

Tailoring Luminescence Properties of Rare Earth Doped Aluminate and Garnet phosphors

Faculty of Natural and Agricultural Sciences

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Tailoring Luminescence Properties of Rare Earth Doped Aluminate and Garnet Phosphors

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Co- Promoter: Prof H.C Swart

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Declaration

This research has not been previously accepted for any degree and is not being currently considered for any other degree at any other university.

I declare that this thesis contains my own research work except where specifically acknowledged.

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Dedication

This thesis is dedicated to my beautiful children, my loving wife and my dear parents.

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Abstract

This work covers several aspects about different phosphors activated with rare earth (RE) metal ions which were synthesised and characterised using different techniques with the sole aim of tailoring their chemical and structural properties so as to optimize their output in order to meet the requirements for industrial and commercial applications.

Eu^{2+} doped and Dy^{3+} co-doped strontium aluminate ($\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$) phosphors were prepared by solution - combustion synthesis technique at 500 °C using urea as a reducer and fuel, a widely known method for preparing nano sized phosphors. The $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ was irradiated with beta (β) rays and thermoluminescence (TL) properties studied with regards to the electron-trapping properties in terms of TL glow curves. The results of the peak shape method showed that the kinetics of the obtained glow curves were of first order.

Blue-green emitting Eu^{2+} and Nd^{3+} doped polycrystalline barium aluminate ($\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$) phosphor was prepared by a solution - combustion method at 500 °C without a post-annealing process. The characteristic variation in the structural and luminescence properties of the as-prepared samples have been evaluated with regards to when the Ba/Al mole ratio changed from 0.1:1 to 1.4:1. The XRD and TEM results reveal that the average particle size of the $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ phosphor is about 60 nm. The broad-band UV-excited luminescence of the phosphors was observed at $\lambda_{\text{max}} = 500$ nm due to transitions from the $4f^65d^1$ to the $4f^7$ configuration of the Eu^{2+} ion. The results indicated that the main peaks in the emission and excitation spectrum of the nanophosphors slightly shifted to the short wavelength because of changes in the crystal field effect due to structural changes caused by the variation of quantity of Ba ion in the host lattice.

Thin films of cerium doped yttrium gadolinium aluminium garnet $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YGAG:Ce) were grown on Si (100) substrates by a pulsed laser deposition (PLD) technique using a 266 nm Nd:YAG pulsed laser under varying deposition conditions. The effect of annealing temperatures on the structure and luminescence properties of the as-deposited (YGAG:Ce) thin films were analysed. A slight shift in the wavelength of the PL spectra was observed from the thin films when compared to the PL spectra of the phosphor in powder form, which is probably due to a change in the crystal field.

Thin films of Strontium Aluminate ($\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}, \text{Nd}^{3+}$) phosphors were grown on Si (100) substrates using a 266 nm Nd-YAG laser. XRD patterns showed that with increasing substrate temperature and argon partial pressure the peaks in the direction (220) shifted to the

lower 2-theta angles. Photoluminescence (PL) data revealed a slight shift in the peak wavelength which is probably due to crystal field effects.

The structural and optical properties of commercially obtained $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ phosphor with respect to substitution of Al^{3+} with Ga^{3+} and Y^{3+} with Gd^{3+} in the $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ garnet structure resulting in $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ and $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ systems respectively were investigated. X ray diffraction (XRD) results show slight shifts in the 2theta angles; to the lower angles when Ga^{3+} was used and to the higher angles when Gd^{3+} was used with respect to the XRD peaks from $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ and JCPDS card No. 73-1370. This could be attributed to the induced crystal field effects due to different ionic sizes of Ga^{3+} and Gd^{3+} as compared to the Al^{3+} and Y^{3+} respectively.

Trap characteristics of commercially obtained $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ phosphor powder is also reported. The effects of UV irradiation time and different heating rates have been discussed. The TL glow curves showed two TL peaks, a maximum centered around 74 °C and a shoulder at around 163 °C when excited with UV radiation. Varying the UV irradiation (exposure) time or hence the absorbed dose and heating rate significantly affected the peak intensity (I_{max}) and peak temperature (T_{max}) of the glow curve. The intensity of the two TL peaks moved to the higher side with an increase in the heating rate.

Key words

- $\text{BaAl}_2\text{O}_4\text{:Eu}^{2+}, \text{Nd}^{3+}$
- $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}, \text{Dy}^{3+}, \text{Nd}^{3+}$
- $\text{Y}_3\text{Al}_5\text{O}_{12}\text{:Ce}^{3+}$
- $\text{Y}_3(\text{Al}, \text{Ga})_5\text{O}_{12}\text{:Ce}^{3+}$
- $(\text{Y}, \text{Gd})_3\text{Al}_5\text{O}_{12}\text{:Ce}^{3+}$
- Morphology
- Luminescence
- Trap/Energy levels
- Decay time
- Electronic transitions

List of abbreviations and symbols

Abbreviations

- ACL - Aperture Angle Control Lens
- AES - Auger Electron Spectroscopy
- AFM- Atomic Force Microscopy
- APPHs - Auger Peak-to-Peak Heights
- $\text{BaAl}_2\text{O}_4\text{:Eu}^{2+}, \text{Nd}^{3+}$ - Barium Aluminate
- CB- Conduction band
- CFT- Crystal Field Theory
- CIE-Commission International de l'Eclairage
- CRTs-Cathode Ray Tubes
- EDS-Energy Dispersive x-ray Spectroscopy
- FTIR – Fourier-Transform infrared
- FEDs-Field Emission Displays
- FWHM- Full Width at Half Maximum
- GCD-Glow Curve Deconvolution
- GUI- Graphical User Interface
- He-Cd- Helium Cadmium
- ICDD-International Centre for Diffraction Data
- ICSD- Inorganic Crystal Structure Database
- IR-Infra Red
- JCPDS-Joint Committee on Powder Diffraction Standards.
- LEDs-Light Emitting Diodes
- OSL-Optically Stimulated Luminescence
- PDF-Powder Diffraction File
- PDP-Plasma Display Panel
- PL-Photoluminescence
- PLD-Pulsed Laser Deposition
- rms-root mean square
- RBS-Rutherford Back Scattering
- RE- Rare Earth
- RT-Room Temperature
- SEM-Scanning Electron Microscopy
- SERS -Surface-Enhanced Raman Scattering
- SOC- Spin-Orbit Coupling
- TEM-Transmission Electron Microscopy
- TL-Thermoluminescence
- TSL-Thermally Stimulated Luminescence
- ToF-SIMS-Time of Flight-Secondary Ion Mass Spectroscopy
- UHV-Ultra High Vacuum
- UV-Vis-NIR- Ultraviolet-Visible-Near-Infrared
- VB- Valence Band
- WLEDs-White Light Emitting Diodes
- XPS -X-ray Photoelectron Spectroscopy
- XRD -X-Ray Diffraction
- YAG-Yttrium Aluminium Garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}\text{:Ce}^{3+}$) -Cubic
- YAM -Yittrium Aluminate Monoclinic ($\text{Y}_4\text{Al}_2\text{O}_9$)
- YAP- Yttrium Aluminate Perovskite
- (YAlO_3) - Yttrium Aluminate Hexagonal
- $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}\text{:Ce}^{3+}$ - yttrium gallium aluminium garnet
- $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}\text{:Ce}^{3+}$ - yttrium gadolinium aluminium garnet

Symbols

- Bq-Becquerel
- MBq-Megabecquerel
- GBq-Gigabecquerel
- Ce^{3+} -Trivalent cerium ion
- $c_\omega, c_\delta, c_\tau, c_\alpha$ and b_α - quantities which describe the kinetic order
- Dy^{3+} -Trivalent Dysprosium ion
- E_g - Band gap energy
- E_t -Trap-depth
- $\text{Eu}^{2+}/\text{Eu}^{3+}$ -Divalent/Trivalent Europium ion
- Ga- Gallium
- Gd- Gadolinium
- Gy- Grays (unit of radiation dose)
- I_m - Peak maximum intensity
- $J = L + S$ - total angular momentum
- J-J coupling- individual total angular momenta
- k - Boltzmann constant
- L - Azimuthal quantum number
- $L - L$ - orbit-orbit interaction
- mCi –millicurie (unit of radioactivity)
- M_J - secondary total angular momentum quantum number
- n_m - high temperature half integral of the glow peak
- Nd^{3+} -Trivalent Neodymium ion (co-dopant)
- s - Frequency factor or “escape frequency”
- S -Spin quantum number
- $s - s$ - spin-spin interaction
- $S - L$ -spin-orbit interaction
- $T_{\max}$ - the peak temperature
- τ_m – time at peak maximum intensity
- μ_g – symmetry factor of a glowcurve
- V_O - Oxygen vacancy,
- V_{Sr} -Strontium vacancy
- α -alpha (rays)
- β - Heating rate
- ω = Full Width at Half Maximum
- χ - x (rays)
- γ -gamma (rays)
- $\delta = T_2 \left(\frac{1}{2} \max \right) - T_{\max}$ – upper half width parameter
- $\tau = T_{\max} - T_1 \left(\frac{1}{2} \max \right)$ - lower half width parameters

Inspiration

A Saying of Prophet Muhammad (May peace be upon him);

"Acquire knowledge. It enables its possessor to distinguish right from wrong; it lightens the way to Heaven; it is our friend in the desert, our society in solitude, our companion when friendless; it guides us to happiness; it sustains us in misery; it is an ornament among friends, and an armor against enemies".

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Chapter 1

General Introduction

1.1. Background

Designing/tailoring of highly optimized phosphor powders for related practical use requires a proper understanding of the dependence of a given optical property of that phosphor on certain physical parameters such as host structure, grain/particle size, presence of impurities/dopants, synthesis method, post synthesis treatment etc. These mechanical or functional parameters control the chemical composition of the phosphor material that will in turn influence the electronic properties of the phosphor and hence luminescence characteristics.

Selection of a suitable host material is very important and can lead to improved luminescence performance of a material. A host material should possess high chemical durability, thermal stability for high-temperature processes and be more chemically stable depending on the potential application. By controlling the host matrix composition via chemical modification for instance, co-doping with metal ions with different ionic radius; Al, Ga, Gd ions etc influences the host chemical environment and hence the resultant optical characteristics [1].

It has been reported that the sulfide component in a sulfide-based phosphor degrade rapidly in moisture and also at high current density necessary for field emission display (FED) while oxide based phosphors have been found to be more stable under these conditions [2]. Silicate oxide phosphors such as $\text{Zn}_2\text{SiO}_4\text{:Mn}$ are more chemically stable than sulfide phosphors under high coulomb loading which makes them useful in Cathode Ray Tube (CRT) applications due to its high efficiency and relatively long persistence [3]. It has also been reported that $\text{Y}_2\text{O}_3\text{S}$ particles are chemically stable materials in acid and basic solution [4].

To obtain the highest up conversion luminescence efficiency, it is important to choose an appropriate host material with lower phonon energy since high phonon frequencies of the host lattice lead to non-radiative relaxation [5]. The other factor which needs to be exploited by researchers is that of thermal heating (annealing/calcination/sintering). The appropriate choice of the temperature and atmosphere for a particular material during the annealing process remains a major challenge. Annealing enhances the luminescence properties of a phosphor. It was found that emission intensity increased significantly with increasing calcination temperature due to the

increase in particle crystallinity and homogenized distribution of the dopant components within the phosphor particles by reducing localized concentration quenching [1]. Also reduction reaction of RE^{3+} and activation of the $\text{e}^{-}\text{-h}^{+}$ pair in the host matrix are strongly dependent on high sintering temperature. As the temperature increases, the $\text{e}^{-}\text{-h}^{+}$ pair gets activated and the trapped electrons are ejected from the network reacting with RE^{3+} to generate RE^{2+} ions [6]. Revaux et al (2011) investigated the optical properties of YAG:Ce nano- particles as a function of annealing temperature [7]. They observed that the higher the temperature, the stronger the emission intensity which they believed was because by annealing the nanoparticles at high temperatures, the formation of YAG phase is completed and the YAG crystallinity is improved and hence the luminescence due to insertion of cerium ions inside the YAG structure in the process [7].

