mixture, which provides higher temperatures for the reaction [14].



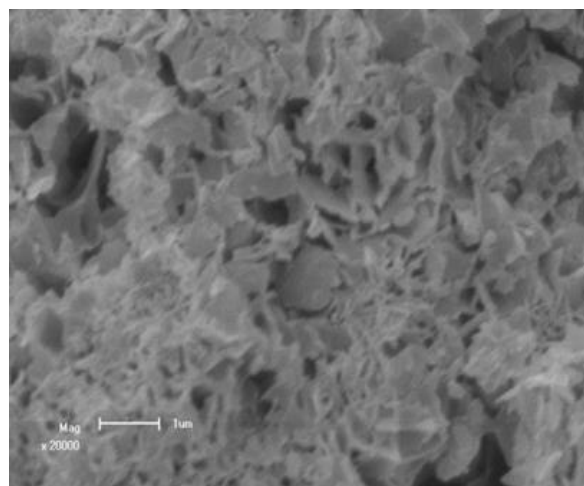
**Figure 4.1** (a) X-ray diffraction patterns of  $\text{CaB}_4\text{O}_7$  phosphors for various Ca:B mole ratio.

**Figure 4.2** (b) X-ray diffraction patterns of  $\text{CaB}_4\text{O}_7$  for different Eu concentrations.

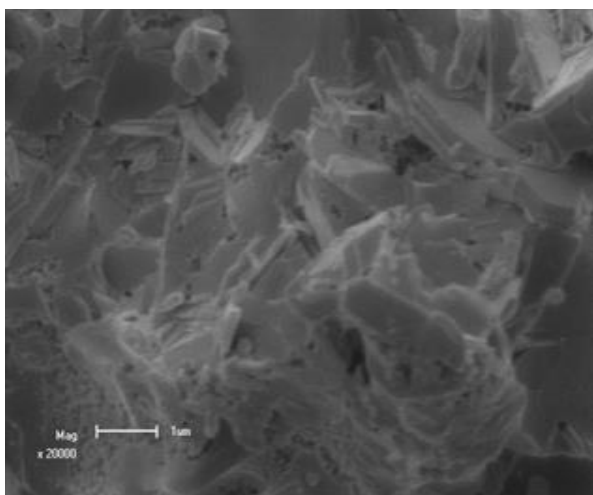
Fig. 4.2 shows the SEM images of sample obtained for different Ca:B molar regular structured with well-developed edges figure (a and b) and Eu ions concentration values figure (c and d) with plate-like particles. From figure (a, b) the SEM pictures of the  $\text{CaB}_4\text{O}_7\text{:Eu}^{3+}$  powder reveals nanorod like, agglomerated, porous for low Ca:B molar ratio but the grains become regular structured with well-developed edges as the Ca:B molar ratio increased, giving rise to the increase in particle size. As for figure (c, d) the SEM pictures shows the plate-like structure with very narrow edges for low Eu concentration but as the Eu concentration increases it reveals mixed plate-like structure and irregular nanoparticles superimposed on them. It was reported that the flame temperature is responsible for agglomeration [15] and the evolution of large amount gaseous products during combustion produces highly porous voluminous powders [16]. When the ignition of the metal nitrate solution with nitrogen-based fuel starts, localization of the heat on the particle boundaries results in a semi-sintered morphology of particles [17]. In the literature, the observed particle size differences/ microstructure of oxides prepared by solution combustion technique using various fuels is usually explained based on the differences in the number of moles of gases liberated during the reaction.



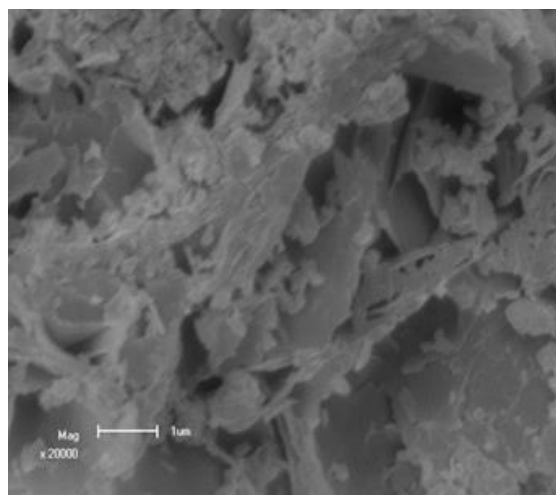
**Figure 4.3** (a) SEM image of  $\text{CaB}_4\text{O}_7:\text{Eu}^{3+}$  Ca:B 1:6 mole ratio sample.



**Figure 4.4** (b) A typical SEM image of samples with 1:12 Ca:B mole ratio sample.



**Figure 4.5** (c) SEM image of  $\text{CaB}_4\text{O}_7:\text{Eu}^{3+}$  samples with 0.53% Eu concentration.



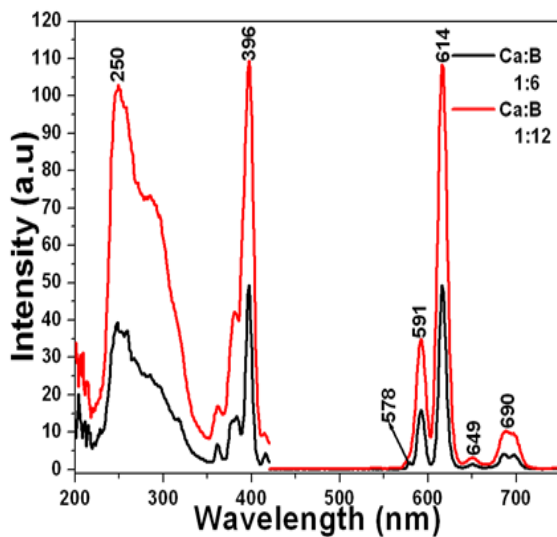
**Figure 4.6** (d) SEM image of samples with 5.3% Eu concentration.

#### 4.2.2 Photoluminescence characteristics

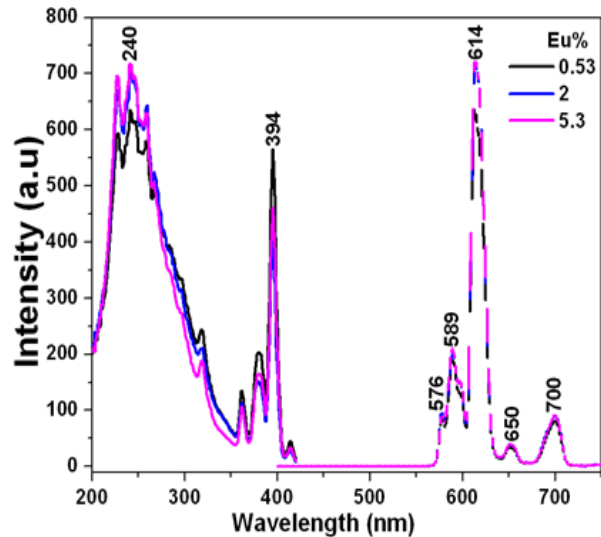
The excitation and emission spectra  $\text{CaB}_4\text{O}_7:\text{Eu}^{3+}$  phosphors are shown in Figure 4.7. From Figure 4.7 the excitation spectra of the  $\text{CaB}_4\text{O}_7:\text{Eu}^{3+}$  phosphor shows 3 bands from 200–400 nm. The excitation spectra by monitoring  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  emission of  $\text{Eu}^{3+}$  in  $\text{CaB}_4\text{O}_7$  can be divided into two regions: the broad excitation band in 220–300 nm regions originates from the charge-transfer transition of the  $\text{Eu}^{3+}-\text{O}^{2-}$  bond (CTB) [18]. The other sharp lines can be assigned, respectively, to the transitions between the ground level  $^7\text{F}_0$  and the excited levels  $^5\text{H}_j$ ,  $^5\text{D}_4$ ,  $^5\text{G}_j$ ,  $^5\text{L}_6$  [19]. The most intense of f-f transitions is  $^7\text{F}_0 \rightarrow ^5\text{L}_0$  band (396 nm). The increase of the amount of the Ca: B molar ratios results in rise of the

intensities of both CT and f-f bands. The emission spectra from Fig. 3(a) consist of transitions from  $^5D_0$  level of  $\text{Eu}^{3+}$  ions to lower level of  $^7F_4$  (680-700 nm),  $^7F_3$  (648-659 nm),  $^7F_2$  (608-633 nm),  $^7F_1$  (583-603 nm) and the ground state  $^7F_0$  (568-580 nm). The  $^5D_0$ - $^7F_2$  band is observed to be the most intense one (with the maximum at 614 nm) for all Ca:B molar ratios. This  $^5D_0 \rightarrow ^7F_2$  band also possesses a high intensity as a result, summary emission color is red.

Similarly from Figure 4.8 similar results were observed with the variation of the Eu concentration. Under the excitation of CTB at 240 nm, it can be seen that the red emission lines at 614 nm originating from the electric dipole transition  $^5D_0 \rightarrow ^7F_2$  is the dominant luminescence in the spectrum. Sharp red emission indicates that  $\text{CaB}_4\text{O}_7:\text{Eu}^{3+}$  is suitable for display phosphors.



**Figure 4.7** Excitation and emission spectra of  $\text{CaB}_4\text{O}_7$  for various Ca:B mol ratio excited at 396 nm.



**Figure 4.8** Excitation and emission spectra of  $\text{CaB}_4\text{O}_7$  at different Eu concentration excited at 240 nm.

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## Chapter 5

# Synthesis and Characterization of $\text{SrB}_6\text{O}_{10}:\text{Eu}^{2+}$ nano-phosphors Prepared Using Solution - Combustion Method

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### 5.1 Introduction

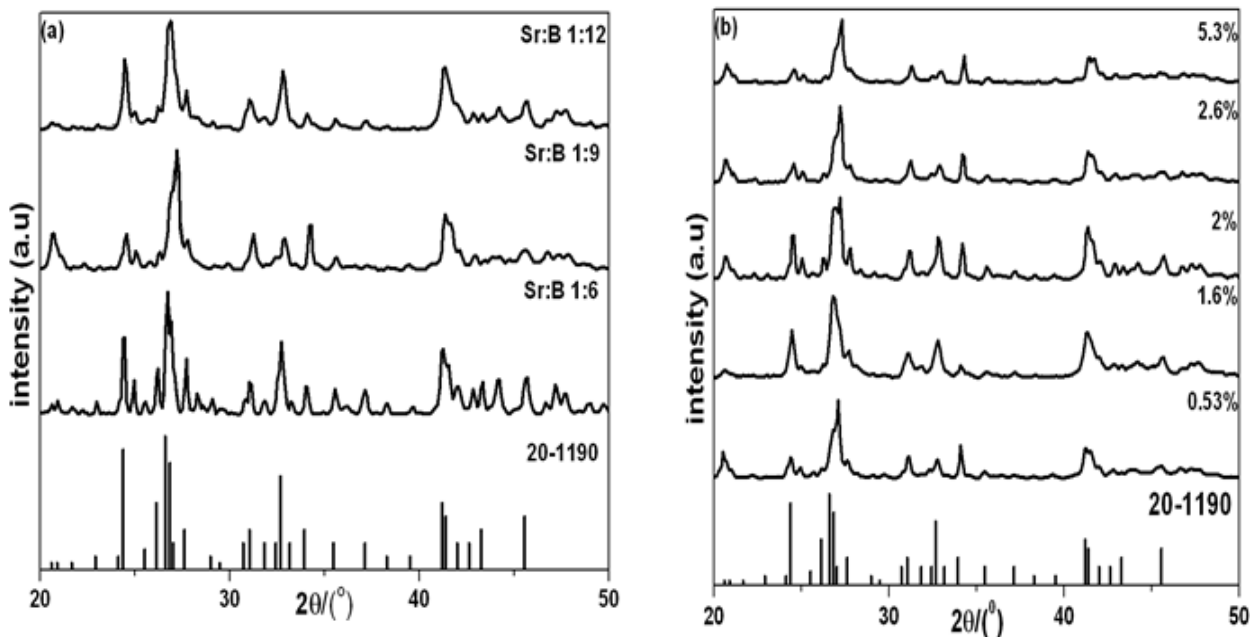
In recent years, more and more attention has been paid to the development of new luminescent nano-materials such as europium doped nano-crystals due to their potential applications in optics and optoelectronics [1, 2]. UV and blue emissions of  $\text{Eu}^{2+}$  has been extensively used in obtaining the blue component of lamp phosphors, colour TV phosphors, X-ray imaging phosphors, and white LEDs [3, 4]. The reduction to  $\text{RE}^{2+}$  ( $\text{RE} = \text{Eu}, \text{Sm}, \text{Yb}$  and  $\text{Tm}$ ) could be performed in air for certain special hosts which meet all the following conditions: (1) the host should not contain any oxidizing ions like  $(\text{NO}_3)^-$ ; (2) the host should provide crystallographic sites suitable for the reduction to  $\text{RE}^{2+}$ ; (3) the cation to be substituted should have a radius similar to that of the  $\text{RE}^{2+}$  ion, and (4) the host should consist of an appropriate structural unit, namely, a rigid tetrahedral unit such as  $\text{BO}_4$ ,  $\text{SO}_4$ , and  $\text{PO}_4$  [5]. In  $\text{SrB}_4\text{O}_7$ , all of the boron atoms are tetrahedrally coordinated and the  $\text{BO}_4$  tetrahedra form a three-dimensional network by sharing all the corners with four neighbours [6, 7]. As for  $\text{SrB}_6\text{O}_{10}$ , no detailed crystallographic structure was reported so far to the best of our knowledge, but the presence of two kinds of anion units,  $\text{BO}_3$  and  $\text{BO}_4$ , was suggested on the basis of infrared spectroscopy [8]. Hence, it may be expected that trivalent rare earth ions could be reduced in air in these hosts, and it was indeed confirmed so in other previous works [5, 9]. Therefore the emission of  $\text{Eu}^{2+}$  is very strongly dependent on the host lattice. The emission transition ( $4f^65d^1 \rightarrow 4f^7$ ) of  $\text{Eu}^{2+}$  is an allowed transition [10]. The exact composition of the starting mixture has important consequences for the afterglow behaviour. A deficit of alkaline earths usually enhances the afterglow, while an excess of strontium in the phosphor can annihilate the persistent luminescence completely. In the variety of alkaline earth borates,  $\text{Eu}^{2+}$  ions exhibit strong photoluminescence. Strontium borate  $\text{SrB}_6\text{O}_{10}$  is an

excellent host material for luminescent ions. The luminescence of divalent rare-earth ions of  $\text{Eu}^{2+}$ ,  $\text{Sm}^{2+}$ ,  $\text{Yb}^{2+}$  and  $\text{Tm}^{2+}$  have been reported in many hosts for long time [11, 12]. Pei [13] reported that the  $\text{Eu}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Yb}^{3+}$  could be reduced to the corresponding divalent rare-earth ions in  $\text{SrB}_4\text{O}_7$  by solid state reaction at high temperature. The procedure was found suitable for producing  $\text{Eu}^{2+}$  doped phosphors. Very intense photoluminescence (PL) was found in these phosphors which are reported here. In the present paper, we investigate the influence of the Sr:B molar ratio and Eu ion concentrations on the structural, morphological and luminescent properties of  $\text{Eu}^{2+}$  doped in  $\text{SrB}_6\text{O}_{10}$ .

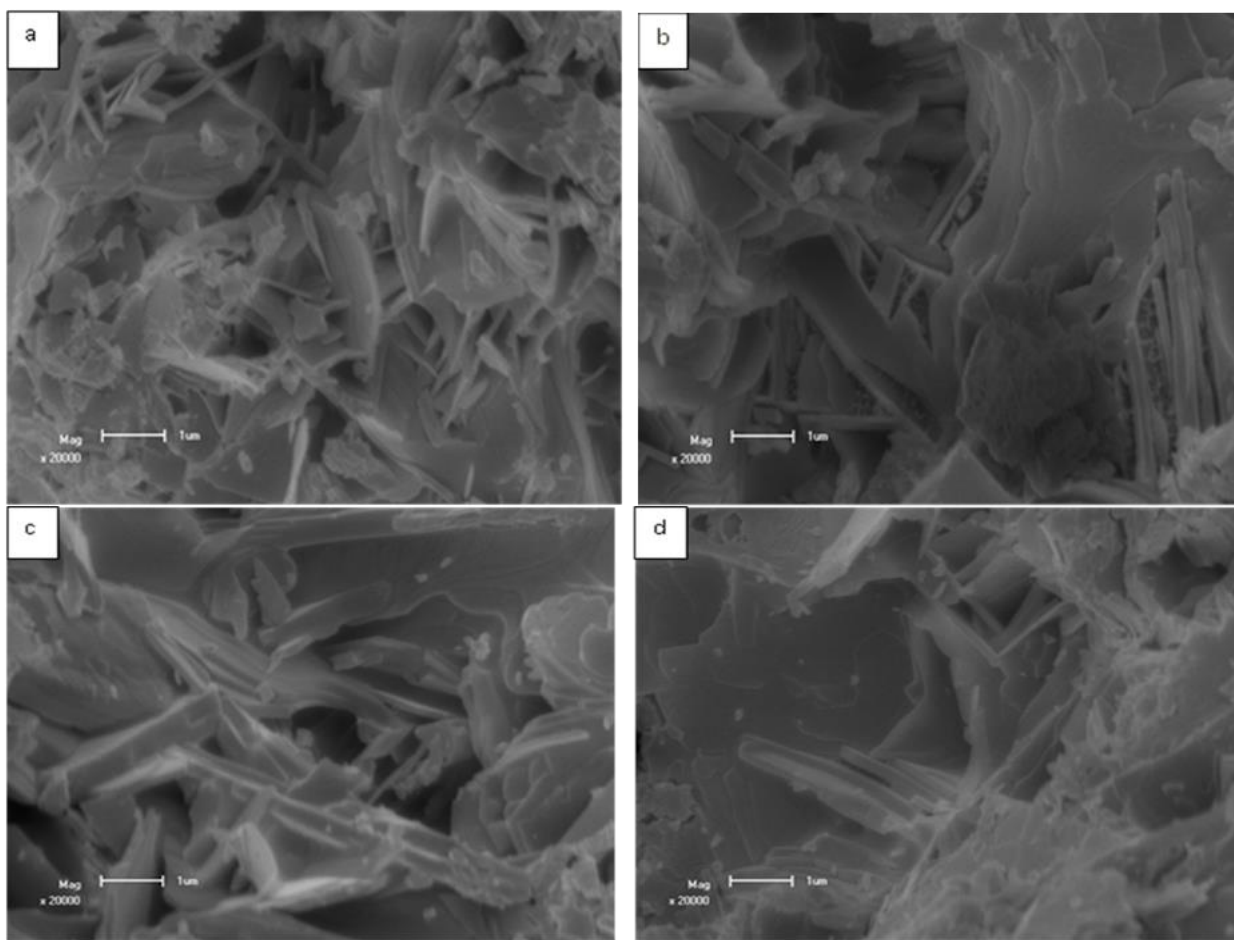
## 5.2 Results and Discussion

### 5.2.1 Structural morphological and properties

Figure 5.1 showed the XRD patterns of different synthesised  $\text{SrB}_6\text{O}_{10}:\text{Eu}^{2+}$  phosphors with (a) Sr:B mol ratio and (b) Eu ion concentrations. The structure of the sample was in good agreement with the (JCPDS: 20-1190) [14]. The increase in Sr:B and Europium ion concentration resulted into elimination of secondary phases. It was observed that the peaks are broad and unsymmetrical. It is apparent that a good crystalline  $\text{SrB}_6\text{O}_{10}$  powder could be obtained at lower temperature by the liquid combustion process, which was lower than that required for the sol-gel method and the solid-state reaction method [15]. The estimated average crystal size was calculated using the maximum intensity peak around ( $2\theta = 26^\circ$ ) was between 16 - 20 nm.



**Figure 5.1** (a) X-ray powder diffraction patterns of the samples obtained by the sol-Combustion method at different Sr:B mol ratio. (b) The XRD patterns for different Europium nitrate concentrations.



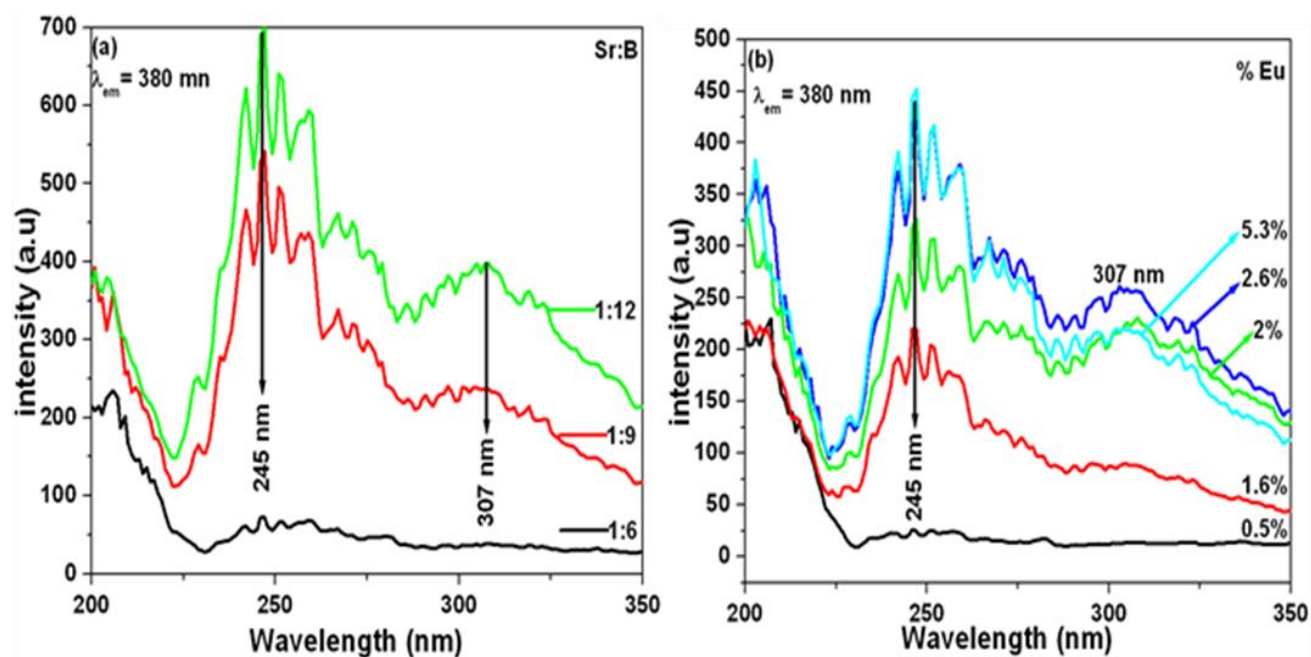
**Figure 5.2** SEM images of (a) Sr:B (1:12), (b) Sr:B (1:6) illustrates the effect of different molar concentrations of Strontium nitrate and SEM image of (a) 0.53% Eu, (b) 2 % Eu

**Figure 5.2(a, b, c, d)** showed the representative SEM images of  $\text{SrB}_6\text{O}_{10}:\text{Eu}^{2+}$  samples obtained for various Sr:B molar ratios and Eu ion concentrations. As can be seen from figures, the micrograph shows the presence of well-packed and randomly oriented platelet-like large grains. It is well known, that the final surface morphology and structure of a specific sample is significantly influenced by the overall bulk composition of the phosphor powder.

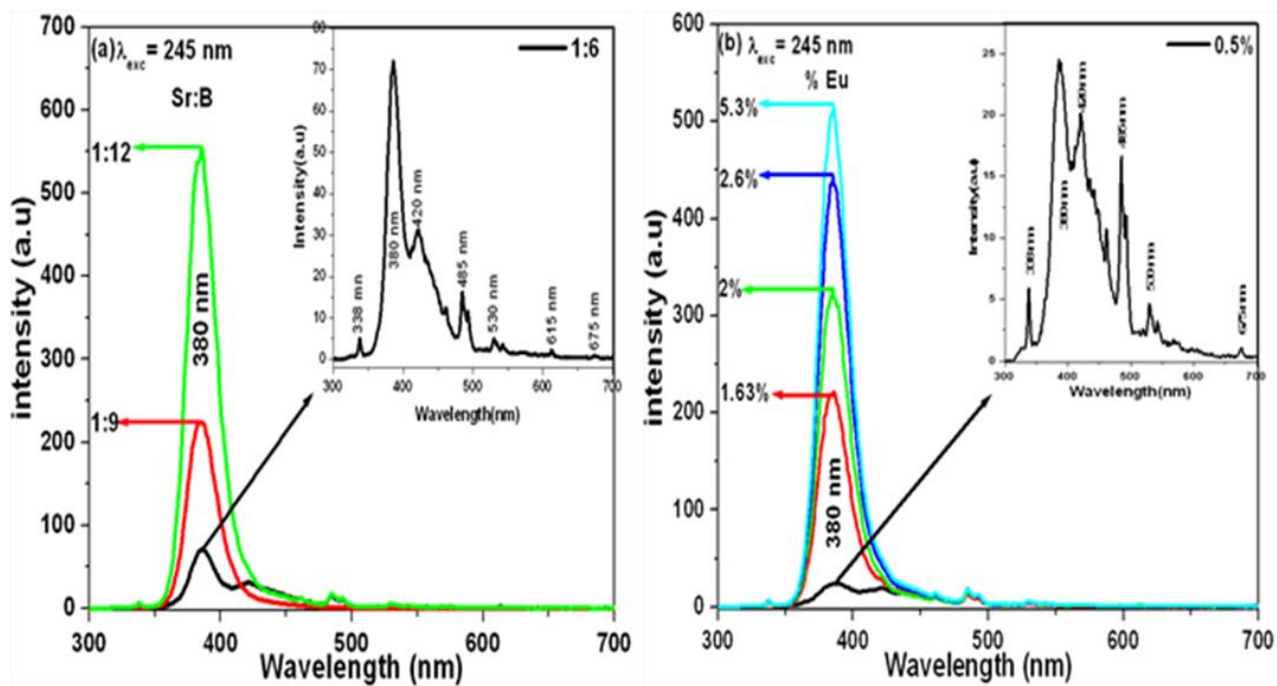
### 5.3.2 Luminescence properties

Figure 4 revealed the effect of (a) Sr:B molar ratio and (b) Eu ions concentrations on the photoluminescence properties of  $\text{SrB}_6\text{O}_{10}:\text{Eu}^{2+}$  phosphor particles prepared by solution-combustion method, respectively. The excitation spectra (Figure 4a and b) obtained by monitoring the emission of the  $\text{Eu}^{2+}$  ion ( $4f^65d \rightarrow 4f^7$  transition), i.e., 380 nm display broad

band's with maxima around 245 nm and 307 nm, which correspond to the splitting of the 5d orbital into  $t_{2g}$  and  $e_g$  components [16]. The excitation spectra of the  $\text{SrB}_6\text{O}_{10}:\text{Eu}^{2+}$  indicated that the emission of the  $\text{Eu}^{2+}$  ions originated from charge transfer bands (CTB) around 245 nm. From Figure 5.3 it was clear that the excitation intensity increased with an increase in the Sr:B molar ratio and Eu ion concentrations. The excitation peak at around 245 nm has higher intensity compared to that around 307 nm therefore we used the excitation wavelength around (245 nm) to probe the emission spectra. There was no shift of excitation bands observed with an increase in both the Sr:B molar ratio and the Eu ion concentrations, and this may attributed to constant crystal field created by the unchanging crystallographic  $\text{SrB}_6\text{O}_{10}:\text{Eu}^{2+}$  phase with the Sr:B molar ratio and the Eu ion concentrations. The PL spectra of the  $\text{SrB}_6\text{O}_{10}:\text{Eu}^{2+}$  phosphors samples synthesized with various Sr:B molar ratio and the Eu ion concentrations samples when excited at 245 nm wavelength are shown in Figure 5.3 (a) and (b). The emission spectrum for most  $\text{SrB}_6\text{O}_{10}:\text{Eu}^{2+}$  phosphors revealed one strong band at 380 nm. Samples with low Sr:B molar ratios and low Eu ion concentrations displaced little bands at 335, 420, 485, 525, 615 and 680 nm as shown in the inset of Figure 5.4.