The annealing atmosphere also plays a major role. For instance, the redox state of Ce ions in YAG:Ce are significantly affected by the annealing atmosphere. When annealed in air, a part of the Ce^{3+} is oxidized to Ce^{4+} which partially quenches the luminescence leading to a very low efficiency, however treatment in a reducing atmosphere ($10\%\text{H}_2/\text{Ar}$) was found to help enhance the initial luminescence by reducing a part of the Ce^{4+} into Ce^{3+} [7]. In another study Yousif et al (2013) reported on structural, photoluminescence (PL) and Cathodoluminescence (CL) properties of $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Tb}$ thin films annealed at different temperatures [8]. They observed an enhancement in the PL intensities as a function of annealing temperatures which was attributed to the improvement of the crystallinity of the films with an increase in the annealing temperature. They also noted that PL intensity increased with an increase in the Ga concentration up to an optimum amount and then decreased with a further increase in the Ga concentration due to diffusion of the Ga to some parts of the surface of the film at $800\text{ }^{\circ}\text{C}$.

A photoluminescence (PL) spectrum shows the emitted light intensity as a function of the excitation wavelength at particular excitation energy. Varying the excitation energy brings about changes in the intensity and peak position of the corresponding emission. This fact can be exploited when controlling optical properties of a phosphor according to the type of application for which it is being designed. Jin He et al (2013) observed a pronounced emission band around 450 nm ascribed to Eu^{2+} ions in mesoporous AlPO_4 glasses doped with Eu ions when the excitation wavelength was 340 nm [6]. As the excitation wavelength was adjusted to 360 nm there was a tendency to increase the fluorescent intensity of Eu^{3+} ions around 590 and 613 nm . The difference in excitation bands for RE^{2+} and RE^{3+} offers a probability to control the fluorescence/luminescence [6].

The nature or form in which a material is used during application such as, powder, pellet, liquid, spray, dyes and films (thin/thick) etc is very paramount and influences its optical output. Phosphors in thin film form have low brightness and efficiencies due to internal reflection compared to those of phosphor powders, but they possess advantages such as better thermal stability, higher lateral resolution, better adhesion to the substrate and less out-gassing in device operation [9,10].

Introduction of impurities (dopants/Co-dopants) into the host generates defects or surface states which influence the band gap such that its absorption edge covers the visible spectrum. Doping induces oxygen vacancies that form electron-trap centers which helps delay the decay of the charge carriers, enhances the visible light absorption property and decreases the electron-hole recombination rate [11]. Modifying of luminescence of RE^{2+} and RE^{3+} can also be achieved by controlling the RE ions concentrations. The fluorescent color can be tuned by controlling the ratio of $\text{RE}^{3+}/\text{RE}^{2+}$ [6].

The properties of materials are strongly associated with geometrical factors, such as shape, dimensionality, size, etc. Crystalline, spherical-shaped, uniform size particles with narrow size distribution with well-defined morphologies can reduce light scattering and produce fine luminescence properties [1].

The presence of adsorbed particles, molecules or groups on the surface of phosphors greatly affects its luminescence behavior. OH and CO groups can significantly quench the luminescence emission. The amount of OH and CO groups adsorbed has been found to decrease with increasing calcination temperature [1]. Smith et al (2005) reported that when a molecule with a chromophore which fluoresces is adsorbed on the SERS (surface-enhanced raman scattering) active metal surface, the fluorescence is almost completely quenched [12].

The development of nanoscience and nanotechnology so far has been made possible by the success in the production of nanomaterials. The preparation of nanomaterials involves control of size, shape and structure of the materials. During the past few years, nanoparticles of ceramic materials have been produced in large quantities by use of physical and chemical techniques. The significant improvements in the preparation of nanomaterials such as long afterglow phosphors, ceramics and semiconductor has been due to the discovery of new various synthesis techniques such as co-precipitation, sol-gel, combustion method, etc.

In this thesis, a systematic investigation was carried out on some aluminate and garnet phosphor powders and thin films. They are aluminates; $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} , and $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ co-doped with $\text{Nd}^{3+}/\text{Dy}^{3+}$ and garnets; $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ and $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$

systems respectively. Particularly the effects of variation of concentration of host matrix composition [mass ratio of Barium to aluminium (Ba:Al)] of $\text{BaAl}_2\text{O}_4\text{:Eu}^{2+}$, Dy^{3+} , Thermoluminescence (TL) behaviour of as-prepared $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$, Dy^{3+} , dopant (Eu^{2+}), Structural and luminescence properties of $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$, Dy^{3+} , Nd^{3+} phosphor thin films grown by pulsed laser deposition (PLD), Characterization of cerium doped yttrium gadolinium aluminate garnet $(\text{Y-Gd})_3\text{Al}_5\text{O}_{12}\text{:Ce}^{3+}$ phosphor thin films fabricated PLD, Effect of Ga^{3+} and Gd^{3+} ions substitution on the structural and optical properties Ce^{3+} -doped yttrium aluminium garnet phosphor nano-powders and Thermoluminescence properties of UV irradiated $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}\text{:Ce}^{3+}$ phosphors with a view of modifying their structures using different techniques so as to tailor their luminescence properties and make them suitable for various commercial applications.

The phosphors were characterized by detailed use of a variety of techniques such as, X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive x-ray Spectroscopy (EDS), Photoluminescence Spectroscopy (PL), Ultra Violet-Visible (UV-VIS) spectroscopy, Thermoluminescence (TL), Atomic Force Microscopy (AFM), Auger electron Spectroscopy (AES), and X-Ray Photoelectron Spectroscopy (XPS) techniques, respectively.

1.2. Statement of the Problem

Presently scientific research is geared towards developing inorganic materials/phosphors that can be effectively and efficiently used in solid state lighting applications such as phosphor lamps, light emitting diodes (LEDs) and new types of high resolution and high efficiency display devices such as field emission displays (FEDs), Plasma display panels (PDPs). Tailoring luminescence properties of a material is significant in the development of efficient materials albeit many challenges faced during the manufacturing in the process of these materials. Researchers and scientist will have to come up with ways that would help overcome these challenges and enhance the luminescence properties of phosphors.

The ability to synthesize tailor-made inorganic materials, which allows fine tuning of luminescence characteristics such as the color, intensity and decay time of a given phosphor, depends on several factors. These optical properties could be influenced by accurately controlling the parameters such as; annealing/ sintering/calcination temperature, excitation wavelengths, host matrix, nature or form in which the material is used for application such as powder, pellet, liquid, spray, dye and thin/thick films, type and concentration of impurities, geometrical factors or size effects, presence of adsorbed groups and the method or synthesis technique used. Since the properties of materials are strongly influenced by these factors the precise manipulation of the parameters remains a major research focus and a challenging issue.

1.3. Objectives of the Study

1.3.1. Main Objective

The main objective of the present study is to develop rare earth (RE) doped aluminate and garnet phosphors.

1.3.2. Specific Objectives

Tailor the optical properties of the phosphors; color, intensity/brightness and decay/glow time by;

1. Modifying their structure through incorporation of impurities (Eu^{2+} , Nd^{3+} , Dy^{3+} , Ce^{3+} , Al^{3+} , Ga^{3+} and Gd^{3+}),
2. Annealing at different temperatures in different atmospheres and by pulsed laser deposition (PLD) under different chamber conditions into thin films.

1.4. Thesis Layout

Chapter 1 begins with a general introductory overview of phosphor materials outlining the need for designing/tailoring of phosphors for practical use while considering optical property of that phosphor vis-à-vis certain physical parameters like host structure, grain/particle size, presence of impurities/dopants, synthesis method, post synthesis treatment etc. It also presents the objectives of this undertaking. The shortcomings encountered and areas that need to be streamlined or emphasised in research works involving phosphor materials are schemed out under the subtopic 'statement of the problem'.

Chapter 2 follows by outlining the theoretical background information relating to phosphors; the structural and electronic properties of phosphors with respect to the crystal structure of the aluminate and garnet host matrices, the crystal field theory and the electronic transitions of the co-activators as per the selection rules.

Chapter 3 gives a brief description of the experimental equipment, environmental and/or atmospheric requirements, techniques used to design, synthesize and characterize alkaline earth aluminate phosphors. The Pulsed laser deposition (PLD) and solution - combustion method used to synthesize the phosphors are discussed in detail. A summary of the different characterization techniques are also given. This includes a description of the operation of each of the techniques such as SEM, TEM, EDX-S, AFM, XRD, XPS, UV-VIS, PL and TL.

Chapter 4 discusses the Thermoluminescence of beta (β)-irradiated $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} phosphors using the heating rate method.

In *Chapter 5*, Combustion synthesis, characterization and luminescence properties of barium aluminate phosphor is presented in details, particularly the effect of Ba/Al molar ratio and its effect on the photoluminescence (PL) and thermoluminescence (TL) properties were studied.

In *chapter 6*, the Characterization of cerium doped yttrium gadolinium aluminate garnet $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ phosphor thin films fabricated by pulsed laser deposition is discussed with respect to the effect of variation of chamber parameters.

Chapter 7 deals with the structural and luminescence properties of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, $\text{Dy}^{3+}/\text{Nd}^{3+}$ phosphor thin films grown by pulsed laser deposition.

In *chapter 8*, the Effect of Ga^{3+} and Gd^{3+} ions substitution on the structural and optical properties of Ce^{3+} -doped yttrium aluminium garnet phosphor nanopowders is presented.

Chapter 9 covers the Trap characteristics of UV activated $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ phosphors.

In *chapter 10*, conclusions and recommendations for possible future works are summarized here.

References

- [1] T.S. Atabaev, H.H. Thi Vu, Z. Piao, Y. H. Hwang, H. K. Kim, *J. Alloys Compd.*, **541** (2012) 263.
- [2] K. Kumar, A. Singh, S. Rai, *Acta Part A*, **102** (2013) 212.
- [3] X. W. Sun, H. S. Kwok, *Appl. Phys. A*, **69** (1999) S39.
- [4] O. Lyuji, Cathodoluminescence and Photoluminescence; Theories and Practical Applications, Taylor & Francis Group, London New York CRC, 2007.
- [5] J. Chen, J. X. Zhao, *Sensors (Basel)*, **12** (2012) 2414.
- [6] J. He, Y. Wang, Y. Liu, K. Wang, R. Li, J. Fan, et al., *J. Phys. Chem. C.*, **117** (2013) 21916.
- [7] A. Revaux, G. Dantelle, N. George, R. Seshadri, T. Gacoin, J. P. Boilot, *R. Soc. Chem.*, **3** (2011) 2015.
- [8] A. Yousif, H. C. Swart, O. M. Ntwaeaborwa, *J. Lumin.*, **143** (2013) 201.
- [9] K. G. Cho, D. Kumar, P. H. Holloway, R. K. Singh, *Phys. Lett.*, **73** (1998) 3058.
- [10] K. T. Hillie, O. M. Ntwaeaborwa, H. C. Swart, *Phys. Stat. Sol.*, **1** (2004) 2360.
- [11] B. Choudhury, A. Choudhury, *J. Lumin.*, **136** (2013) 339.
- [12] E. Smith, G. Dent, Modern Raman Spectroscopy – A Practical Approach, John Wiley & Sons Ltd, 2005.

Chapter 2

Review of Theoretical Concepts

2.1. Structural and Electronic Properties of Phosphors

A phosphor is a material that absorbs energy from radiations and converts it into light. Essentially it emits light by converting one type of energy into another thereby acting as a transducer or a photon-converter. Luminescence, which includes both fluorescence and phosphorescence, is defined as a phenomenon in which the electronic states of a substance is excited by some kind of external energy and the excitation energy is given off or emitted as light of various wavelengths [1]. Thus, a phosphor is referred to as being luminescent because it emits energy from an excited electron as light over and above thermal radiation [2]. The excitation of the electron is caused by absorption of energy from an external source such as another electron, a photon or an electric field [3]. Photoluminescence (PL) which is luminescence in the visible range involves a radiative transition between the energy levels within the band gap of a material's host lattice followed by photo (light) excitation [4]. Generally during luminescence, a higher energy photon is absorbed and a lower energy photon is emitted a process known as Stokes process. The energy difference (excess energy) is absorbed by the solid and appears as lattice vibrational (heat) energy [5].