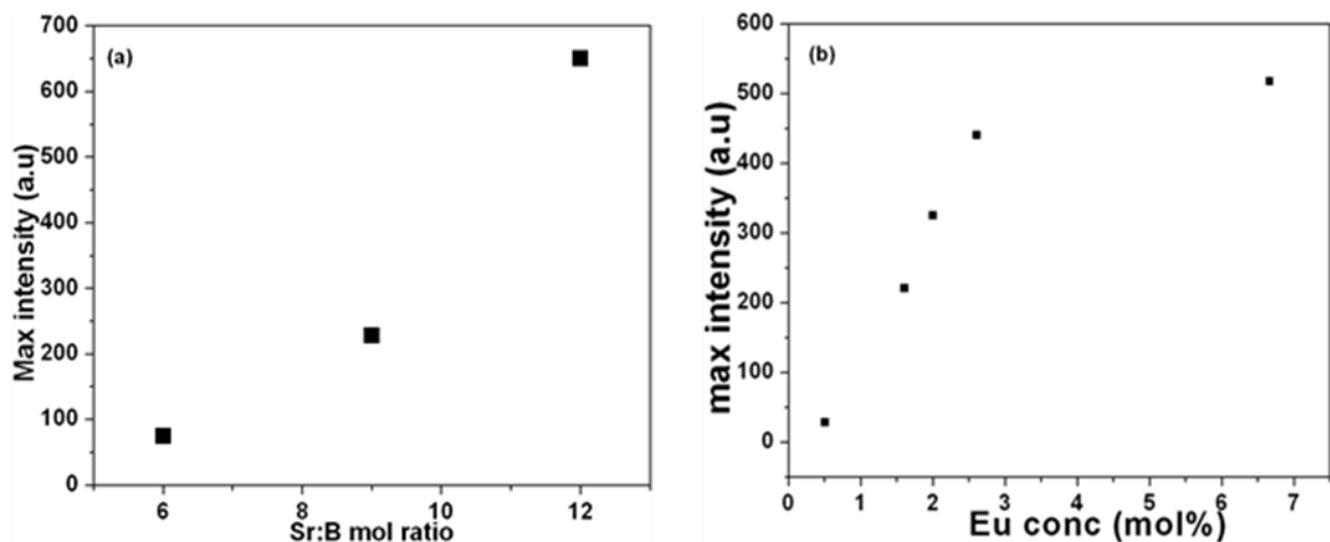


**Figure 5.3** (a) and (b) shows the excitation spectra ( $\lambda_{\text{em}} = 380 \text{ nm}$ )  $\text{SrB}_6\text{O}_{10}:\text{Eu}^{2+}$  obtained at various Sr:B mol ratio and Strontium nitrate concentrations.



**Figure 5.4** (a) and (b) shows emission spectra ( $\lambda_{\text{exc}} = 245 \text{ nm}$ ) of  $\text{SrB}_6\text{O}_{10}:\text{Eu}^{2+}$  obtained at various Sr:B mol ratio and Europium nitrate concentrations.

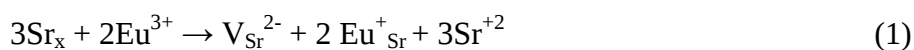
The emission at around 335, 380 and 420 nm may be attributed to  $\text{Eu}^{2+}$  transition from  $4f^65d \rightarrow 4f^7$  [17]. The peak at 615 nm is associated with  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transitions while the peak located at 680 nm was due to the transitions from  $^5\text{D}_0 \rightarrow ^7\text{F}_3$  levels in  $\text{Eu}^{3+}$  respectively [15]. The narrow red emissions in the region (600-630 nm) arise from the transitions of the remnant unreduced  $\text{Eu}^{3+}$  ion. The red emission only appears for samples with lowest Sr: B mole ratios. This was also confirmed by XRD measurement showing presence of binary phases at low Sr: B mole ratios. The results indicate that the luminescent intensity of  $\text{SrB}_6\text{O}_{10}:\text{Eu}^{2+}$ , phosphor increased with both increase in the Sr:B molar ratio and the Eu ion concentrations as shown in Figure 5.5 (a) and (b), respectively.



**Figure 5.5** (a) and (b) shows emission intensity of  $\text{SrB}_6\text{O}_{10}:\text{Eu}^{2+}$  at different Sr:B mol ratio and Europium nitrate concentrations respectively.

The increase in emission intensity may be due to increase in oxidiser: fuel mole ratios as the strontium: boron mole ratios increased which increased the energy transfer from  $\text{Sr}^{2+}$  to  $\text{Eu}^{2+}$  [16]. The  $\text{SrB}_6\text{O}_{10}:\text{Eu}^{2+}$  phosphors can be used as UV sensors. The change in the oxidation state of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  ion was well documented in the literature under a high-temperature treatment in air [13, 17, and 19].

In previous research it has been shown that the reduction of the  $\text{Eu}^{3+}$  to the  $\text{Eu}^{2+}$  ion could be explained by the charge compensation model. As  $\text{Eu}^{3+}$  ions are doped into  $\text{SrB}_6\text{O}_{10}$ , they may replace  $\text{Sr}^{2+}$  ions; although in order to maintain electrical neutrality of the compounds, two  $\text{Eu}^{3+}$  ions would be needed to substitute for three  $\text{Sr}^{2+}$  ions (the total charge of the two  $\text{Eu}^{3+}$  ions is equivalent to three  $\text{Sr}^{2+}$  ions). Therefore, one vacancy defects of one vacancy defect of  $\text{V}_{\text{Sr}}^{2-}$  with two negative charges, and two positive  $\text{Eu}_{\text{Sr}}^{+}$  defects would be created by each substitution of every two  $\text{Eu}^{3+}$  ions in the compound. The vacancy  $\text{V}_{\text{Sr}}^{2-}$  would act as a donor of electrons, while the two  $\text{Eu}_{\text{Sr}}^{+}$  defects may become acceptors of electrons. Consequently, by thermal stimulation in air, the negative charges in the vacancy defects of  $\text{V}_{\text{Sr}}^{2-}$  would be transferred to the  $\text{Eu}^{3+}$  sites and reduce  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  ions[18]. The whole process can be expressed by the following equations:





By adding Equation (2) - (3)



It was also observed that the ions in the compounds in which the reduction of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  has taken place in air had the same feature, i.e. a rigid crystal structure and the existence of tetrahedral anion group's viz.  $\text{BO}_4$ ,  $\text{AlO}_4$ ,  $\text{SO}_4$ , and  $\text{PO}_4$  [19].

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# Chapter 6

## Synthesis and Characterization of $\text{BaB}_8\text{BO}_{13}:\text{Eu}^{2+}$ nanophosphors Prepared Using Solution Combustion Method.

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### 6.1 Introduction

$\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  ions exhibit strong photoluminescence in variety of alkaline earth borates and are well known as activators in phosphors [1-4]. The  $\text{Eu}^{2+}$ -doped phosphors emit blue light, which originated in  $4f_65d \rightarrow 4f_7$  transition of  $\text{Eu}^{2+}$  ions while the  $\text{Eu}^{3+}$ -doped phosphors emit red light, which originated in  $5D_0 \rightarrow 7F_J$  transition of  $\text{Eu}^{3+}$  ions [5-7]. For example,  $\text{BaB}_8\text{BO}_{13}:\text{Eu}^{2+}$  and  $\text{BaMgAl}_2\text{O}_4:\text{Eu}^{3+}$  was used as blue and red phosphors, respectively, for plasma display panels [8]. Among various host materials for europium-doped nanocrystals, borates, especially barium borates have attracted much interest because of their rich varieties in structure, high transparency and exceptional optical damage threshold [9]. Barium octaborate  $\text{BaB}_8\text{O}_{13}$  is an excellent host material for luminescent ions. The structures of  $\text{BaB}_8\text{O}_{13}$  consist of two interlocking three dimensional infinite networks as triborate and pentaborate groups, which form  $\text{BO}_3$  triangle and  $\text{BO}_4$  tetrahedral units [10-11]. In the  $\text{BaB}_8\text{O}_{13}$  lattice, the rare earth ions are isolated from each and therefore exhibit an intense luminescence. In this investigation  $\text{BaB}_8\text{O}_{13}:\text{Eu}^{2+}$  phosphor was prepared using solution combustion method. The synthesis is based on the exothermic reaction between the fuel (urea) and oxidizer (ammonium nitrate). The material properties were characterized by various techniques. Then, the influence of Eu-doping on the crystallization of the parent glasses was investigated using various techniques and the luminescent properties of the parent glasses and the obtained glass-ceramics were estimated. Under UV excitation (250 nm),  $\text{BaB}_8\text{O}_{13}:\text{Eu}^{2+}$  shows intense broad emission band peak at 400 nm. The effect of concentration of Ba:B molar ratios and concentration of  $\text{Eu}^{2+}$  ions and annealing temperature on the PL intensity were also studied.

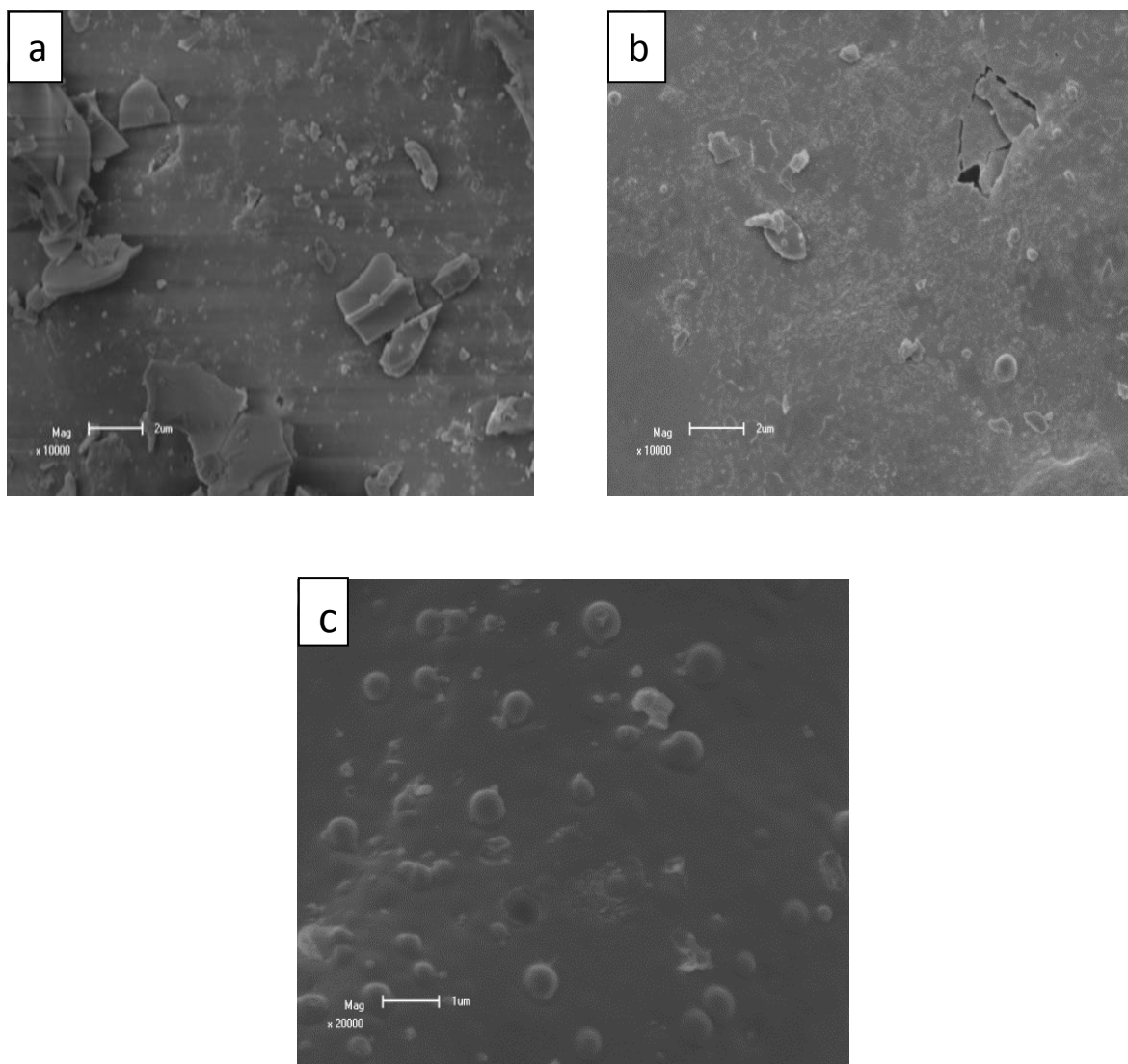
## 6.2. Results and discussions

### 6.2.1 Morphological and structural properties

It is well known, that the final surface morphology and structure of a specific sample is significantly influenced by the overall bulk composition of the phosphor powder. The variations in morphology and structural features of the phosphor powders dependence on the bulk composition were therefore closely monitored for the various samples that were prepared with the different Ba:B molar ratios and various Eu ion content. Figure 1(a) shows the representative SEM images of  $\text{BaB}_8\text{O}_{13}:\text{Eu}^{2+}$  samples obtained for various Ba:B mole ratios. As can be seen from figure, the products are mainly large agglomerated microparticles that appear to contain particles with sizes in nano ranges as primary source. The as-prepared powder reflects the foamy and agglomerate particle nature of the powder. The foamy structure of  $\text{BaB}_8\text{O}_{13}:\text{Eu}^{2+}$  reflects the inherent nature of the reaction. Theoretical equation assuming complete combustion may be written for blue phosphor  $\text{BaB}_8\text{O}_{13}:\text{Eu}^{2+}$  using urea as follows:



The equation above can only describe an ideal process. A typical SEM image figure 1 (b) of samples with Eu ions reveals that the sample is composed of more uniform nano particles with relatively less agglomerates. It indicates that the amount of Eu concentration has no obvious influence on the morphology and size. For the solution-combustion synthesis of oxides, metal nitrates are employed as oxidizer and urea is employed as a reducer. Figure1(c) shows SEM image when annealed at high temperature ( $700^\circ\text{C}$ ) gives large grains size and better crystallization.



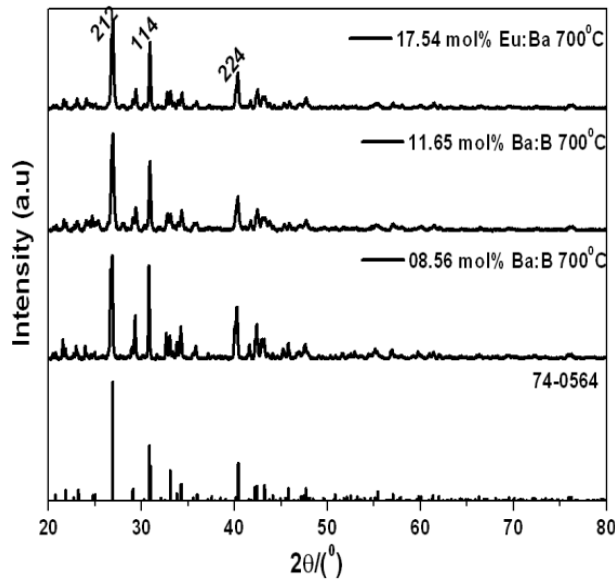
**Figure 6.1** (a) SEM image of Ba-B-O: Eu<sup>2+</sup> of samples with 9 mol% Ba:B mole ratio. (b) A typical SEM image of samples with 12 mol% Ba:B mole ration. (c) A typical SEM image of samples annealed at temperature (700 °C) of 12 mol% of Ba:B mole ration.

Figure 2 gives the XRD pattern of Eu<sup>2+</sup> doped BaB<sub>8</sub>O<sub>13</sub> as-prepared and annealed phosphors for several Ba:B mole ratios and varying amount of Eu content. All the as prepared samples annealed up to 600<sup>0</sup>C shows the presence of significant amount of Ba(NO<sub>3</sub>)<sub>2</sub>. All diffraction peaks of samples annealed at temperature above 700<sup>0</sup>C corresponds to the tetragonal phase of BaB<sub>8</sub>O<sub>13</sub> (JCPDS no. 74-0564) structure. Comparing the given XRD patterns, the positions and intensities of the main peaks are nearly the same. No diffraction line resulted from the source materials and other impurity crystal structures. Figure 2 (b) shows the behaviour of temperature influence on the structure of BaB<sub>8</sub>O<sub>13</sub>. Further, the crystal structure of BaB<sub>8</sub>O<sub>13</sub> showed no obvious change after Eu<sup>2+</sup> doping. The average structural unit distance was

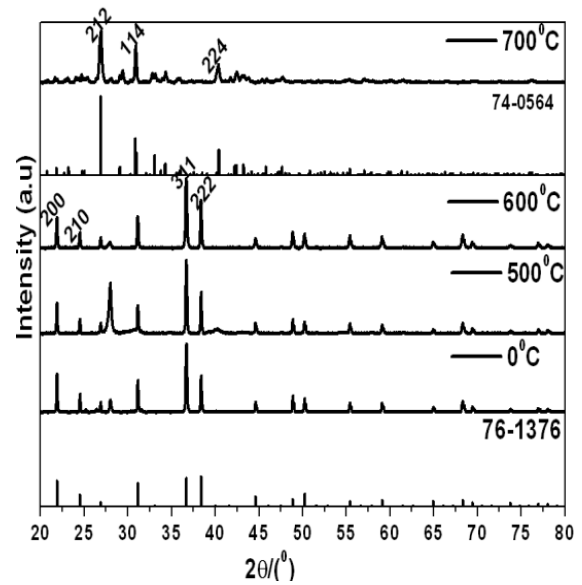
estimated from the full width at half maximum of the diffraction peak by the Scherrer equation:

$$D = \frac{k\lambda}{B \cos \theta}$$

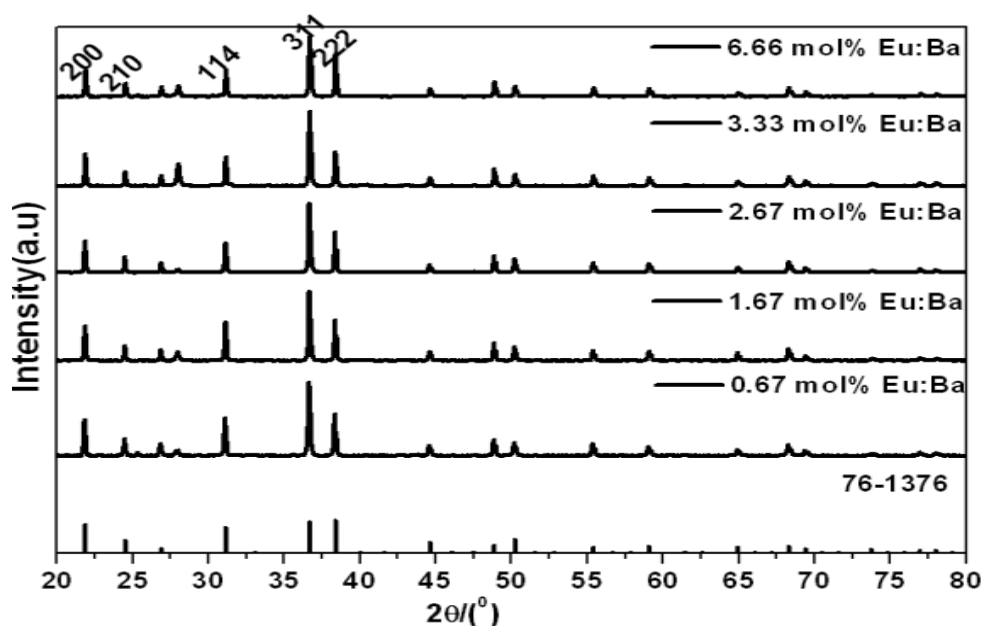
Where  $D$  is the mean crystallite diameter,  $k$  (0.89) is the Scherrer constant,  $\lambda$  is the X-ray wavelength (1.5406 Å) and  $B$  is the full width half maximum (FWHM) of the  $\text{BaB}_8\text{O}_{13}:\text{Eu}^{2+}$  diffraction peak. The average crystallite sizes ( $D$ ) of the annealed  $\text{BaB}_8\text{O}_{13}:\text{Eu}^{2+}$  particles is about 14.13 nm calculated using the most intense reflection at  $2\theta = 26.88^\circ$ .



**Figure 6.2 (a)** X-ray diffraction patterns of  $\text{BaB}_8\text{O}_{13}$  phosphors annealed at 700 °C for various Ba:B mole ratio.



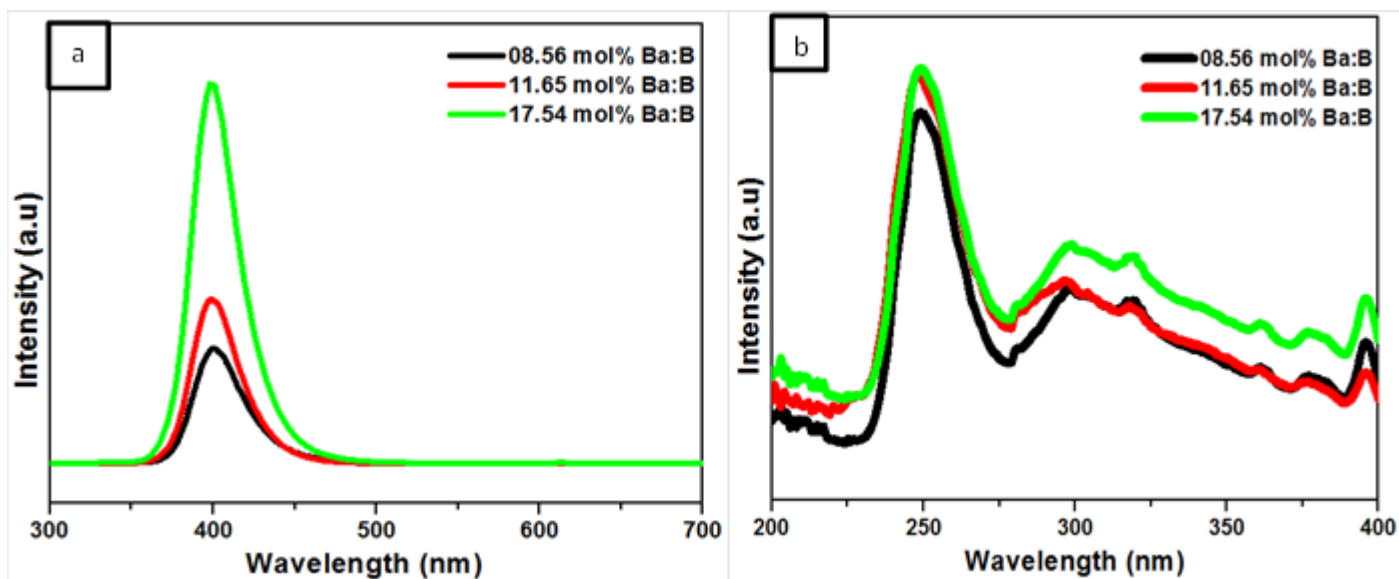
**Figure 6.3 (b)** X-ray diffraction patterns of  $\text{BaB}_8\text{O}_{13}$  different annealing temperature of Ba:B mole ratio.



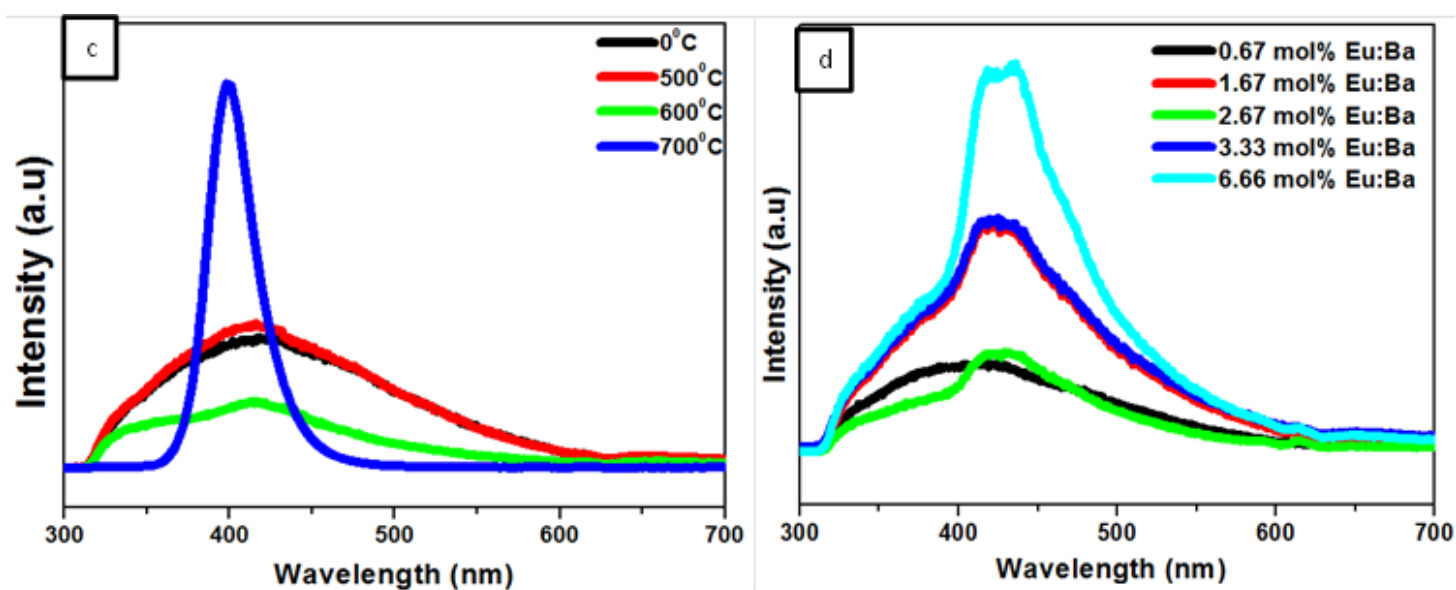
**Figure 6.4 (c)** X-ray diffraction patterns of as prepared phosphors with Eu:Ba mole ratio annealed below 600 °C.

### 6.2.2 Optical properties

The excitation and emission spectra of  $\text{BaB}_8\text{O}_{13}:\text{Eu}^{2+}$  are shown in figure 3. From figure 3(a) the  $\text{Eu}^{2+}$  ion shows strong UV absorption and efficient emission in  $\text{BaB}_8\text{O}_{13}$ . Variation of Ba:B mole ratios has no significant effects on the structure. Excitation spectra show strong excitation bands attributed to a charge transfer band (CTB) of  $\text{Eu}^{2+}$  band in the short UV region (250 nm) and broad band maximum at 325 nm, attributed to host excitation band. This is good evidence that the Eu ions exist as  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  inside the two as-made  $\text{BaB}_8\text{O}_{13}$  phosphors. The emission spectra peaks at 400 nm assigned to  $4f_65d \rightarrow 4f_7$ . In order to investigate the energy migration different samples doped with different Ba:B mole ratios and concentrations of  $\text{Eu}^{2+}$  ions were prepared under the same conditions. The concentration dependence of the emission intensity of prepared  $\text{Eu}^{2+}$  doped  $\text{BaB}_8\text{O}_{13}$  phosphors annealed at 700°C are showed in figure 3(b). Figure 3(c) shows the temperature influence that annealing at different temperature changes the sharp of the sample, annealing up to 600°C is for  $\text{Ba}(\text{NO}_3)_2$  at (700°C) is for  $\text{BaB}_8\text{O}_{13}$  as it was seen on XRD. The intensity of sample changes as the annealing temperature increase changing also the structure of the phosphor. Figure 3(d) shows variations of Eu concentrations significantly affect the initial luminescent intensity with an increase in  $\text{Eu}^{2+}$ . It can be observed the Ba: B mole ratio changes the luminescence property of the phosphors.



**Figure 6.5** (a) Excitation spectra ( $\lambda_{em} = 400$  nm) of  $BaB_8O_{13}$  for various Ba:B mole ratio. (b) Emission spectra of  $BaB_8O_{13}$  ( $\lambda_{exc} = 230$  nm) for various Ba:B mole ratio annealed at 700 °C.