When designing a phosphor for a particular kind of application one needs to understand the properties of the constituents of the phosphor. Generally inorganic phosphors consist partly of a host material (insulator or semiconductor) which makes up the bulk and partly impurities (rare earth, transition metal) called dopants/activators, purposely incorporated in small amounts into the host. The luminescence observed in phosphors emanates either directly from the host or from the dopants [5] or both simultaneously. An activator/dopant is an impurity ion which is incorporated into the host lattice and forms a luminescence centre which absorbs the energy and gives off luminescence when excited. In some cases when the activator ions show weak absorption other impurities known as sensitizers, co-activators or co-dopants can be added to

enhance the luminescence. They absorb the energy from the primary excitation and subsequently transfer it to the activator [6].

Having briefly looked at the basic principles of an inorganic phosphor let's discuss in detail the characteristics of these ingredients;

2.2. Host Structure

In a given host, the emission of from the luminescent centre is influenced by a number of factors. For a phosphor to exhibit the required properties, the essential requirements of the host are [4,7,8];

- Purity. It should be free from all other impurities except the intentionally incorporated activators/dopants hence high color purity.
- Close lattice matches to dopant ions for achieving high doping levels.
- Adequate optical transparency within the wavelength range of interest,
- Low phonon energy,
- High optical damage threshold,
- Low thermal expansion,
- Low acoustic loss,
- Hardness,
- Stability against chemical and mechanical changes/ strain fields induced by the application of an external stress or electric field,
- Covalency,
- Size of the cations and anions,
- Strength of the crystal field,
- Alignment-directions of linear chains in the lattice,
- high quantum efficiency and
- luminescence lifetime

In light of the above we will study the crystal structures of two host systems: *aluminates* (MAl_2O_4); BaAl_2O_4 , SrAl_2O_4 and *garnets* (YAG); $\text{Y}_3\text{Al}_5\text{O}_{12}$, $\text{Y}_3(\text{Ga},\text{Al})_5\text{O}_{12}$ and $(\text{Y},\text{Gd})_3\text{Al}_5\text{O}_{12}$.

2.2.1. Crystal Structure of Alkaline Earth Aluminates

The crystal structures of the aluminate compounds studied in this research are all derivatives of the stuffed tridymite structure. In this type of structure there are large open channels in the framework, which provide suitable sites for large cations[9]. Phosphor hosts based on the alkaline earth aluminate can be grouped into three categories; (a) Binary alkaline earth aluminates (MAl_2O_4), where $\text{M} = \text{Ba}$, Ca and Sr , such as; BaAl_2O_4 , CaAl_2O_4 and SrAl_2O_4 (b) Hexaaluminates which are hexagonal poly-aluminates having a structure related to either that of beta(β)-alumina (ideal formula $\text{NaAl}_{11}\text{O}_{17}$) or magnetoplumbite (ideal formula $\text{PbFe}_{12}\text{O}_{19}$) have a similar hexagonal symmetry of space group $\text{P6}_3/\text{mmc}$. Alkaline earth hexaaluminates ($\text{MAl}_{12}\text{O}_{19}$) such as $\text{CaAl}_{12}\text{O}_{19}$ and $\text{SrAl}_{12}\text{O}_{19}$ related to magnetoplumbite and beta-alumina and their superstructures and (c) Rare earth hexaaluminates with the magnetoplumbite structure. The large cation is 9-coordinated in the beta-alumina structure and 12-coordinated in the magnetoplumbite structure [10,11].

In contrast, the compound Ba magnetoplumbite, $\text{BaAl}_{12}\text{O}_{19}$ does not exist except as a mixture of two distinct non-stoichiometric phases, referred to as phase I and phase II in which one is deficient in barium and the other one with excess barium, that were shown to have the beta-alumina structure[11]. Also the magnetoplumbite-type crystals, like $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}^{2+}$ and $\text{CaAl}_{12}\text{O}_{19}:\text{Eu}^{2+}$ have close packed structures of 19 oxygen ions and one large cation, with smaller cations occupying the interstitial sites. In this structure no preferential orientation of d orbitals of Eu^{2+} on a large cation site can occur, and a blue Eu^{2+} emission will be observed [9].

The compounds MAl_2O_4 , $\text{M} = \text{Ba}$, Ca and Sr are formed of a three-dimensional framework of corner-sharing AlO_4 tetrahedra. Each oxygen is shared with two aluminium ions so that each tetrahedron has one net negative charge [10]. The charge balance is achieved by the large divalent cations like Ba^{2+} , Sr^{2+} , Ca^{2+} etc. which occupy interstitial sites within the tetrahedral framework. The tetrahedra framework is isostructural with the tridymite structure. The stuffed tridymite structures are derived from the structure of SiO_2 β - tridymite [12] (figure 2. 1).

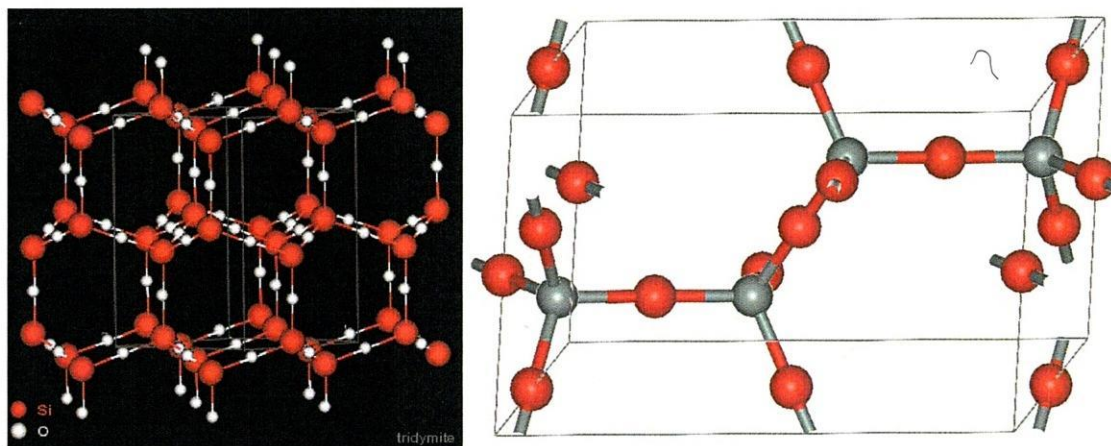


Figure 2.1: Structure of (a) SiO_2 β -tridymite along [001] direction [12, 13] and (b) β - tridymite (red are oxygen atoms) [14]

Barium Aluminate (BaAl_2O_4) has the ideal stuffed tridymite structure with a high-melting-point of 1815 °C and good dielectric, pyroelectric, and hydraulic-hardening properties [15]. The BaAl_2O_4 materials investigated in this study at ambient temperature possess the hexagonal superstructure with space group: $P6_322$, no. 182, having unit cell parameters $2a$, c , where a and c correspond to the hexagonal tridymite lattice parameters with $a = 5.218 \text{ \AA}$, $c = 8.781 \text{ \AA}$ and $Z: 2$ [16]. The structure consists of Ba^{2+} ions located within the channels consisting of six interconnected AlO_4 tetrahedra (figure 2) with two Ba, four Al and six O sites [17]. As Al^{3+} replaces Si^{4+} in the tetrahedra of SiO_2 tridymite, Ba will occupy sites in channels parallel to the c -axis [12].

According to the BaAl_2O_4 crystal structure in which the channels are along the c axis, there are two different Ba^{2+} sites occurring in separate chains; one occurs 3 times more frequently than the other. The less frequently occurring Ba^{2+} site forms chains in which the Ba^{2+} ions are exactly above each other. The other Ba^{2+} chain, which contains the more frequently occurring Ba^{2+} sites, is not exactly linear. In the latter chain the distance between two successive Ba^{2+} ions is slightly longer than in the perfectly linear chain [9]. Also the first Ba^{2+} site (2a) has the multiplicity of two and a site symmetry of C_3 while the second one (6c) has six and C_1 . Both Ba^{2+} sites have nine-coordination and the sites are similar in average size ($d(\text{Ba}-\text{O})_{\text{Ave}} = 2.86$ and $2.87 \text{ \AA}$) [18]. However, the lower symmetry site has also shorter Ba–O distances ($2.69 \text{ \AA}$) corresponding to those typical of $\text{Eu}^{2+}-\text{O}$ (2.68) hence the Eu^{2+} ion is expected to substitute for Ba^{2+} in both nine coordinated sites (Ba1 (2a) and Ba2 (6c), with C_3 and C_1 site symmetries, respectively. The Eu^{2+} ion prefers the smaller Ba1 site ($0.077 \text{ \AA}$) because of being statistically 12 % smaller than Ba^{2+} [17] it would therefore seem reasonable that this 6c site is filled preferentially [18].

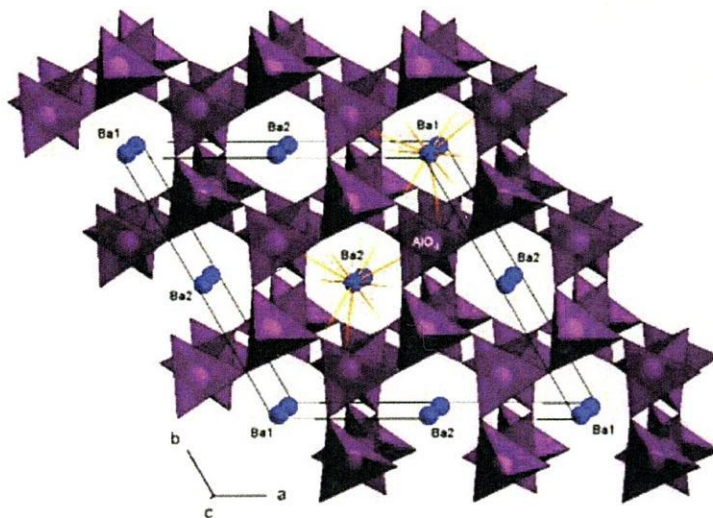


Figure 2.2: The BaAl_2O_4 hexagonal structure (space group P63) with Ba^{2+} ions situated within channels of AlO_4 tetrahedra [16].

Structural changes may also occur due to the size difference between Eu^{2+} (1.30 Å) and Ba^{2+} (1.47 Å) [17,19]. On the other hand Eu^{2+} cannot not fit into the four coordinated Al^{3+} site (0.39 Å) which is much too small also for Eu^{3+} (CN: 9, 1.12; CN: 6, 0.95 Å; Al^{3+} with CN 6: 0.54 Å) [17]. Also the rather complicated structural chemistry of the MAl_2O_4 host as well as the considerable size mismatch between the host (Ba^{2+}) and the main dopant (Eu^{2+}) cations may affect the luminescence efficiency of the Eu^{2+} when compared to that from the Ca^{2+} and Sr^{2+} aluminates [18]. When heated, BaAl_2O_4 has been observed to undergo a phase transformation over a wide temperature range of between 400–670 K [20].

SrAl_2O_4 also belongs to distorted stuffed β - tridymite type structure, which is a member of the nepheline family, constructed by corner-shared $[\text{AlO}_4]^{-5}$ tetrahedron framework composed of lattice distortions which form large interstitial cavities that accommodate Sr^{2+} ions to compensate for the charge mismatch. The AlO_4 tetrahedral connect together to form six-member rings whereby each oxygen ion (O^{2-}) is shared by two aluminium ions (Al^{3+}) so that each tetrahedron has one net negative charge [21]. The SrAl_2O_4 structure consists of two nine coordinated crystallographic low symmetry sites occupied by Sr^{2+} sites which occur in equal amounts in the lattice and have channels/chains in the a - and c -directions where the Sr chains are located along the a -axis [9,22].

The chains are not perfectly linear and the two sites are said to only differ by a slight distortion of their square planes [23]. The distance between two successive strontium ions is 3.9 and 4.6 Å, respectively while the bond length between the Sr^{2+} and the neighbouring O^{2-} are different for the two strontium sites. In one site, the O atoms are at a larger distance from the Sr^{2+} than the other [10]. The ionic sizes of Eu^{2+} (1.20 Å), Eu^{3+} (1.01 Å), Dy^{3+} (0.97 Å) and Sr^{2+} (1.21 Å) are

very similar, so that Eu^{2+} (1.20 Å), Eu^{3+} (1.01 Å), and Dy^{3+} (0.97 Å) ions can readily occupy the sites of Sr^{2+} . Therefore, it is expected that Eu^{3+} or Eu^{2+} should also lie in these two kinds of low symmetric sites one of the sites has centro- symmetrical surrounding, while the other has no symmetry of inversion [24].

SrAl_2O_4 exists in two different phases, namely monoclinic (M) with space group $P2_1$ and cell parameters; $a = 8.447$ Å, $b = 8.816$ Å, $c = 5.163$ Å, $\beta = 93.42^\circ$) and hexagonal with space group $P6_322$ and cell parameters; ($a = 5.140$ Å and $c = 8.462$ Å [23]. At room temperature, SrAl_2O_4 is monoclinic with space group $P2_1$ and stable. The stuffed tridymite monoclinic structure (space group $P2_1$), has the lowest symmetry in the SrAl_2O_4 species and is constructed of corner-sheared AlO_4 tetrahedra forming distorted quasi- hexagonal rings, and Sr ions penetrate to the void space of the honeycomb-like framework structure for charge compensation.

During heating it undergoes a phase transition from a low-temperature monoclinic structure to a distorted form of hexagonal SrAl_2O_4 at high temperatures (950 K) with space group $P6_322$ [25]. The change from space group $P6_3$ to its subgroup $P2_1$ eliminates the triad axis of the former phase. Thus, the distortion causes a reduction in the symmetry of the trigonally distorted rings. The disappearance of the triad axis would also result in the formation of three twin domains, which are related to the other by the lost symmetry axis. Structural phase transitions also occur between these two structure types during cooling. It has long been suggested that at high temperatures the hexagonal SrAl_2O_4 structure is isomorphous with that of BaAl_2O_4 [4, 8, 20]. Fukuda et al (2005) [20] investigated the crystal structure of SrAl_2O_4 at 1073 K and observed that $[\text{Al}_1\text{O}_4]$ and $[\text{Al}_2\text{O}_4]$ tetrahedra are alternatively linked in trigonally distorted rings, with tetrahedra pointing up and down, to form layers perpendicular to the c-axis (Fig. 2.4). The layers are stacked as in tridymite with a two layer repeat and joined by tetrahedral apices a derivative of stuffed tridymite, in which all of the Si^{4+} is replaced by Al^{3+} and the charge balancing cation Sr^{2+} occupy the channels between the rings of tetrahedra [20].

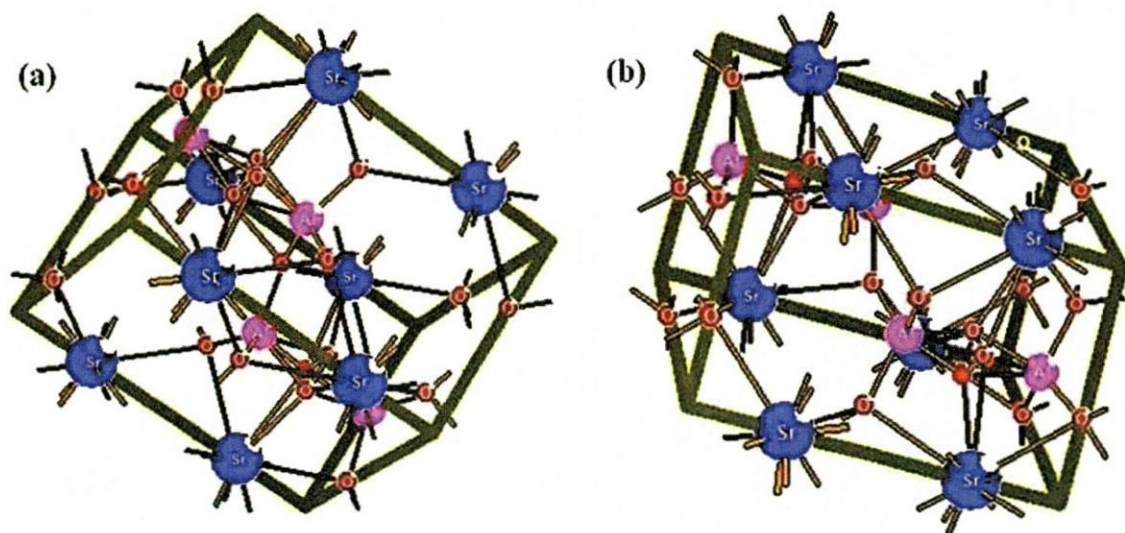


Figure 2.3: (a) Monoclinic phase and (b) Hexagonal unit cells of SrAl_2O_4 .

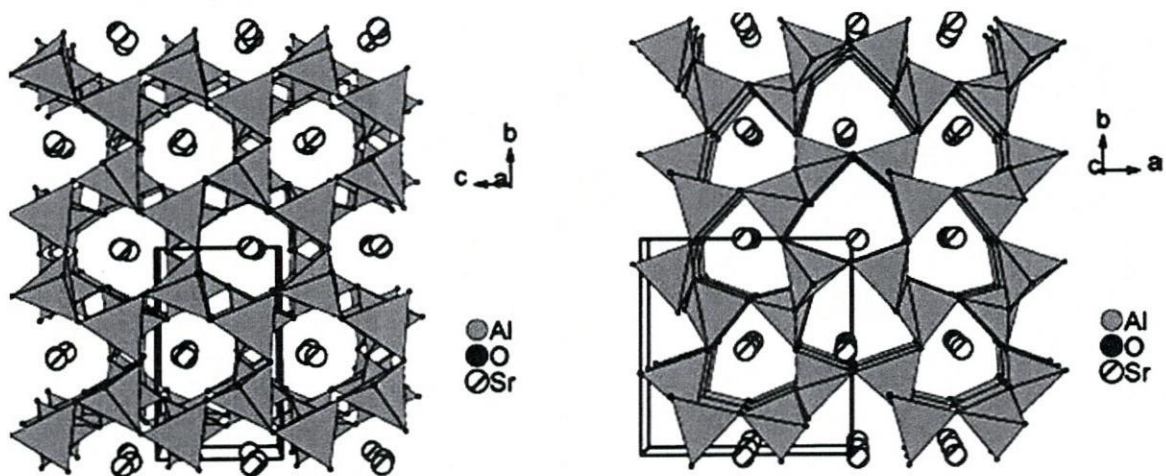


Figure 2.4: Structures of the SrAl_2O_4 monoclinic phase along the a- and c-directions [20, 26].

The crystal structures of hexagonal SrAl_2O_4 and BaAl_2O_4 differ distinctly in the linkage pattern of the $[\text{AlO}_4]^{-5}$ tetrahedra. In SrAl_2O_4 structure, all of the tetrahedral rings are equivalent and trigonally distorted. In BaAl_2O_4 , there are two types of tetrahedral rings; trigonal rings and asymmetrical rings. In the BaAl_2O_4 – SrAl_2O_4 system it has been observed that at ambient temperature there exists another superstructure of $\sqrt{3}A$ and C with probable space group $P6_3$ [20]. A related study by Carpenter et al (2010) on the elastic and inelastic properties of a ceramic $\text{SrAl}_2\text{O}_4\text{:Eu}$ also highlighted on the reports of the existence of an intermediate structure with $P6_3$ space group and unit cell with a -dimension $\sqrt{3}$ times that of the $P6_322$ parent structure [8]. They observed that neither of the $P6_322$ or $P6_3$ ($\sqrt{3}A$) structures is expected to contain a microstructure, such as ferroelastic twin walls, which would be displaced by the application of an external stress. A feature common to both structures is the tilting of AlO_4 tetrahedra such that

the apical oxygen between successive sheets is located away from the three-fold symmetry axis. They concluded that the $P6_322 \leftrightarrow P6_3 (\sqrt{3}A)$ transition behaves in respect of its strain and elastic relaxation as a normal displacive transition which is close to tricritical in character and that the elastic and inelastic properties of $SrAl_2O_4:Eu$, in the $P2_1$ form which has the properties of current interest for elasticoluminescence, are dominated by the influence of phase transitions [8].

2.2.2. Crystal Structure of Garnets

The unit cell of yttrium aluminium garnet compound ($Y_3Al_5O_{12}$) or YAG with a general chemical formula, $(\{A\}_3(B)_2[C]_3O_{12})$ contains eight formula units where A,B,C are metal ions Y^{3+} and Al^{3+} located at different symmetry sites [27]. It has a symmetrical cubic structure in which A, B, and C are at the dodecahedral, octahedral and tetrahedral sites respectively [28]. A and B are usually di- and tri-positive cations. It has a bcc structure (space group $Ia\bar{3}d$ or O_h^{10}) with 160 (80) atoms in the cubic (primitive) cell (Figure 2.5). The Y ions (A atoms) occupy the 24(c) sites and each is dodecahedrally coordinated to eight O. The O atoms occupy the 96(h) sites whose exact locations depend on three structural parameters x, y, and z and are different for different garnet oxides. There are two different sites for Al, Al_{oct} (B atom) occupy the 16(a) site with an octahedral point symmetry ($C3i$) and Al_{tet} (C atom) occupy the 24(d) sites with a tetrahedral point symmetry (S_4) [29]. The garnet structure can be viewed as interconnected octahedrons, tetrahedrons, and dodecahedrons with shared O atoms at the corners. Each oxygen is a member of two dodecahedra, one octahedron and one tetrahedron [27].

There are three crystalline phases in a $Y_2O_3-Al_2O_3$ pseudobinary system, i.e. orthorhombic **perovskite** (YAP) and hexagonal YAH ($YAlO_3$), **monoclinic** $Y_4Al_2O_9$, (YAM) and **cubic garnet** $Y_3Al_5O_{12}$ (YAG) [32]. The different phases occur depending on the molar ratio and thermodynamic conditions whereby the Y_2O_3/Al_2O_3 ratio in orthorhombic YAP ($YAlO_3$) and hexagonal YAH ($YAlO_3$) is 1:1, in YAM it is 2:1 and in YAG it is 3:5 [33]. In as much as the synthesis of YAG is carried out under stoichiometric conditions of Y_2O_3 and Al_2O_3 mixture, other phases, YAM and YAP, often appear as by-products [34]. It has been reported that as the firing temperature is increased YAM forms first, followed by YAP second and finally YAG [35].

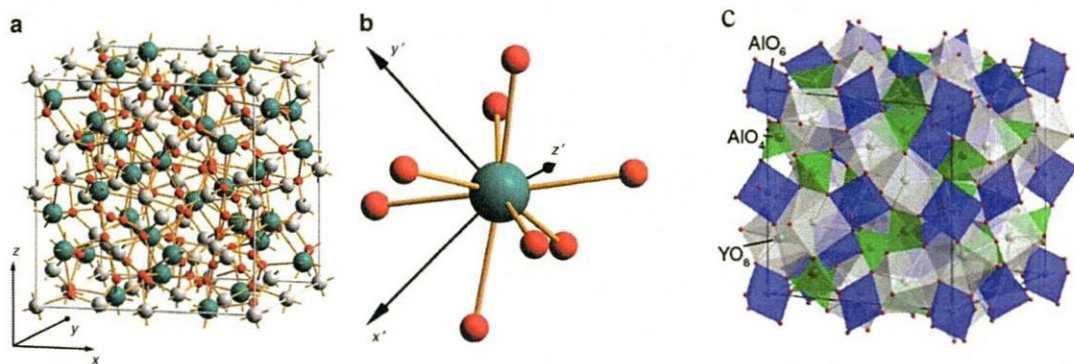


Figure 2.5:(a) Unit cell of YAG crystal -Green, white and red sites are occupied by yttrium, aluminium and oxygen, respectively (b) The local surrounding of one yttrium site[29] and (c) garnet structure of $Y_3Al_5O_{12}$ compound showing linked AO_8 (Y-sites), BO_4 (green-Al sites) and MO_6 (blue- Al sites) polyhedral [31].

The **$YAlO_3$ phase** has a perovskite structure (YAP) of the $GdFeO_3$ type [35]. In YAP, the Y and Al are both octahedrally coordinated in a distorted octahedron formed by the O atoms [37]. YAP contains 20 atomic % Y and 20 atomic % Al or in terms of mol% it is 50 mol% Al_2O_3 in Y_2O_3 . At thermal equilibrium more than 50 mol% but less than 62.5 mol% Al_2O_3 in Y_2O_3 forms a mixture of YAP and YAG while a combination of less than 50 mol% but greater than 33.3 mol% Al_2O_3 in Y_2O_3 , forms a YAP plus YAM mixture[38].