**Figure 6.6** (c) Emission spectra of  $BaB_8O_{13}$  ( $\lambda_{exc} = 250$  nm) for 12 mol% of Ba:B annealed at different Temperature. Emission spectra ( $\lambda_{exc} = 250$  nm) of  $BaB_8O_{13}$  obtained for various Eu:Ba annealed below 600 °C

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# Chapter 7

## Effects of precursor concentration On Morphological and Structure Characterization of $\text{TiO}_2$ via sol-Gel method

### 7.1 Introduction

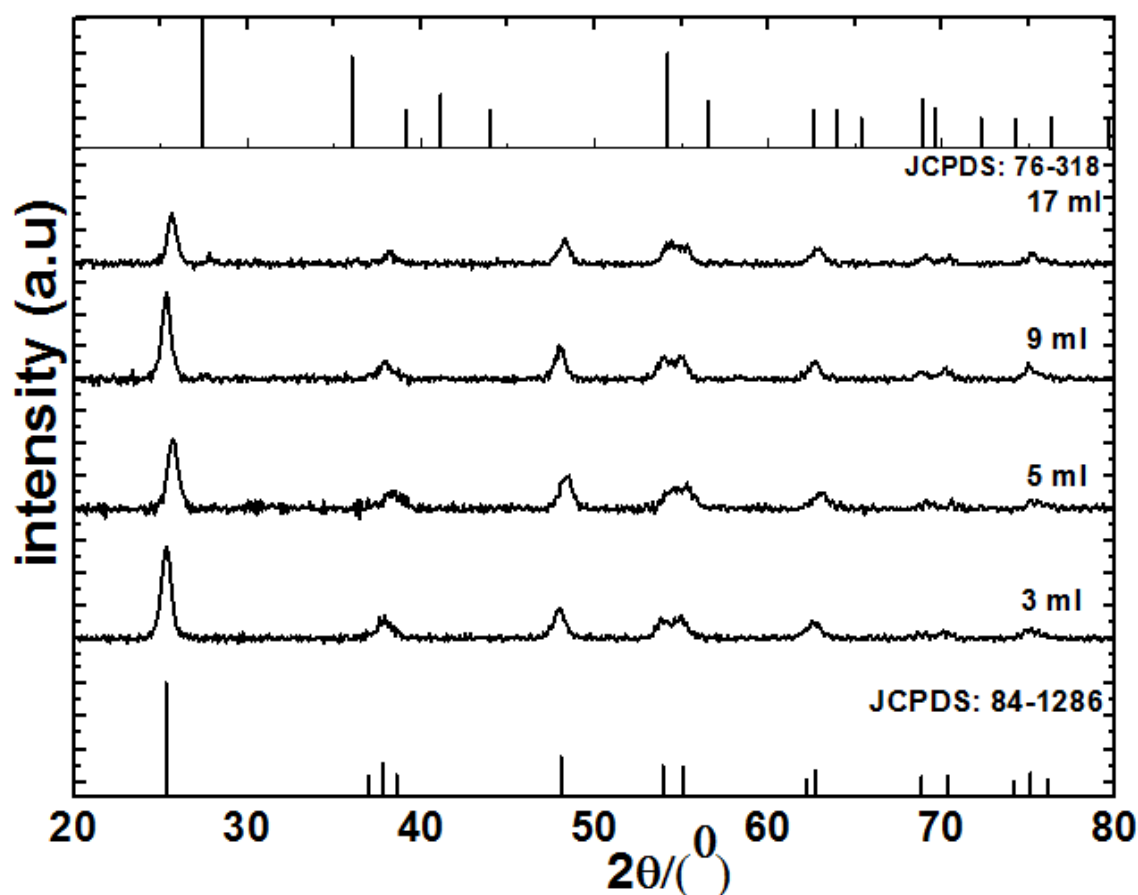
Nano-crystalline  $\text{TiO}_2$  thin films have been intensively investigated in recent years, because of their different potential applications including air purification [1–5], water purification or water treatment [6–9], sterilization or disinfections [10–11], solar energy cells [12–13] and gas sensors [14]. Heterogeneous solar photocatalysts effectively utilize the ultraviolet (UV) energy from the sunlight, a renewable energy, for the photocatalytic reactions that can potentially reduce the treatment costs. Normally,  $\text{TiO}_2$  exhibits polymorphs with three phases; anatase, rutile as tetragonal whereas brookite orthorhombic.

While rutile phase is optically active and the most stable of these three; anatase phase has attracted much attention because of its higher photocatalytic activity for photocatalysis [15] and solar energy conversion [16–17]. At present, the  $\text{TiO}_2$  photocatalytic thin films can be prepared by a number of methods such as dip-coating, sol-gel method, thermal oxidation of metal or reactive magnetron sputtering [3–9]. Sol-gel process is one of the most common methods used for producing photocatalytic  $\text{TiO}_2$  material in the form of powder or coatings.

In this study the effect of Tetra-n-butyl-orthotitanate on the structure, morphology and optical properties of the synthesized  $\text{TiO}_2$  nanoparticles was investigated. The primary aim of the investigation was to evaluate the effect of Tetra-n-butyl-orthotitanate on the stability of  $\text{TiO}_2$  nanoparticles particularly for the use of wide band gap, high temperature devices such as LEDs and a variety of other sensing devices.

## 7.2 Results and discussion

### 7.2.1 XRD analysis



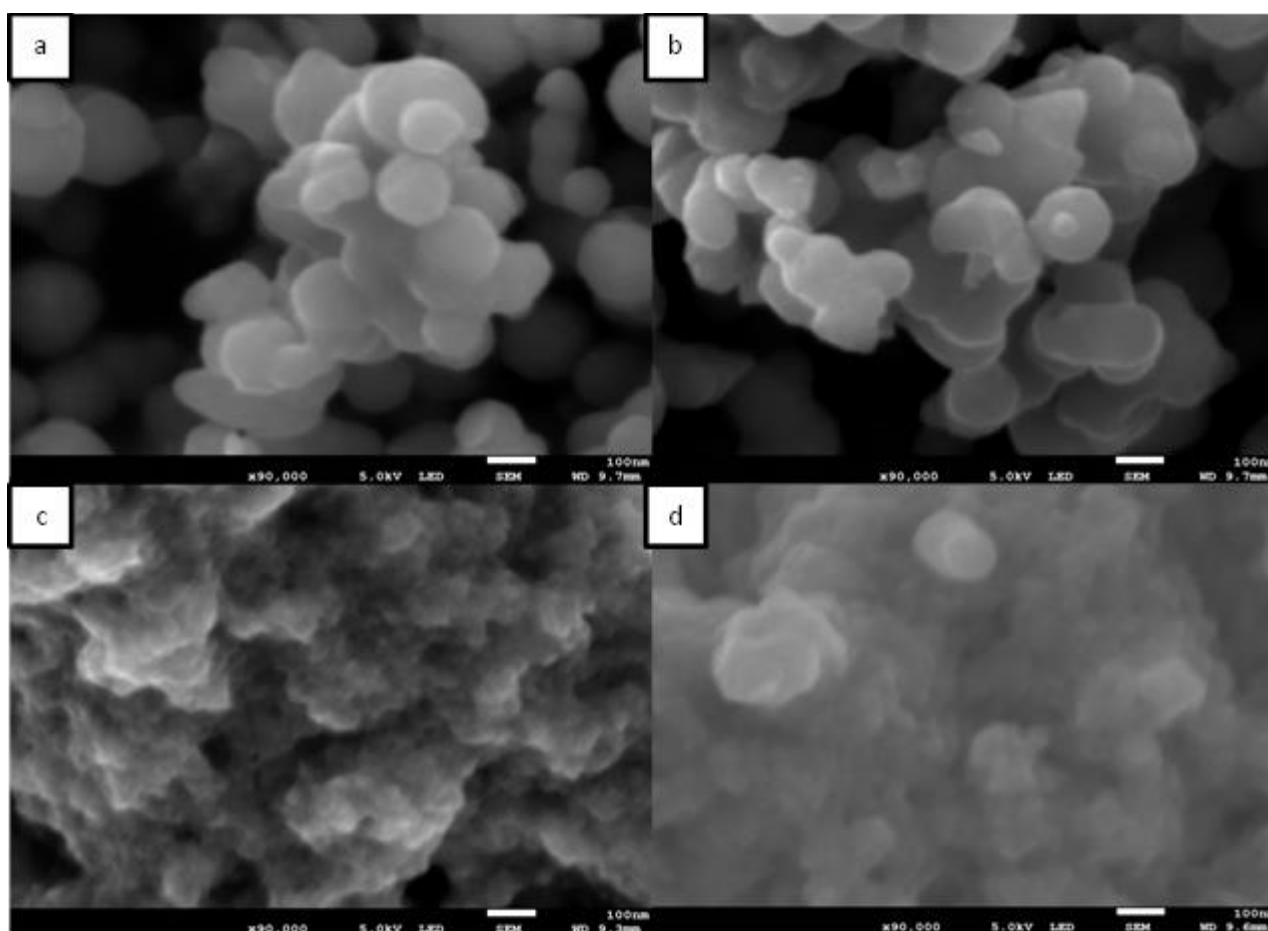
**Figure 7.1** XRD patterns of TiO<sub>2</sub> nanoparticles prepared at different concentrations of Tetra-n-butyl-orthotitanate.

Powder x-ray diffraction (XRD) was used for identification of the particles size, crystal structures, crystal orientation and lattice parameter. X-ray powder diffraction (XRD) was used to characterize the TiO<sub>2</sub> powder at different concentrations of Tetra-n-butyl-orthotitanate to determine the crystal structure of material. Figure 1 shows the XRD patterns of TiO<sub>2</sub> powder prepared using the sol-gel solution. The XRD pattern for all the samples prepared at 3 ml clearly shows anatase TiO<sub>2</sub> well consistent with tetragonal structure with lattice constants  $a = 3.81 \text{ \AA}$ ,  $c = 9.498 \text{ \AA}$  indexed to JCPDS card no. 84-1286. The crystallite sizes were estimated using (101) diffraction peaks according to the Scherrer equation (7.1) [18],

$$T = \frac{K\lambda}{\beta \cos\theta} \quad (7.1)$$

where  $t$ ,  $K$ ,  $\lambda$ ,  $\beta$  and  $\theta$  are the grain size, constant (0.94), wavelength of X-ray ( $\text{CuK}\alpha$ -1.54184 Å), the true half-peak width and the half diffraction angle in degree, respectively. The crystallite sizes of all powder are 16, 17,25,38,41 nm respectively.

### 7.2.2 SEM analysis

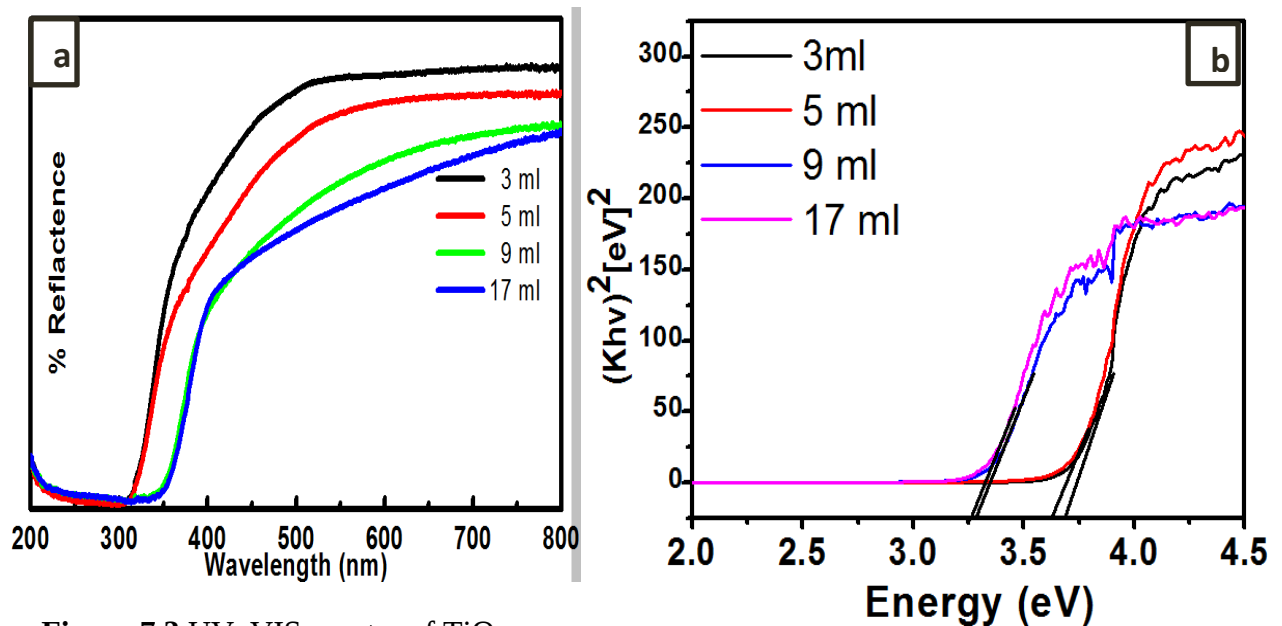


**Figure 7.2** SEM of  $\text{TiO}_2$  nanoparticles prepared at different concentrations of Tetra-n- butyl-orthotitanate.

Scanning electron microscopy (SEM) studies was used to examine morphology and shape of nanomaterials. From figure 7.2, at low concentration of Tetra-n-butyl-orthotitanate spherical nanoparticles were observed. As the concentrations of precursors increases the nanoparticles

become more agglomerated. It can be seen that high homogeneity emerged in sample by increasing the concentrations of Tetra-n-butyl-orthotitanate. Whenever the concentration of precursor was low, the samples were less agglomerated with small voids between nanoparticles. The observed voids were due to degassing of nitrates during the annealing process [19]. Voids between the nanoparticles decreased with the increase in the concentrations of precursor. The morphology of nanoparticles became highly clustered with small spherical shapes at high concentration of Tetra-n-butyl-orthotitanate. Thus, concentration of Tetra-n-butyl-orthotitanate played an important role on the surface morphology of the nanoparticles because the size of the nanoparticles decreased with increasing precursor's concentration.