The **$Y_4Al_2O_9$ phase** has a monoclinic structure (YAM), with Y/Al ratio of 2/1 [37]. It is one of the three compounds that occur within the pseudo-binary system between aluminum oxide (Al_2O_3) and yttrium oxide (Y_2O_3) [39]. Yamane et al (1998) reported that at room temperature the space group of the crystal structure of monoclinic $Y_4Al_2O_9$ is $P2_1/c$ [40]. In the unit cell of $Y_4Al_2O_9$, the Al atoms are connected to four oxygen atoms and the Y atoms connected to either six or seven oxygen atoms with site symmetry C_1 [41,42]. Two of the Y ions are sevenfold coordinated and the other two are six fold coordinated, while all of the Al ions are tetrahedrally coordinated. The Oxygen sites are more complex with four distinct arrangements among the nine sites[37]. YAM contains 13.3 atomic % Al and 26.7 atomic % Y. YAM is 33.3 mol% Al_2O_3 in Y_2O_3 . At thermal equilibrium a mixture containing more than 33.3 mol% and less than 50 mol% Al_2O_3 in Y_2O_3 is a combination of YAM plus YAP. While less than 33.3 mol% Al_2O_3 in Y_2O_3 forms a combination of YAM and Y_2O_3 at thermal equilibrium [38].

The **$Y_3Al_5O_{12}$ phase** has a cubic structure of the garnet type (YAG) and is also known as yttrium aluminium garnet or YAG. YAG has a complicated structure with 160 atoms in the cubic cell. In YAG, there are two Al sites, an octahedral and a tetrahedral, and Y is eightfold coordinated[36] as shown in Fig.5. YAG contains 15 atomic % Y, and 25 atomic % Al or 62.5 mol% Al_2O_3 in Y_2O_3 . At thermal equilibrium more than 62.5 mol% Al_2O_3 in Y_2O_3 is a mixture of YAG and

Al₂O₃. A combination with less than 62.5 mol% but greater than 50 mol% Al₂O₃ in Y₂O₃ consists of a mixture made of YAG and YAP at thermal equilibrium [38].

2.3. Crystal Field Theory (CFT)

Crystal Field Theory (CFT) is a model that describes the interaction between a central metal ion that is surrounded by anions (ligands) in a crystal. It describes the effect of the attraction between the positive charge of the metal cation and negative charge on the non-bonding electrons of the ligand. It describes the breaking of degeneracies of electron orbital states (having the same quantum energy level), usually d or f orbitals, due to the effect of the static electric field produced by a surrounding charge distribution (anion neighbours). Crystal field theory states that d or f orbital degeneracy can be broken by the electric field produced by ligands, stabilizing the complex [43]. The simplest form of crystal field theory is the point charge electrostatic model (PCEM). Each anion that coordinates the metal ion is represented by a monopole having the valence value of the anion. They produce a crystal field consisting of a spherically symmetric part and a non-spherical part. The interaction of the non-spherical part with the 5d electron causes the crystal field splitting [43, 44]. This splitting is affected by:

- The nature of the metal ion
- The metal's oxidation state (a higher oxidation state leads to a larger splitting)
- The arrangement of the ligands around the metal ion
- The nature of the ligands surrounding the metal ion

The interactions between the metal ion and the ligands are purely electrostatic (ionic). The ligands are regarded as point charges. If the ligand is negatively charged, ion-ion interaction occurs. If the ligand is neutral the interaction is described as, ion-dipole interaction. The electrons on the metal are under repulsive from those on the ligands. In metals the electrons occupy the d-orbitals farthest away from the direction of approach of ligands.

The other analogy is the effect of moving a set of negative point charges (anions) close to a metal ion on a metal d or f orbital energies. The energies of the d orbitals would rise as the negative charges approach the metal ion, due to the repulsive force between the orbital electrons and the surrounding charge. When point charge enters a region of high electron density, the orbital energy rises significantly owing to the repulsion between the electron and the point charge. If the surrounding anion is spherically symmetric, all the orbitals will be equally affected. However the surrounding negative charge is never spherically distributed, because the charge is associated with specific ions that occupy specific positions. As a result each orbital is

affected differently depending on the geometry of the surrounding point charges. This effect is clearly seen in the splitting of the energy levels of the orbitals.

The perturbing crystal field reduces the symmetry of the free-ion Hamiltonian and splits each free-ion energy level into a set of crystal-field levels. The numbers and degeneracies of these crystal-field levels are determined both by the numbers and dimensions of the point-group irreducible representations contained in the subduced representations and by additional degeneracies arising from time-reversal invariance.

The efficiencies and emission wavelength bands of solid state devices are being modified based on color centres via crystal field engineering by use of transition-metal ions and rare-earth ions as impurities or defects in crystals. It involves improving performance by tailoring the environment of an isolated optical centre in a crystal through the crystal growth process in which the structure and composition of the unit cell is modified in a controlled and known manner [44, 45]. CFT has been used to describe various spectroscopies of transition metal coordination complexes, in particular optical spectra (colors).

The impurities intentionally incorporated in to the host lattice perturb the band structure of the host by creating local quantum states that lies within the band gap. Luminescence mechanism is generally an electron-hole recombination process which involves transitions from conduction band to acceptor level, donor level to valance band or donor level to acceptor level (Figure 2.6).

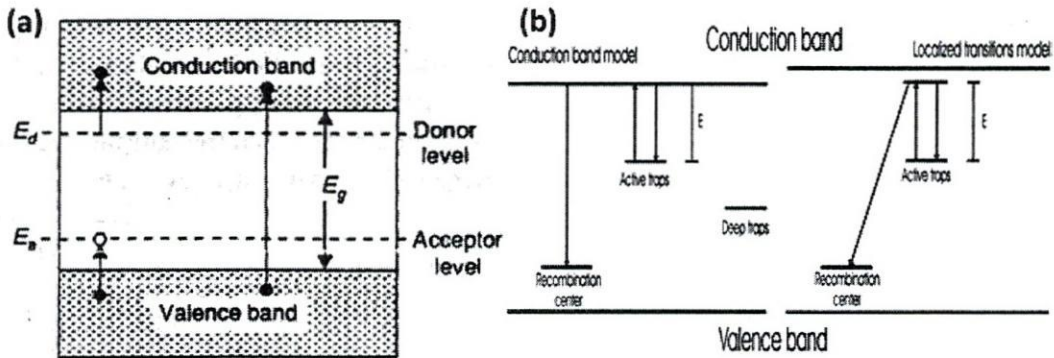


Figure 2.6: (a) Transitions from conduction band to acceptor level, donor level to valence band or donor level to acceptor level. (b) Trap (impurities or defects) levels in a crystal band gap

In some cases, this mechanism is localized on the activator atom center. However, these localized transitions are only allowed when two selection rules are met [3]:

1. Spin selection rule, i.e. $\Delta s = \pm 1$, where s is the spin quantum number, and
2. LaPorte selection rule $\Delta l = 0$, where l is the orbital angular momentum quantum number.

2.4. Electronic Transition in RE Metal Ions

The Rare Earth (RE) metals constitute a group of seventeen elements, which include fifteen lanthanides (commonly symbolized as Ln), Scandium (Sc) and Yttrium (Y). The atomic numbers of lanthanide elements increase from 57 (lanthanum-La) to 71 (lutetium-Lu). They are found in the 6th and 7th periods or rows of the periodic table. Apart from Lu which is a d-block element, all of the La elements belong to the f-block characterized by the filling of the 4f electron shell. All La elements form trivalent cations (Ln^{3+}) whose ionic radii decrease from La to Lu. However they can occur as activators in phosphors in their divalent (Ln^{2+}) charge state.

Lanthanides have their electron configuration in the form; $[\text{Xe}]4f^n 6s^m$. As atoms or as free ions the 6s shell can be empty ($m = 0$), occupied by one electron ($m = 1$) or occupied by two electrons ($m = 2$). The dominant oxidation state of the lanthanides is (III) and that the electron configuration of a trivalent lanthanide ion is of the form $[\text{Xe}]4f^n$ [45, 46]. In compounds, the 6s shell is empty, and moving through the lanthanide series from La to Lu, the 4f shell is partially filled with at most $n = 14$ electrons. They are effectively shielded from the environment by the closed $5p^6$ and $5s^2$ shells of the $[\text{Xe}]$ configuration. Hence the $4f^n$ energy levels are inert to the crystal field environment but the shielding of an electron in a 5d orbital is relatively poor and its energy is very sensitive to the environment and can be easily split by the crystal field effect [47]. The magnitude of the splitting of the 5d levels depends strongly on the shape and the size of the anion polyhedron coordinating the Ln dopant ion [48].

Emission of light from phosphors doped with lanthanide ions as luminescent centers is mainly due to two types of electronic transitions: 4f - 4f and $4f^n - 4f^{n-1}5d$ transition. 4f - 4f transitions are generally characterized by sharp emission lines, long lifetimes and excellent coherence properties while the $4f^n - 4f^{n-1}5d$ transitions show broad band, shorter lifetimes and large oscillator strength [49,50]. Since the 4f electronic energy levels of lanthanide ions are characteristic of each ion [51], the energy $E(n, m, Q, A)$ needed to excite an electron from the ground state of the $4f^n 6s^m$ configuration to the lowest energy of the $4f^{n-1} 6s^m 5d$ configuration depends on the type of lanthanide ion (characterized by n , m and its ionic charge Q) and the host crystal denoted by A . Figure 2.7 shows $E(n, m, Q, \text{free})$ for the lanthanides in free space ($A = \text{free}$) as a function of n [46].

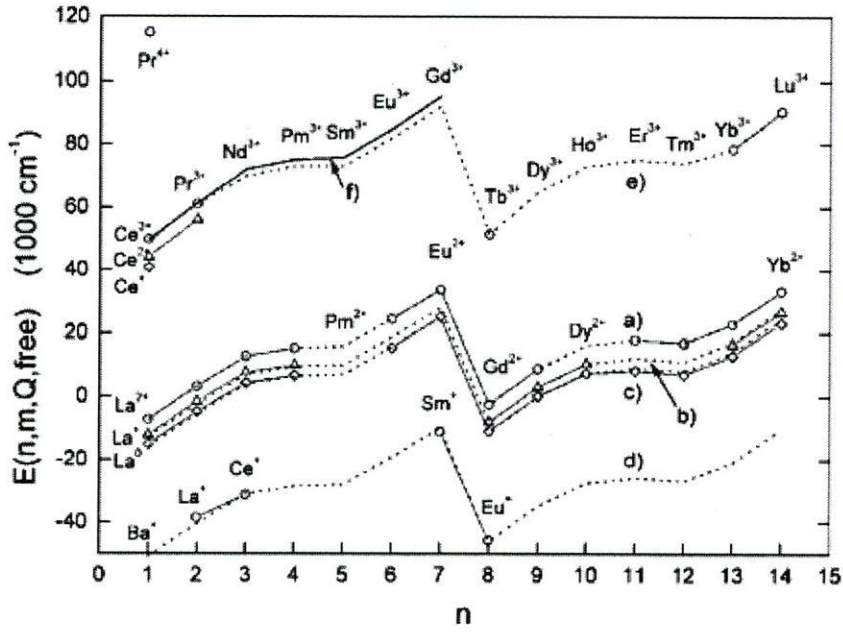
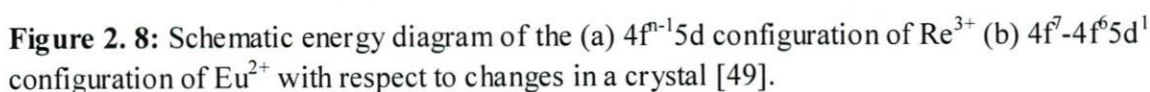


Figure 2.7: f-d transition energies $E(n, m, Q, \text{free})$ for the free atomic and ionic lanthanides as a function of n [47].