### 7.2.3 UV-vis analysis

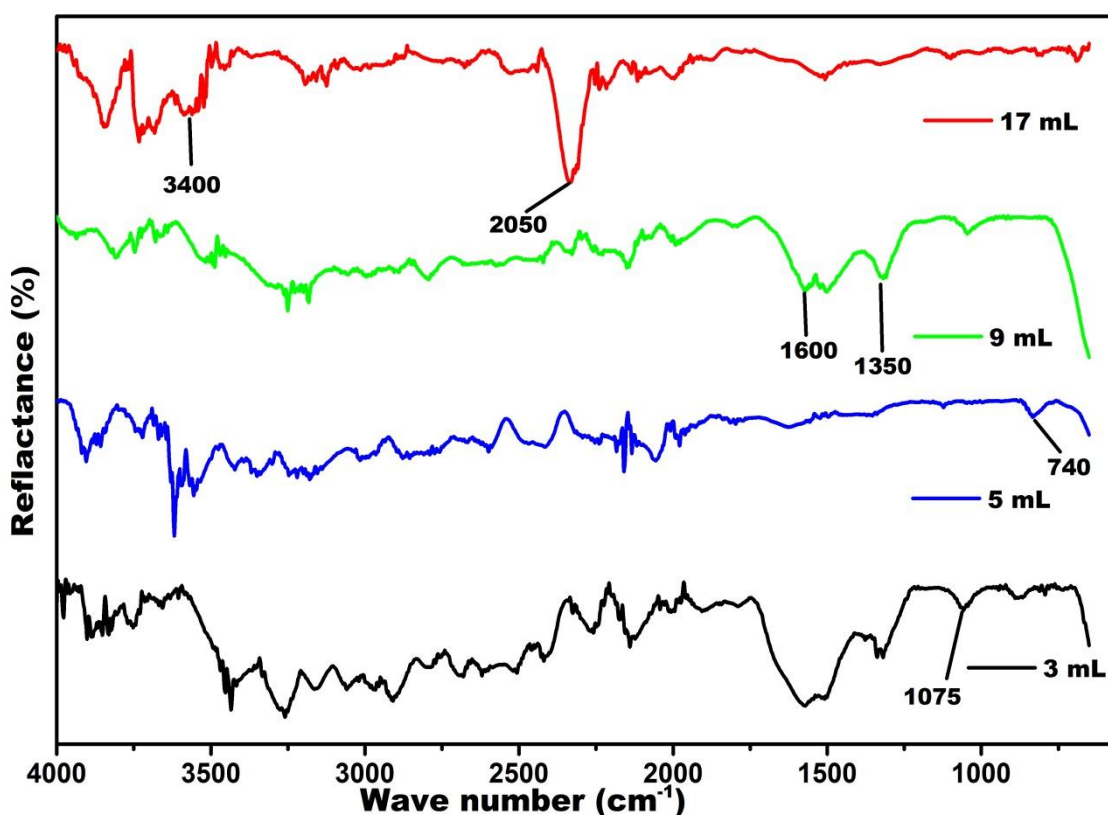


**Figure 7.3** UV–VIS spectra of TiO<sub>2</sub> nanoparticles prepared at different concentrations of Tetra-n- butyl-orthotitanate.

Figure 7.3 shows the diffuse reflectance spectra of pure TiO<sub>2</sub> prepared at different concentrations of Tetra-n-butyl-orthotitanate. The method adopted to acquire the absorption spectra of powder samples in DRS mode is that of Kubelka-Munk [20]. The equation for the Kubelka Munk method is represented by  $F(R) = (1 - R)^2/2R$ , where  $R$  is the reflectance and  $F(R)$  is the absorbance [20]. Samples exhibit an absorption peak at 330 nm corresponding to the maximum absorption when electrons are excited from the valence to the conduction band.

The synthesized  $\text{TiO}_2$  nanomaterials band gap energy (3.7, 3.6, 3.3, 3.3 eV) are larger than the value of 3.2 eV for the bulk  $\text{TiO}_2$  nanomaterials. This is true due to the fact that the band gap energy of the semiconductors depends on the particle size [21–22]. With increasing the concentration of Tetra-n-butyl-orthotitanate, the reflectance in the UV region obviously decrease and the absorption edge shifts slightly to a higher wavelength region. The red shift of the absorption peak should be due to quantum-size effects [23]. The band gap decreasing with increases particle size and the absorption edge is shifted to a lower energy (red shift) with increasing particle size. The band gap values validates our crystallite size results according to which smaller crystallite size should have larger band gap and large crystallite size should have smaller band gap [24]. Thus, from XRD results the crystalline size increased when increasing concentration of Tetra-n- butyl-orthotitanate which results in decrease in band gap energy.

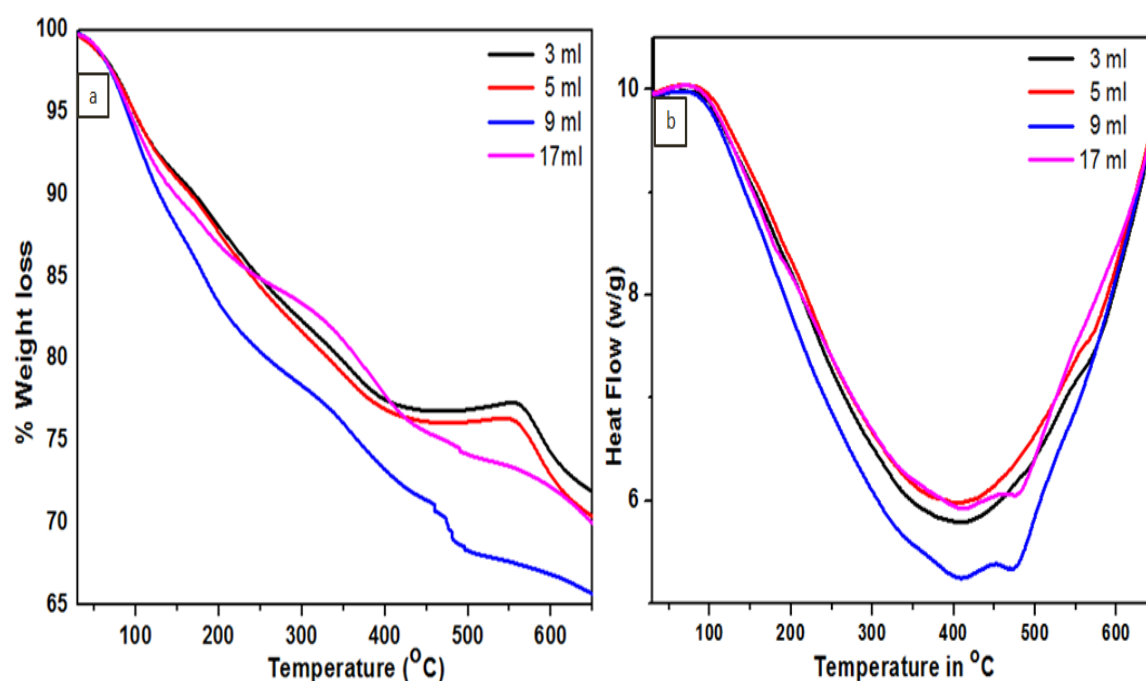
#### 7.2.4 FTIR analysis



**Figure 7.4** FTIR spectra  $\text{TiO}_2$  nanoparticles prepared at different concentrations of Tetra-n-butyl-orthotitanate.

The characterization of functional groups on the nanopowders was important to understand the photoinduced super-hydrophilicity on the surface. An FTIR spectrum obtained from the surface of nanopowders in figure 7.4. Adsorption band at about  $3400\text{ cm}^{-1}$  is assigned to the stretching modes of O-H bonds and is related to surface about water. The adsorption band at  $1600\text{ cm}^{-1}$  is attributed to the bending vibration of H-O-H bonds. The adsorption band at about  $440\text{ cm}^{-1}$  is due to the stretching vibrations of Ti-O-Ti and Ti-O bonds [24]. While the adsorption band at about  $1075, 1150\text{ cm}^{-1}$  is due to O-H bending stretching vibrations and O-H bending vibration at  $740\text{ cm}^{-1}$  [25].

### 7.2.5 TGA & DSC analysis

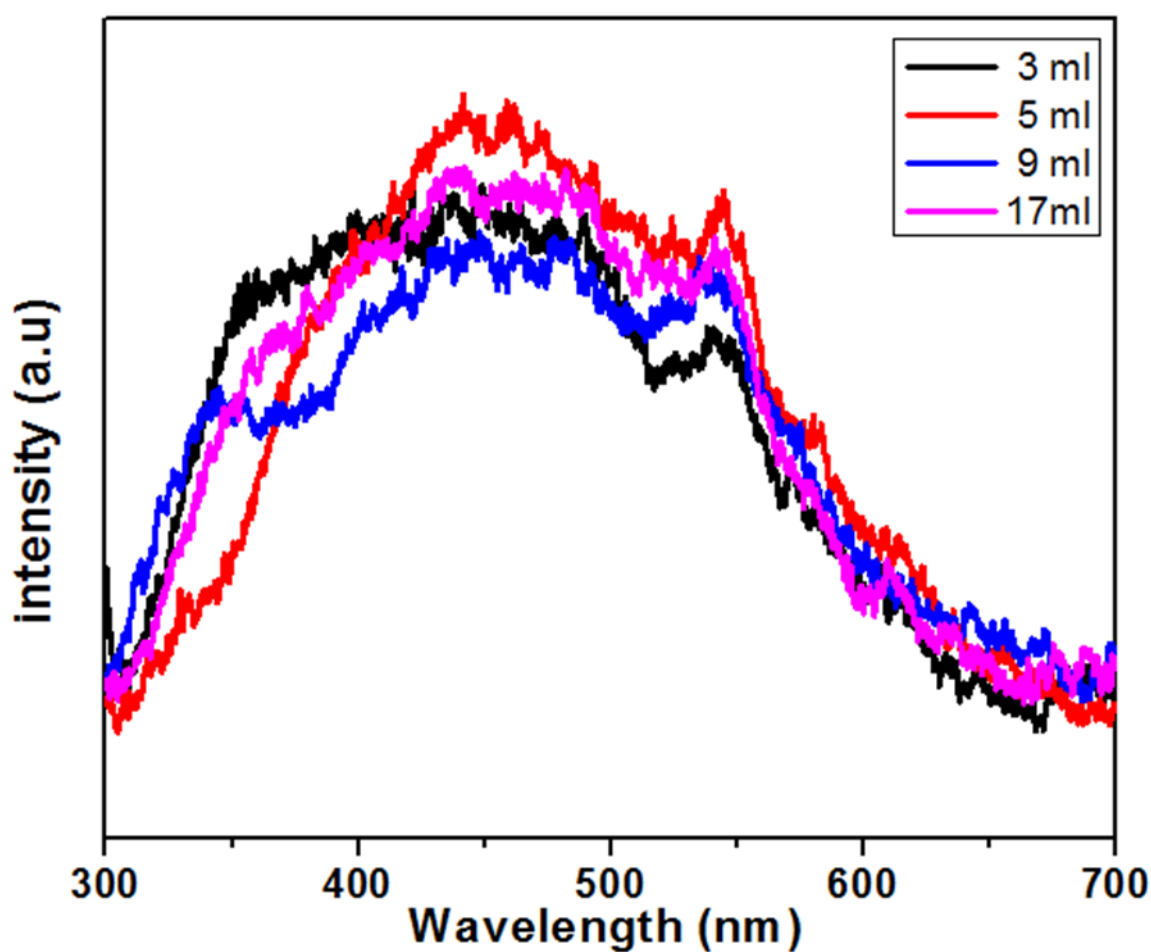


**Figure 7.5** (a) TGA of TiO<sub>2</sub> nanoparticles, (b) DSC of TiO<sub>2</sub> nanoparticles prepared at different concentrations of Tetra-n-butyl-orthotitanate.

The TGA-DSC curves of anatase nanopowder with various weight percentages are shown figure 7.5. To understand the thermal properties of the TiO<sub>2</sub> nanomaterials, TGA and DSC were employed to determine the change in weight loss and enthalpies, respectively. Figure 7.5 (a) and (b) shows the TGA and DSC curves of sol-gel derived TiO<sub>2</sub> nanoparticles. In

figure 7.5 (a), the total weight loss of  $\text{TiO}_2$  precursors is about 23 – 35 %. The thermal decomposition of gel-precursors is almost finished at about 400 °C. Up to this temperature, the weight loss is associated with water and organic compounds removal [25]. The DSC plot in figure 7.5 (b) shows a broad endothermic curve centred at around 400 °C. DSC curves indicate strong endothermic effects correlated with the precursor/organic compounds thermal dissociation and water evaporation [26].

### 7.2.6 PL analysis



**Figure 7.6** PL emission spectra of  $\text{TiO}_2$  powder prepared at different concentrations of Tetra-n-butyl-orthotitanate ( $\text{C}_{16}\text{H}_{38}\text{O}_4\text{Ti}$ ).

The  $\text{TiO}_2$  sample revealed a broad intensity band centered at 460 nm with a weak band at higher wavelength (560 nm). These two emissions were assigned to photon incident lines and oxygen defect trap exciton peak, respectively [27]. This visible luminescence band arises

from the radiative recombination of electrons via intrinsic surface states of  $\text{TiO}_2$  nanoparticles.

It is well known that in case of nanoparticles, surfaces play important roles as the surface-to-volume ratio becomes increasingly large at a nanometer size. As  $\text{TiO}_2$  is a strongly ionic metal oxide, the filled valance band is mainly composed of the outermost 2p orbitals of oxygen atoms, and the lowest conduction band is derived from titanium 3d orbitals [28].  $\text{TiO}_2$  nanoparticles, and the size of particle was fine so that the average distance the electrons could move freely was very short. These intrinsic surface states act as luminescence centers under an appropriate excitation as can be seen in the present work.