The 5d-electron has a strong interaction with the neighboring anion ligands in the compound since the 5d orbital is not shielded from the surrounding crystal environment and thus the 5d energy level is perturbed by changes in the band gap of the material. Figure 2.8 shows that changes in the 5d energy level of the RE^{3+} are influenced by factors such as; the shift of the energy centroid (E_c) of the 5d orbit, the Coulomb interactions between 4f and 4f electrons ($E_{\text{Coul}}(\text{ff})$) and between 4f and 5d electrons ($\Delta E_{\text{Coul}}(\text{fd})$) and the effect of the crystal field (E_{cf}) [49]. The centroid of $4f^{n-1}5d$ level in crystals are lower than in the free ions and the reduction is similar for all lanthanides since it is affected only by the interaction of the outer 5d electrons with the surrounding anion ligands [44].



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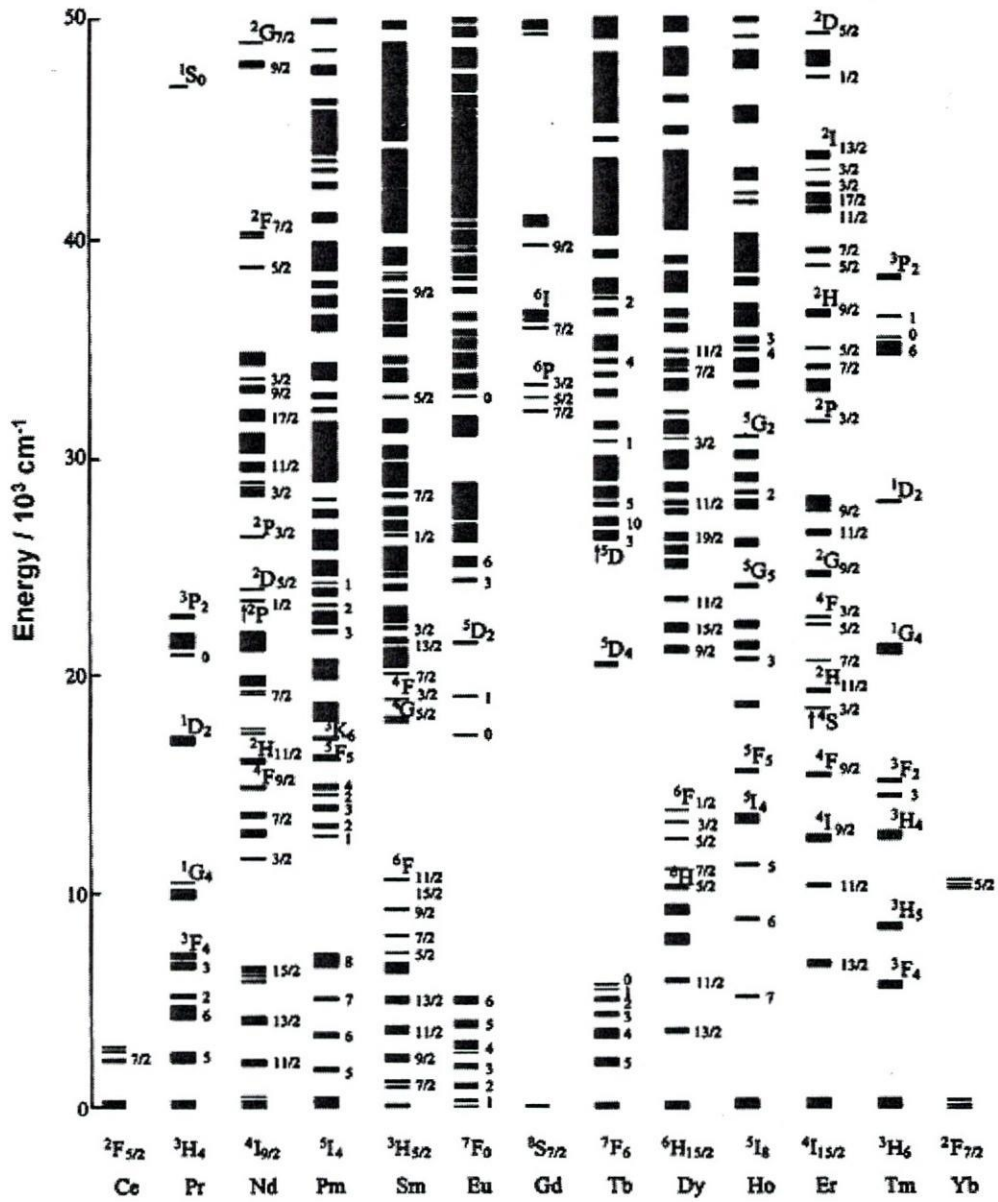


Figure 2.9: Energy level diagram of $4f^n$ in trivalent Ln^{3+} ions doped in a low-symmetry crystal (LaF_3) [55].

Temperature variations during or post-synthesis also affects the crystal field. Xia et al (2005) reported a little shift/increase in the 2θ value of XRD diffraction peaks of $\text{YAG}:\text{Ce}^{3+}$ phosphors due to the change of crystal field around Ce^{3+} ions as the lattice parameter decreased with increasing of sintering temperature [54].

2.5. Selection Rules

Only a fraction of all possible transitions are observed. The possibility or **probability** of a transition to occur (**allowed**) or not (**less likely/not allowed**) and its intensity are determined by what is known as selection rules. These are a set of restrictions governing the likelihood that a physical system will change from one state to another or will be unable to make such a transition. Allowed transitions are electric dipole interaction transitions which have high probability of occurring and high intensity while forbidden transitions have low probability, weak intensity and are non-electric dipole interaction. Selection rules for electronic, vibrational, and rotational transitions in molecules and compounds have been formulated and may differ depending on the technique used to characterize the transition. The following selection rules apply;

2.5.1. Angular Momentum: ($\Delta l = \pm 1$)

It states that the only allowed transitions are those in which the orbital quantum number of an electron changes by one and its magnetic quantum number remains the same or changes by one for instance $p \rightarrow d$ or $d \rightarrow p$ are allowed but $d \leftrightarrow d$ transitions are not allowed.

2.5.2. Spin-Selection Rule: ($\Delta S = 0$)

The multiplicity of a state is calculated as the total number of unpaired electrons + 1, or twice the total spin + 1 written as $2S+1$. It is the number of possible orientations of spin angular momenta. Multiplicity is used to distinguish between several degenerate wave functions that differ only in the orientation of their angular spin momenta. It is defined as $2S+1$, where S is the angular spin momentum. When all electrons are paired $S = 0$, and the multiplicity = $2(0) + 1 = 1$. This case is called a **singlet**. If a molecule has 1 unpaired electron $S = +\frac{1}{2}$ and $2S + 1 = 2$, which is called a **doublet**. Two unpaired electrons would result in a **triplet**, etc. Atoms and molecules with odd multiplicities are usually more stable than those with even multiplicities. The singlet ground state is S_0 , excited singlet states are S_i where i is the number of states above ground state it is, for doublet states it's D_i , for triplet states it's T_i , etc. As a result of spin orbital interactions energy levels may split into $2S+1$ sublevels [56]. The **spin** selection rules specifies that there should be no change in the number of unpaired electrons. Spin allowed transitions occur between states which have the same spin multiplicity for instance, $^2T \rightarrow ^2E$ transitions are allowed. Spin forbidden transitions are those that occur between states with different spin multiplicity for instance, $^2T \rightarrow ^1E$ are not allowed. For the electron to change its spin energy must be used up and so any spin forbidden transitions are usually very weak. The spin forbidden

transitions can occur due to the help of **spin-orbit coupling**. In heavy atoms spin-forbidden transitions are more intense usually larger spin-orbit coupling.

2.5.3. LaPorte Rule (parity): ($\Delta l = 0$)

This is based on the inversion symmetry of the complex. For centro-symmetric molecules, transitions between energy levels with the same symmetry with respect to the centre of inversion ($g \rightarrow g$, $u \rightarrow u$) are not allowed for example, $T_{2g} \rightarrow E_g$ are forbidden and also transitions between like atomic orbitals such as s-s, p-p, d-d, or f-f, transitions are forbidden but transitions between states of different inversion symmetry ($g \leftrightarrow u$) are allowed. All transitions of octahedral and square planar complexes are LaPorte forbidden. The Laporte selection rule can however be overcome (i.e LaPorte forbidden transitions can occur) due to the following reasons [57];

- As a result of distortions from centro-symmetry that occurs continuously as the complex vibrates. These distortions cause d-p mixing and set up transitions between states with varying amounts of p character. Various ligands around the molecule disrupt the perfect symmetry around the complex, or because the molecule can vibrate to remove the centre of symmetry. The vibration-induced breakdown of the LaPorte Rule makes the d-d transitions vibronically allowed. The intensity of vibronic bands increases with temperature as vibrational amplitudes increase.
- Lack of inversion symmetry. Tetrahedral ML_4 complexes (T_d) have no inversion symmetry which allows easier mixing of levels to give more intense transitions with higher molar absorptivities ($\epsilon \approx 100 - 1000$). This is further magnified by the fact that the t_2 orbitals in T_d complexes have the same symmetry as the $(n+1)p$ orbitals, so $e \rightarrow t_2$ has a partly d-p character. For this reason, d-d transitions for tetrahedral complexes are LaPorte allowed.
- Charge transfer (CT) transitions are ($g \leftrightarrow u$) and are LaPorte allowed hence possess very high molar absorptivities ($\epsilon \gg 10^3$).

2.5.4. Magnetic dipole transitions

Magnetic dipole transitions describe the effect of the coupling to the magnetic part of the electromagnetic wave. Depending on the frequency at which they are observed, magnetic dipole transitions fall into two categories:

2.5.5. Optical magnetic dipole transitions

These can occur at frequencies in the infrared, optical or ultraviolet between sublevels of two different electronic levels

2.5.6. Magnetic Resonance transitions

These occur at microwave or radio frequencies between angular momentum sublevels within a single electronic level. These are further subdivided into two [57];

- **Electron Paramagnetic Resonance (EPR) transitions**- those transitions associated with the electronic angular momentum of the atom or molecule and
- **Nuclear Magnetic Resonance (NMR) transitions**- those associated with the nuclear angular momentum

The selection rules for magnetic dipole transitions states that only transitions between states in which the matrix elements of either **L** or **S** are nonzero are magnetic dipole allowed. Therefore the magnetic dipole selection rules are:

- (1) No change in electronic configuration,
- (2) No Parity is changed,
- (3) $\Delta J = 0, \pm 1$,
- (4) $\Delta M_J = 0, \pm 1$,
- (5) $\Delta J = 0$ together with $\Delta M_J = 0$ is not allowed; in particular, $J = 0 \leftrightarrow 0$ is not allowed;
- (6) $\Delta L = 0$;
- (7) $\Delta S = 0$

2.5.7. Electric dipole transitions

Electric dipole transitions due to the effect of interaction of an electron in an atom with the electromagnetic field as it jumps between the energy levels in a system. Between certain electron states the electric dipole transition may occur or not according to one or more selection rules, particularly the angular momentum selection rule in which a case, the transition is termed electric dipole allowed or forbidden. Selection rules for magnetic dipole transitions states that only transitions between states in which the matrix elements of either **L** or **S** are nonzero are magnetic dipole allowed. Therefore the electric dipole selection rules are:

- (1) Only one electron changes its nl state;
- (2) Parity must change;
- (3) $\Delta J = 0, \pm 1$;
- (4) $\Delta M_J = 0, \pm 1$;
- (5) $J = 0 \leftrightarrow 0$ is not allowed;
- (6) $\Delta L = 0, \pm 1$;

(7) $L = 0 \leftrightarrow 0$ is not allowed;

(8) $\Delta S = 0$;

Where $\mathbf{J} \equiv \mathbf{L} + \mathbf{S}$ is the total orbital plus spin angular momentum

2.5.8. Spin-orbit coupling (SOC).

Spin-orbit coupling originates from the movement of electrons in a crystal's intrinsic electric field. It links a particle's velocity to its quantum mechanical spin thereby uniting a particle's spin with its momentum. In spectroscopy the magnitude of a spin-orbit coupling is measured as a splitting of spectral lines. Spin-orbit coupling requires the introduction of a new quantum number j , and is caused by the magnetic moments due to electron orbit and electron spin. In fact, $j = l \pm 1/2$, which gives rise to a splitting of each energy level into two levels, unless $l = 0$ (no orbital magnetic moment) [3]. The principal characteristics of spin-forbidden transitions induced by spin-orbit coupling are their weakness relative to spin-allowed transitions, but with strength strongly dependent upon the atomic numbers of the atoms in the molecule. The latter is often called the "heavy atom" effect, and is very familiar to spectroscopists of substituted π -electron systems [58].

2.5.9. L-S coupling (Russell-Saunders Coupling)

LS- or Russell-Saunders coupling is an appropriate way of describing small electronic configurations because the spin-orbit coupling is weak in comparison to the electrostatic effects. In light atoms ($Z < 30$) the spins and the orbital momenta are interacting with themselves, i.e. spin-spin ($s - s$) and orbit-orbit ($L - L$) interactions are larger than the individual spin-orbit ($S-L$) interactions. The spins can be combined into a total spin and the L 's into a total orbital angular momentum. The interaction between the resulting L and S is called Russell-Saunders coupling or L-S coupling. The allowed LS terms of a configuration consisting of two nonequivalent groups of electrons are obtained by coupling the S and L vectors of the groups in all possible ways, and the procedure may be extended to any number of such groups. The total angular momentum J then can be calculated as $\mathbf{J} = \mathbf{L} + \mathbf{S}$. The presence of large external magnetic fields would decouple these two momenta.

2.5.10. J-J coupling

In heavier atoms with bigger nuclear charges spin-orbit coupling is frequently as large as or larger than the spin-spin or orbit-orbit interactions. In those cases not the total spins and orbital

momenta, but the individual total angular momenta $J_k = L_k + S_k$ must be combined, this is called j-j coupling.

Summary

In ground configurations of heavy atoms and in many excited configurations of light and heavy atoms, the spin-orbit energy of the valence electrons contributes to a larger fraction of the energy perturbation than the residual electrostatic energy. LS coupling inadequately describes the observed states in these cases. The levels given by j-j - coupling may then be used to explain the absences of multiplets predicted by LS coupling, as well as the presence of LS-forbidden transitions that are allowed by j j-coupling selection rules.

2.5.11. Judd-Ofelt theory

In this theory, the initial and final states of an absorption transition are written as $|SLJ\rangle$ and $|S'L'J'\rangle$, respectively, where S, L, and J denote the quantum numbers for the total spin, orbital angular momentum, and total angular momentum, respectively [6]. The Judd-Ofelt theory is based on the **static**, **free-ion** and **single configuration** approximations. In the static model, the central ion is affected by the surrounding host ions via a static electric field, referred to as the ligand or crystal field. In the free-ion model, the host environment produces the static crystal field, and is treated as a perturbation on the free-ion Hamiltonian. In the single configuration model, the interaction of electrons between configurations is neglected. In simple terms, the Judd-Ofelt theory describes the intensities of lanthanide and actinide transitions in solids and solutions [59, 60].

From the Judd-Ofelt theory, some general rules have been derived for ED transitions between $4f^n$ states of $(RE)^{3+}$ ions in crystals [60]:

- $\Delta J \leq 6$; $\Delta S = 0$, and $\Delta L \leq 6$.
- For ions with an even number of electrons:
 - (i) $J = 0 \leftrightarrow J' = 0$ is forbidden;
 - (ii) $J = 0 \leftrightarrow \text{odd } J'$ values are weak transitions;
 - (iii) $J = 0 \leftrightarrow J' = 2, 4, 6$ should be intense transitions.

These rules can be useful in establishing initial predictions, although the actual rules that govern a particular transition must be determined by group theory considerations. Table 2.1 shows the selection rules for allowed transitions.

Table 2.1: Allowed transitions; $J=L+S$ is the total angular momentum, L is the Azimuthal quantum number, S is the Spin quantum number, and M_J is the secondary total angular momentum quantum number [62].

Allowed transitions		Electric dipole (E1)	Magnetic dipole (M1)	Electric quadrupole (E2)	Magnetic quadrupole (M2)	Electric octupole (E3)	Magnetic octupole (M3)
Rigorous rules	(1)	$\Delta J = 0, \pm 1$ ($J = 0 \not\rightarrow 0$)		$\Delta J = 0, \pm 1, \pm 2$ ($J = 0 \not\rightarrow 0, 1; \frac{1}{2} \not\rightarrow \frac{1}{2}$)		$\Delta J = 0, \pm 1, \pm 2, \pm 3$ ($0 \not\rightarrow 0, 1, 2; \frac{1}{2} \not\rightarrow \frac{1}{2}, \frac{3}{2}; 1 \not\rightarrow 1$)	
	(2)	$\Delta M_J = 0, \pm 1$		$\Delta M_J = 0, \pm 1, \pm 2$		$\Delta M_J = 0, \pm 1, \pm 2, \pm 3$	
	(3)	$\pi_f = -\pi_i$		$\pi_f = \pi_i$		$\pi_f = -\pi_i$	
LS coupling	(4)	One electron jump $\Delta l = \pm 1$	No electron jump $\Delta l = 0,$ $\Delta n = 0$	None or one electron jump $\Delta l = 0, \pm 2$	One electron jump $\Delta l = \pm 1$	One electron jump $\Delta l = \pm 1, \pm 3$	One electron jump $\Delta l = 0, \pm 2$
	(5)	If $\Delta S = 0$ $\Delta L = 0, \pm 1$ ($L = 0 \not\rightarrow 0$)	If $\Delta S = 0$ $\Delta L = 0$	If $\Delta S = 0$ $\Delta L = 0, \pm 1, \pm 2$ ($L = 0 \not\rightarrow 0, 1$)	If $\Delta S = 0$ $\Delta L = 0, \pm 1, \pm 2, \pm 3$ ($L = 0 \not\rightarrow 0, 1, 2; 1 \not\rightarrow 1$)	If $\Delta S = 0$ $\Delta L = 0, \pm 1, \pm 2, \pm 3$ ($L = 0 \not\rightarrow 0, 1, 2; 1 \not\rightarrow 1$)	If $\Delta S = 0$ $\Delta L = 0, \pm 1, \pm 2, \pm 3$ ($L = 0 \not\rightarrow 0, 1, 2; 1 \not\rightarrow 1$)
Intermediate coupling	(6)	If $\Delta S = \pm 1$ $\Delta L = 0, \pm 1, \pm 2$		If $\Delta S = \pm 1$ $\Delta L = 0, \pm 1, \pm 2, \pm 3$ ($L = 0 \not\rightarrow 0$)	If $\Delta S = \pm 1$ $\Delta L = 0, \pm 1$ ($L = 0 \not\rightarrow 0$)	If $\Delta S = \pm 1$ $\Delta L = 0, \pm 1, \pm 2, \pm 3, \pm 4$ ($L = 0 \not\rightarrow 0, 1$)	If $\Delta S = \pm 1$ $\Delta L = 0, \pm 1, \pm 2$ ($L = 0 \not\rightarrow 0$)

As a general remark, one can state that in cases where the rare-earth ion occupies a site with inversion symmetry, the selection rule states: $\Delta J = 0, \pm 1$. In cases where $\Delta J = 0$, any transition to another state with $J = 0$ is forbidden as well. In such a case, $\Delta|J|$ is necessarily ± 1 . These are all magnetic dipole transitions. In lattices without inversion symmetry there is also electric dipole emission. For these transitions, the selection rule is: $\Delta|J| \leq 6$. Here again, for initial or final states with $J = 0$, other selection rules are operative. In such a case, for electric dipole transitions, $\Delta|J| = 2, 4$, or 6 . Therefore the presence of an inversion center opens up the possibility to tune the emission spectrum to a small extent [6].

2.5.12. Zeeman Effect

Zeeman Effect is the effect of splitting a spectral line into several components in the presence of a **static magnetic field**. Zeeman Effect is as a result of distortion of the electron orbitals where the angular momentum quantum state undergoes a displacement from degeneracy because of the magnetic field. The presence of a magnetic field and its strength corresponds with the pattern

and amount of splitting. The splitting is associated with the orbital angular momentum quantum number L of the atomic level. This quantum number can take non-negative integer values. The number of split levels in the magnetic field is $2L + 1$. Figure 2.10 illustrates the Zeeman Effect.

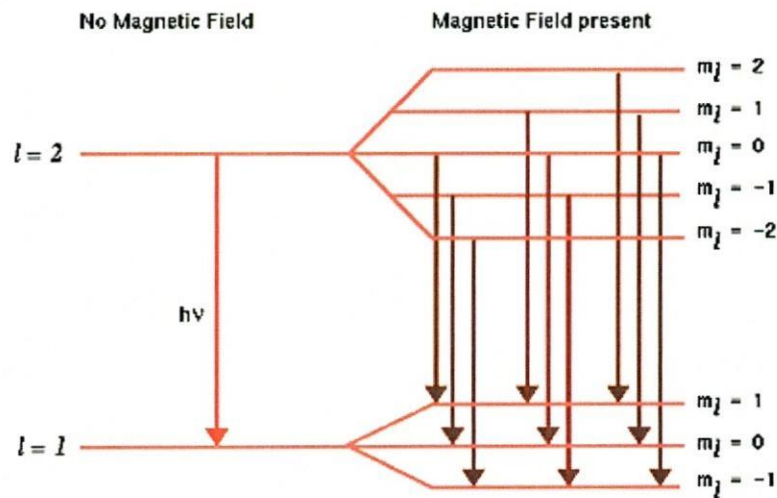


Figure 2.10: Zeeman Effect [63]

Zeeman Effect can be divided into three groups as follows [63];

- **Normal Zeeman Effect**- whereby for some atoms, the spectral lines split in three under a magnetic field.
- **Anomalous Zeeman Effect** – in which case the spectrum displays a more complex pattern of splitting.
- **Paschen-Back Effect** – as the magnetic field becomes stronger, some spectral lines merge and the anomalous Zeeman splitting joins into a normal splitting

2.5.13. Stark effect

Stark effect is the shifting and splitting of spectral lines of atoms and molecules due to presence of external electric fields. The amount of splitting and or shifting is called the Stark splitting or Stark shift. Stark effect can be classified into two [62];

- **First-order** Stark effect which is linear in presence of electric field.
- **Second order** Stark effect is quadratic in presence of the electric field.

The splitting of the energy levels by an electric field first requires that the field polarize the atom and then interact with the resulting electric dipole moment. That dipole moment depends upon the magnitude of M_j , but not its sign, so that the energy levels are split into $J+1$ or $J+1/2$ levels, for integer and half-integer spins, respectively.

2.5.14. Jahn–Teller effect

The Jahn–Teller effect, describes the geometrical distortion of molecules and ions that is associated with certain electron configurations. The Jahn–Teller theorem essentially states that any nonlinear molecule with a spatially degenerate electronic ground state will undergo a geometrical distortion that removes that degeneracy, because the distortion lowers the overall energy of the species. The distortion reduces the symmetry and energy of a non-linear molecular system that The distortion normally takes the form of elongating the bonds to the ligands lying along the z axis, but occasionally occurs as a shortening of these bonds instead When such an elongation occurs, the effect is to lower the electrostatic repulsion between the electron-pair on the Lewis basic ligand and any electrons in orbitals with a z component, thus lowering the energy of the complex. If the undistorted complex would be expected to have an inversion centre, this is preserved after the distortion [64].

2.6. Optical transition in Lanthanide Ions

Rare Earth (RE) metals constitute a group of seventeen elements, which include fifteen lanthanides (Commonly symbolized as Ln), Scandium (Sc) and Yttrium (Y). Since the objective of the present study is to develop rare earth (RE) doped aluminate and garnet phosphors and tailor their optical properties; color, intensity/brightness and decay/glow time by modifying their structure through incorporation of impurities (Eu^{2+} , Nd^{3+} , Dy^{3+} , Ce^{3+} , Al^{3+} , Ga^{3+} and Gd^{3+}), we briefly study the optical transitions of these ions.