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## Chapter 8

# Effect of Temperature on the synthesis and Characterization of Titanium dioxide powder prepared by a sol-gel method for solar energy applications

### 8.1 Introduction

Since the discovery of photocatalytic water splitting on  $\text{TiO}_2$  electrodes [1-2], titanium dioxide has been extensively studied and proven to be a very efficient and versatile material with remarkable properties in several technological applications, such as photocatalysis [3], photovoltaic solar cells and sensors [4]. Such applications have become even more important with the urgent need for effective sustainable energy solutions, and for alternative methods for decontamination of air and water streams.

The bulk material of  $\text{TiO}_2$  is widely nominated for three main phases of rutile, anatase and brookite. Among them, the  $\text{TiO}_2$  exists mostly as rutile and anatase phases which both of them have the tetragonal structure. This structure is less stable than rutile and transforms to rutile in the 700–900 °C temperature range.

Titanium oxides is very promising candidate for future technology of thin layers because of its interesting mechanical, thermal and chemical properties. Titanium oxide ( $\text{TiO}_2$ ) is a cheap, non-toxic, and non-biodegradable material, hence it's widely used in various industries [5]. Moreover, it is a semiconductor which is insensitivity to visible light due to its band gap (3.2 eV) which enables it to absorb in the near ultraviolet region [6]. When irradiated with UV light,  $\text{TiO}_2$  nanosized powder shows strong oxidizability and reducibility [7, 8].

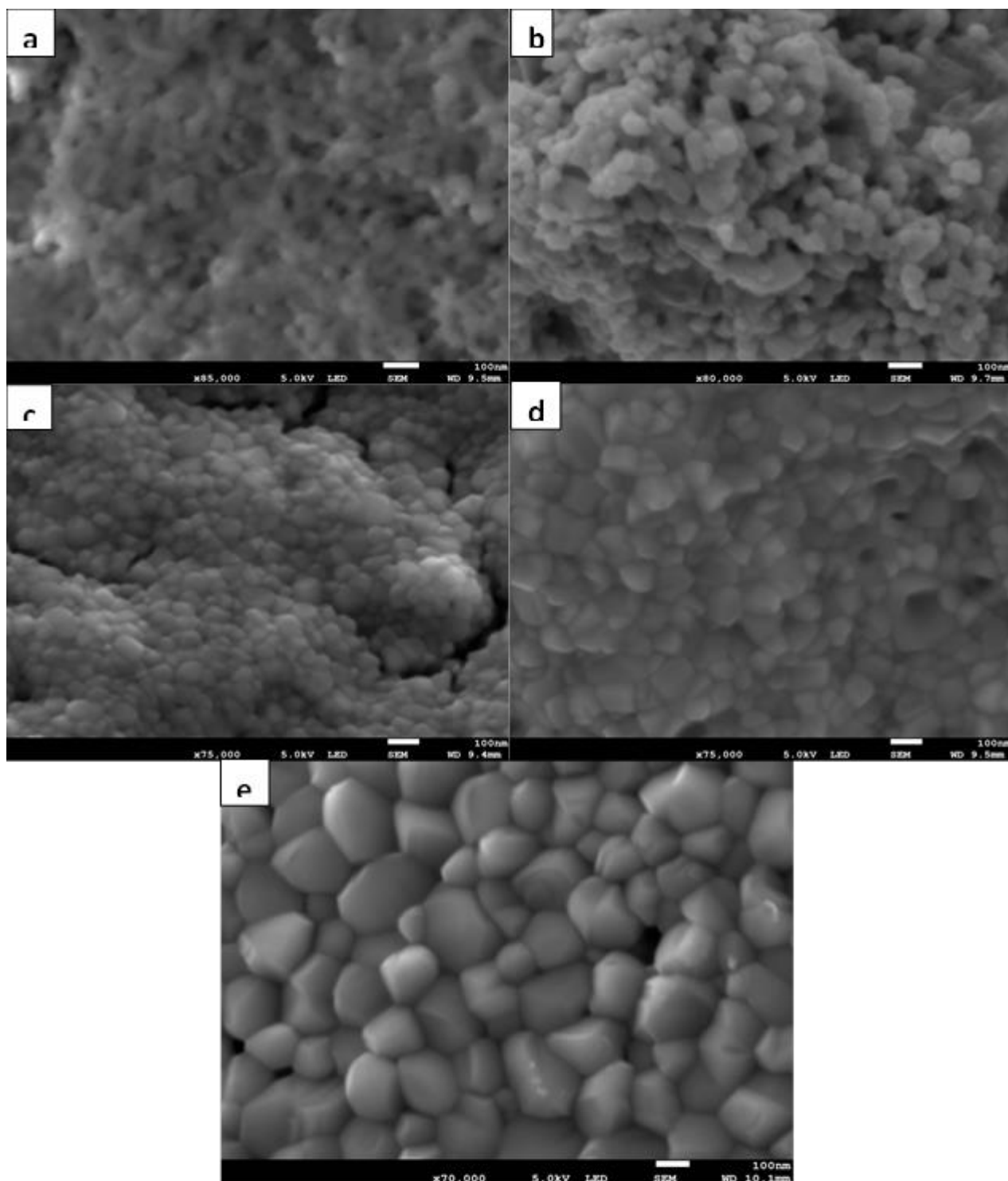
The preparation of TiO<sub>2</sub> nanoparticles has been extensively studied recently using different synthesis methods with the aim of developing materials with improved TiO<sub>2</sub> activity [9]. This preparation techniques include wet chemical methods such as chemical precipitation method [10], chemical vapour deposition (CVD) [11], the sol-gel technique [12] and combustion method [13]. But, these techniques require long period post treatment, high temperature, costly reagents and other are too expensive. Within these methods the sol-gel method has been considered to be a promising route for the synthesis of nanoparticles for photo-catalytic materials.

In this work, impact of annealing temperature on TiO<sub>2</sub> nanoparticles has been studied. The phase transformation was investigated by an X-ray diffractometer (XRD). The nanostructure was characterized by a scanning electron microscope (SEM), Energy dispersive x-ray spectroscopy (EDS) was used to study elemental analysis or chemical characterization of a sample.

## **8.2 Results and discussion**

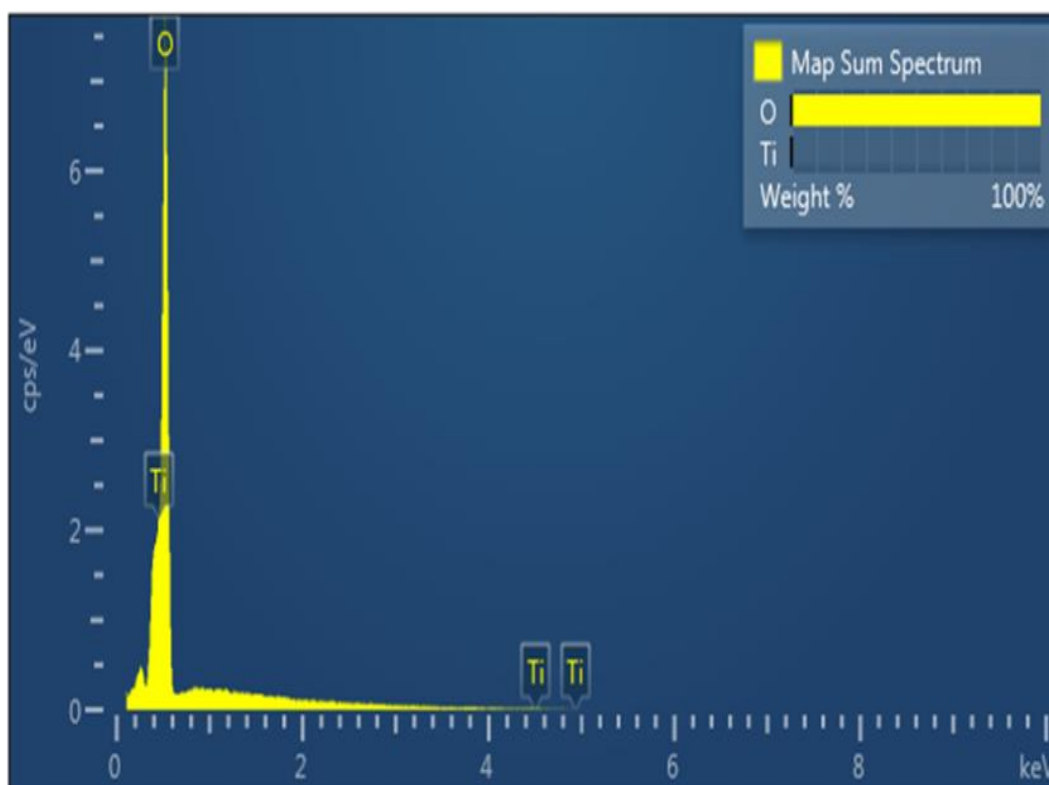
### **8.2.1 SEM analysis**

Figure 8.1 (a-d) show SEM micrographs of the TiO<sub>2</sub> powder prepared by sol-gel method calcined at different temperature 500 - 900 °C. The EDS (Energy dispersive x-ray spectroscopy) was connected to the SEM machine and used to study the elemental composition our sample. Scanning electron microscopy (SEM) studies were used to examine morphology and shape of nanomaterials. From the figures, the most of the particles are almost spherical in shape with uniform size distribution. A closer examination of these figures reveals a well-defined particle like morphology, having abundance of spherical-shaped particles, with the average agglomerated particle size in the range of 14-20 nm. The spherical shape is significantly important not only for the design of surface properties and surface area, but also for tuning the electronic structure i.e., to make the visible light spectrum more active for the better photocatalytic activity [14].



**Figure 8.1:** The SEM images of the synthesized TiO<sub>2</sub> nanomaterial (a) Calcination of 600 °C, (b) Calcination of 700 °C, (c) Calcination of 800 °C, (d) Calcination of 900 °C.

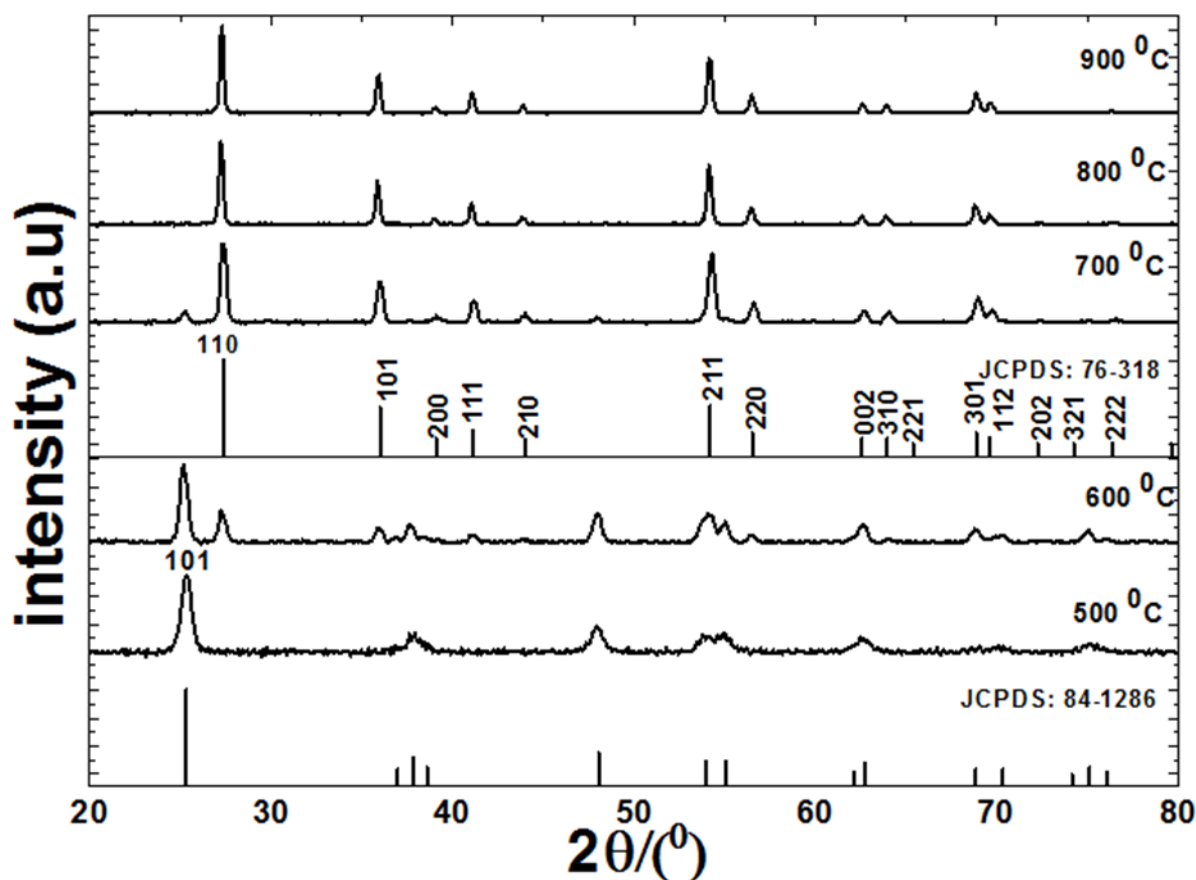
### 8.2.2 EDS analysis



**Figure 8.2:** Energy dispersive x-ray spectroscopy (EDS) of TiO<sub>2</sub> nanoparticles

Energy dispersive x-ray spectroscopy (EDS) is an analytical technique used for the elemental analysis or chemical characterization of a sample. Energy Dispersive Spectroscopy (EDS) allows one to identify what those particular elements are and their relative proportions (Atomic percentage). EDS analysis usually involves the generation of an X-ray spectrum from the entire scan area of the SEM. The elemental analyses of the synthesized TiO<sub>2</sub> nanomaterials are clearly shown below in figures 2. The EDS results provided evidences that the required phase of titanium (Ti) and oxygen (O) were present in the sample at calcination temperature of 900 °C.

### 8.2.3 XRD analysis



**Figure 8.3:** XRD pattern of the prepared nanoparticles at the different calcination temperature.

The figure shows that the X-ray diffraction (XRD) patterns of the powder samples for different calcination temperature. XRD patterns shows that the samples calcined at  $T = 600\text{ }^{\circ}\text{C}$  have both anatase and rutile structure of  $\text{TiO}_2$  nanoparticles with a dominance of anatase structure. The XRD pattern for the samples annealed at  $500\text{ }^{\circ}\text{C}$  clearly shows anatase  $\text{TiO}_2$  well consistent with tetragonal structure with lattice constants  $a = 3.81\text{ \AA}$ ,  $c = 9.498\text{ \AA}$  indexed to JCPDS card no. 84-1286. As the calcined temperature rose to  $700\text{ }^{\circ}\text{C}$ , the rutile structure becomes dominant over the anatase structure. At calcined temperature  $800\text{ }^{\circ}\text{C}$  and  $900\text{ }^{\circ}\text{C}$ , the anatase structure disappears and the samples show monostructure. The rutile phase appeared in XRD peaks when calcined at the temperature above  $700\text{ }^{\circ}\text{C}$  and it was confirmed with the JCDPS card No. 76-318. Therefore, it was concluded that the anatase to rutile transformation occurred at a temperature between  $700\text{ }^{\circ}\text{C}$  and  $800\text{ }^{\circ}\text{C}$ . The factors

affecting reaction rate of anatase to rutile are transformation reported in literature [15]. The mean particle size (D) was calculated using the Debye–Scherrer equation given below. where K is a constant equal to 0.9  $\lambda$  is the wavelength of the Cu K $\alpha$  radiation,  $\beta$  is the half-peak width of the diffraction peak in radiant and  $\theta$  is the Braggs angle of (101) plane.

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (8.1)$$

where  $\beta$  is full width half maxima,  $\theta$  is angle of reflection. The grain size increases as the temperature increases as increase in crystal size.

#### 8.2.4 FTIR analysis

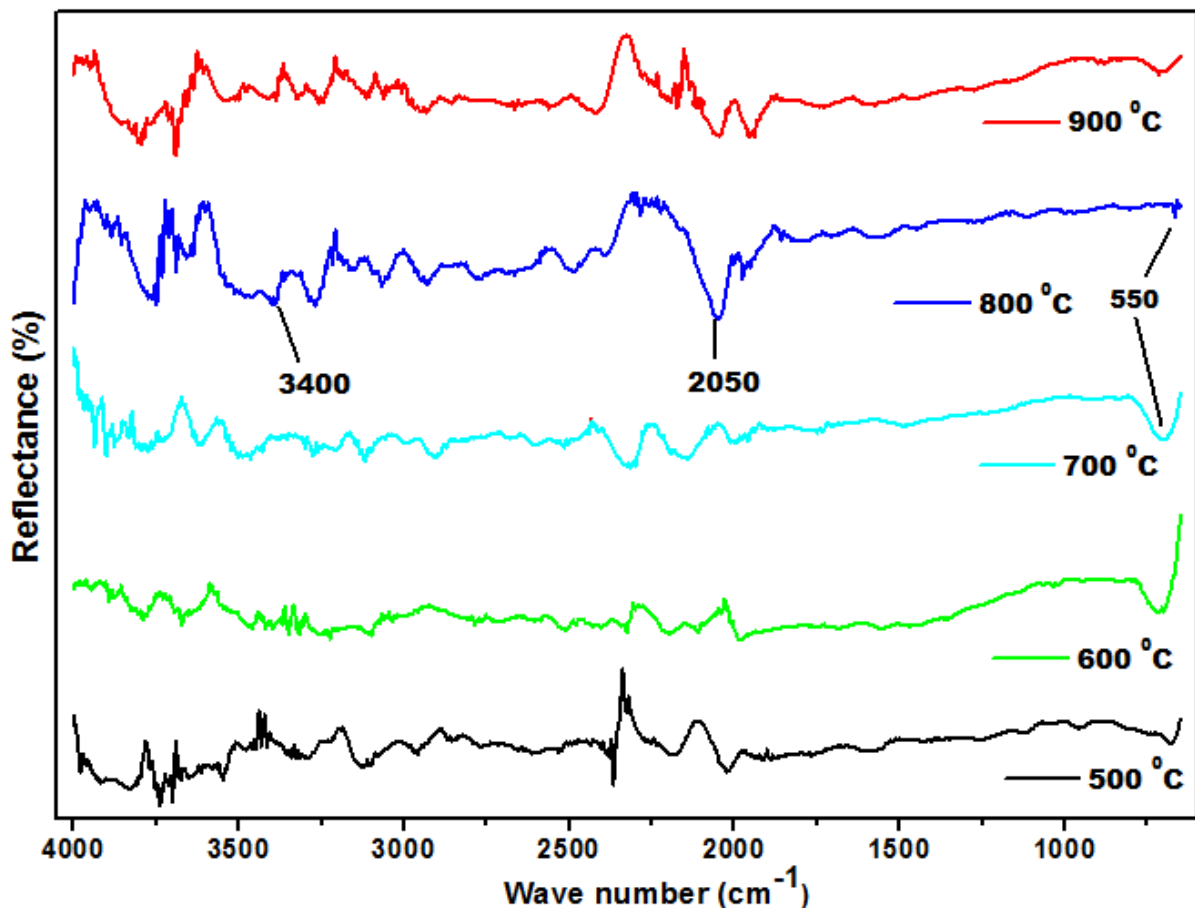
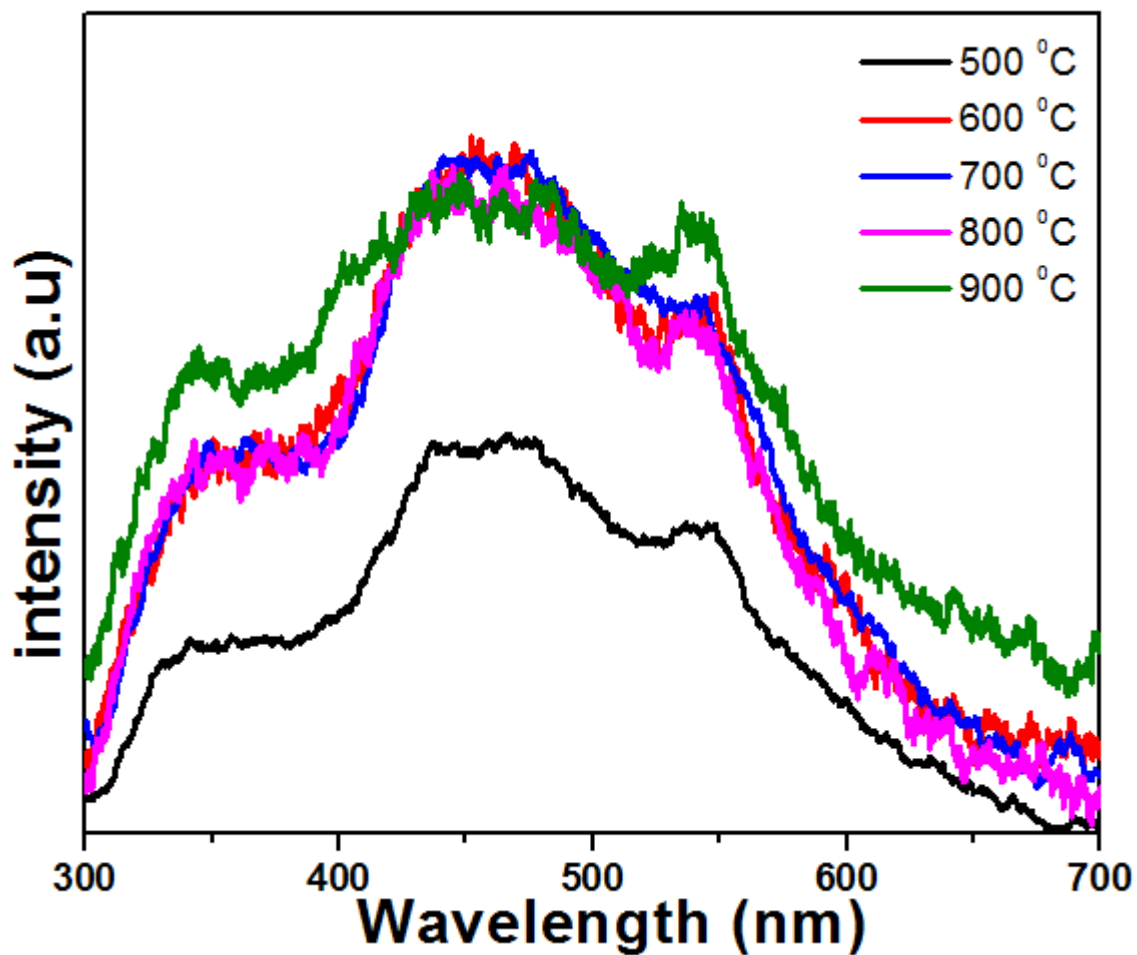


Figure 8.4: FT-IR Spectroscopy of TiO<sub>2</sub>

Figure 8.4 represents the FT-IR spectra of sol-gel derived  $\text{TiO}_2$  calcined at different temperature ( $500^\circ\text{C} - 900^\circ\text{C}$ ). The peaks at  $3400$  and  $1650\text{ cm}^{-1}$  in the spectra are due to the stretching and bending vibration of the  $-\text{OH}$  group. In the spectrum of pure  $\text{TiO}_2$ , the peaks at  $550\text{ cm}^{-1}$  show stretching vibration of  $\text{Ti-O}$  and peaks at  $1450\text{ cm}^{-1}$  shows stretching vibrations of  $\text{Ti-O-Ti}$ . These factors could make the oxygen vacancies. As can be seen, one dominant feature centred around  $2250\text{ cm}^{-1}$ , which is characteristic of the  $\text{TiO}_2$  [16], was observed.

### 8.2.5 PL analysis



**Figure 8.5:** PL spectra of  $\text{TiO}_2$  at different annealing temperature.

Figure 8.5 shows the PL spectra of  $\text{TiO}_2$  nanoparticles calcined at different temperature range 500 - 900 °C. Photoluminescence spectra were recorded at room temperature on the prepared nano  $\text{TiO}_2$  prepared by sol-gel synthesis. The Photoluminescence spectrum of anatase phase nano $\text{TiO}_2$  resulted from three origins: self-trapped excitons surface states and oxygen vacancies [17-18]. Oxygen vacancy peaks normally observed at 391nm and 409 nm. In our samples, we observed the peaks around 340 460 and 540 nm. This shows the Photoluminescence emission due to the presence of oxygen vacancies of nano  $\text{TiO}_2$ .

From the PL spectra, we also notice that PL intensity increase with increase in calcined temperature. In other words, temperature increased has a direct relationship with the PL intensity, even though the relationship between the two is not entirely linear as shown in Figure 8.5. Nevertheless, more electron-hole pairs were generated by the light absorption of the temperature, the probability of electrons transitioned from the defect energy levels to the valence band also increased, producing a higher PL intensity [16].

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# Chapter 9

## Summary and Conclusion

MBxOy:Eu (M = Ca, Sr, Ba) phosphors with different Ca:B /Sr:B and Ba:B molar ratio and with constant Eu concentration have been synthesized by a solution combustion method at initial reaction temperature of 500 °C for 15 minutes.

XRD analysis of phosphor shows a monoclinic phase for Ca:B. From XRD analysis, it was observed that the increase in Sr:B molar ratio and Eu ion concentration resulted into the elimination of secondary peaks. It was found that the grain size determined from XRD peaks does not change with increase in the Sr:B molar ratio and Eu ions concentration. The XRD results show the pure Ba:B phase obtained when annealed at 700 °C.

The SEM pictures of the  $\text{CaB}_4\text{O}_7:\text{Eu}^{3+}$  powder reveals nanorod like, agglomerated, porous for Ca:B molar ratio but the grains become flake-like as the Ca:B molar ratio increased, giving rise to the increase in particle size. SEM shows the presence of well-packed and randomly oriented platelet-like large grains. The particle like morphology was obtained for various Ba/B ratios. Porosity (at large magnification)–due to production of super-heated gases ( $\text{N}_2$ ,  $\text{CO}_2$ ) escaping from the reaction

PL results shows the excitation spectra by monitoring  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  emission of  $\text{Eu}^{3+}$  in  $\text{CaB}_4\text{O}_7$ , can be divided into two regions. The luminescent intensity of the  $\text{CaB}_4\text{O}_7:\text{Eu}^{3+}$  phosphor increase with increase in both the Ca:B molar ratio and Eu ions concentration. PL results shows that the luminescent intensity of the  $\text{SrB}_6\text{O}_{10}:\text{Eu}^{2+}$  phosphor increase with increase in both the Sr:B molar ratio and Eu ions concentration. The particle homogeneity and luminescence intensity improved by sol-combustion process. The position of the emission peak in blue domain does not change but intensity change with Eu concentrations. Addition of Eu concentrations up to optimum value improves luminescence and afterglow.

Titanium dioxide ( $\text{TiO}_2$ ) powder was prepared by a sol-gel method. At all concentration values of precursor values from 1 ml to 17 ml, the anatase structure of  $\text{TiO}_2$  were obtained after calcination at 500 °C. At a higher calcining temperature of 800 °C for 2 h, a multi-phase of the anatase and rutile structures of  $\text{TiO}_2$  was obtained at 3 ml. The particles of  $\text{TiO}_2$  were

highly agglomerated and irregular in shape with the particle sizes in the range from 14 – 41 nm. The size of both the rutile and anatase phases increased with the concentration values of precursor and calcination temperatures increased from 1ml to 17 ml and 500 °C to 900 °C, respectively.

### **International Conferences**

- **T. M. Sithole**, B. F. Dejene, L. F. Koao, Synthesis and Characterization of SrB<sub>6</sub>O<sub>10</sub>:Eu<sup>2+</sup> nano-phosphors Prepared Using Solution - Combustion Method, 5th Conference on Photo-Responsive Materials, Kariega Game Reserve, South Africa, May 2013.

### **National Conferences**

- **T. M. Sithole**, B. F. Dejene, L. F. Koao, Synthesis and Characterization of CaB<sub>4</sub>O<sub>7</sub>:Eu<sup>3+</sup> nano-phosphors Prepared Using Solution - Combustion Method. SAIP at UKZN July 2013.
- **T. M. Sithole**, B. F. Dejene, L. F. Koao, Synthesis and characterization of BaB<sub>8</sub>BO<sub>13</sub>:Eu<sup>2+</sup> nanophosphors prepared using solution-combustion method. SAIP at UP July 2012.