2.6.1. Cerium (Ce^{3+})

As one of the RE elements in the lanthanides group, Cerium (Ce) has electron configuration of $[\text{Xe}] 4f^1 5d^1 6s^2$. The $4f^n$ energy levels are not affected by the host environment because they are completely shielded by the filled $5p^6$ and $5s^2$ shells of the $[\text{Xe}]$ configuration [63]. However an electron in a 5d orbital is not completely shielded and its energy is very susceptible to changes in the crystalline environment [63]. The ground and excited electronic configurations of Ce^{3+} ion are $4f^1$ and $5d^1$ and it has only one electron in the 4f state. The excited $5d^1$ level strongly interacts with the host lattice due to the large spatial field of the 5d wave-function and the crystal field splitting dominates over the split spin-orbit interaction. Therefore emission transition is an allowed one since the $5d \rightarrow 4f$ transition is parity and spin-allowed/ electric-dipole allowed. As a consequence, the emitting level has a short life- time, a common property in certain phosphors

[65, 66]. The $5d \rightarrow 4f$ transitions of Ce^{3+} ion are electric-dipole allowed. Figure. 2.11 shows the energy level diagram of the $4f-5d$ configuration of Ce^{3+} ion in a garnet structure.

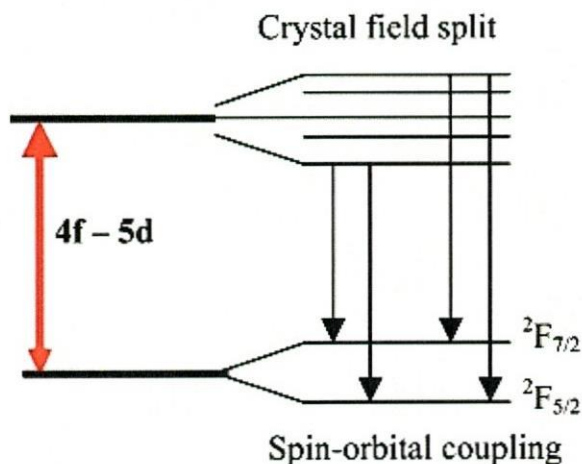


Figure 2.11: A simplified energy level scheme and crystal field splitting of the Ce^{3+} ion ($4f^1$) [68].

Emission observed from cerium differs greatly with the type of host material. In $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, there are two Ce^{3+} absorption bands in the region between 250 and 500 nm. They centred at 342 and 462nm due to the crystal-field splitting of the $5d$ state. During the $4f-5d$ transition, upon excitation with the electron in $4f^1$ ground state is photo-excited to the $5d^1$ levels leaving the $4f$ shell empty, relaxes and then gets de-excited and returns to $4f^1$ state thereby emitting light photon which covers a broad band from 450 to 650 nm with a maximum in the green-yellow region (530 nm) as a result of electronic transitions within Ce^{3+} between the $[\text{Xe}]4f^15d^06s^0$ ($^2F_{5/2}, ^2F_{7/2}$) and $[\text{Xe}]4f^05d^16s^0$ ($^2D_{3/2}$) states. In the ground ($4f$) state Ce^{3+} splits up into a doublet $2F_j$ ($j = 5/2$ and $7/2$) state due to spin-orbit coupling [53]. Sun and Kwok (1999) observed that $\text{Y}_2\text{SiO}_5:\text{Ce}^{3+}$ showed a blue emission band peak at around 400 nm attributed to the $5d \rightarrow 4f$ transition of Ce^{3+} [67].

2.6.2. Europium $\text{Eu}^{2+} (4f)^7$

Europium (Eu) has electron configuration of $[\text{Xe}] 4f^7 6s^2$. **Divalent europium (Eu^{2+})** ion gives a very intense and broad emission spectrum in the visible range due to the inter-configurational electronic $f^7(^8S_{7/2}) - f^6d$ (f-f) transition. The transition of one f electron from an f to d- orbital occurs between two configurations of opposite parity and therefore it is electric dipole allowed transition [69,70].

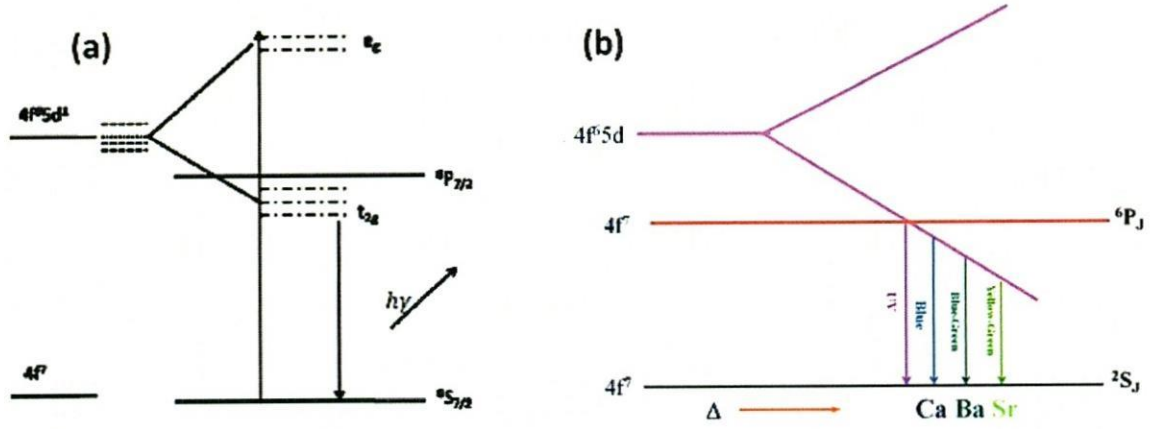


Figure 2.12: Energy level diagram showing (a) the $4f^7 (^8S_{7/2}) - 4f^6 5d^1$ configuration of Eu^{2+} ion [71]. (b) Crystal field and distortion in the MAI_2O_4 (Ca, Ba, Sr) phosphors [72].

The energy of the $4f^6 5d^1$ state depends on the crystal field, because unlike the 4f electrons the 5d electron is in the outer shell and not shielded by the $5p^6$ and $5s^2$ shells [69]. As a result the $5s^2 p^6$ excited 5d energy levels are split by the crystal field into t_{2g} and e_g components as illustrated by figure 2.12 (a).

The Eu^{2+} emission is caused by the electronic transition from the lowest excited state to the $4f^7 (^8S_{7/2})$ state. The interaction of the crystal field strength will determine whether the lowest $4f^6 5d^1$ is above or below the excited $4f^7$ multiplets which are not affected by the host lattice [25]. When the lowest excited state $^6P_{7/2}$ of $4f^7$ - configuration is located below the lowest state of the $4f^6 5d^1$ - configuration, a sharp emission line will be observed [70]. On the contrary, when there is no 4f state below the $^6P_{7/2}$ the broad emission band in Eu^{2+} will arise from $4f^6 5d^1 - 4f^7$ dipole allowed transition. Furthermore, the emission wavelength depends on the strength of the crystal field around the Eu^{2+} ion [70].

The PL characteristics obtained from Eu^{2+} doping also depends on the crystal field strength imposed by the host matrix structure. The 5d excited states are not shielded from the surrounding electronic shell, and the d-electron wave function is greatly affected by the crystal field and strong coupling to the lattice can take place. The d-orbit is generally 5-fold degenerate in free space and it may split further under the action of the crystal field and the split interval should be proportional to the crystal field strength. Cheng et al (2009) studied the room-temperature (RT) photoluminescence excitation (PLE), photoluminescence (PL), and afterglow spectra of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} bulk and nanostructures [73]. The PLE spectrum for the nanostructures, monitored at 518 nm, showed four sub-bands peaking at about 273, 325, 365 and 418 nm,

clearly demonstrating the crystal field splitting of five-fold degenerate 5d excited level of Eu^{2+} ions. In the PL spectra under different excitation wavelengths, they observed only one greenish-yellow broad band emission peak located around 518 nm, corresponding to the $4f^65d^1 - 4f^7(^8S_{7/2})$ electric dipole-allowed transition of Eu^{2+} [74].

Compared to those of its bulk counterpart, the PL, PLE, and afterglow peaks of the nanostructured $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ slightly shifted to shorter wavelength. They observed a conspicuous change in the relative intensity and position of the excitation peak in the blue region. For the nanostructured SrAl_2O_4 , the unit cell volume becomes small and the width of the band gap becomes large. And thus the energy centroid of the 5d configuration ascends correspondingly since the 5d energy level has a closer relation to the conduction band of the compound [75]. Furthermore, the 5d states are vulnerable to the surrounding electronic shell, and the d-electron wave function is greatly affected by the crystal field and strong coupling to the lattice can occur. Eu^{2+} ions, substituting for the Sr^{2+} sites, in monoclinic SrAl_2O_4 phase also possess no symmetry [76]. The relatively large contraction of the lattice constants b and c also indicates the existence of deformation in distorted quasi-hexagonal rings, and therefore, the crystal symmetry around the Eu^{2+} ions is further lowered due to the nanometre size of the crystallites. As a consequence, there is a smaller split of the mixed states of 4f and 5d due to the weakness of the crystal field strength which resulted in a blue shift of Eu^{2+} - related optical transitions [77].

Wako et al (2014) also investigated the excitation and emission spectra of $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Nd}^{3+}$ with various concentrations of Eu^{2+} and Nd^{3+} ions. They observed that the excitation spectra of $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}$ phosphor were similar in shape and showed a broad band from 280 to 400 nm which contained two excitation peaks; one main peak at 325 nm and a shoulder at 260 nm both due to $4f^65d^1 - 4f^7$ transition of Eu^{2+} . The emission spectra were all symmetrical in the blue region and peaked around 440 nm also attributed to the $4f^65d^1 - 4f^7$ transition of Eu^{2+} although the luminescent intensities varied greatly. They also observed that high concentrations of Eu^{2+} generally reduced both intensity and lifetime of the phosphor powders. Compared with the $\text{CaAl}_2\text{O}_4: 0.01\text{Eu}^{2+}$ phosphor, they found out that $\text{CaAl}_2\text{O}_4: 1\text{mol}\% \text{Eu}^{2+}, \text{Nd}^{3+}$ showed relatively higher luminescence intensity and a longer duration. This may be explained in two ways: Firstly, the co-doped Nd^{3+} ions efficiently transferred the absorbed energy to the Eu^{2+} emitter. Secondly, the depth of traps formed by the co-doped Nd^{3+} ions was more suitable [78].

In another experiment on the effect of varying the Ba:Al molar ratios on the luminescence characteristics of the $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Nd}^{3+}$ phosphor, Wako et al (2014) observed two maxima

curve fits, peaking at 490 and 525 nm (blue-green) in the PL spectra of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Nd}^{3+}$ which arise from the two emissions of Eu^{2+} in the two Ba^{2+} sites within in the BaAl_2O_4 structure[15]. These are due to the transitions from the lowest 2D level of the excited $4f^65d^1$ configuration to the ground $^8S_{7/2}$ level of the $4f^7$ configuration of the Eu^{2+} ion [17] .

2.6.3. Europium $\text{Eu}^{3+} (4f)^6$

Among the rare-earth ions, Eu^{3+} is an efficient red emitter because this ion has a large energy gap between the emitting 5D_0 level and next lower 7F_6 level [79, 80] as represented in the energy level diagram of Eu^{3+} shown in figure 2.13. The emission of this ion usually consists of sharp emission lines in the red spectral region which arise from the f-f transition of the Eu^{3+} .

For Eu^{3+} ions in free state, The $^5D_0 \rightarrow F_0$ emission is forbidden due to the electric dipole rule ($\Delta S = 0$) and is not usually observed. The $^5D_0 \rightarrow ^7F_2$ transition is forbidden according to magnetic dipole ($\Delta S = \Delta L = 0, \Delta J = 0, \pm 1$) and electric dipole ($\Delta S = 0$) selection rules. According to the theory of Judd (1962) and Ofelt (1962) [60, 81], the $^5D_0 \rightarrow ^7F_2$ transition becomes electric-dipole allowed, due to an admixture of opposite parity $4f^{n-1} 5d$ state through an odd parity crystal field component. The $^5D_0 \rightarrow ^7F_{3,5}$ transitions show first order magnetic-dipole and second order electric-dipole character [82,83]. The $^5D_0 \rightarrow ^7F_{4,6}$ transitions have electric dipole character [82].

combination of $4f^{n-1}5d$, $4f^{n-1}5g$, etc and transitions can occur. $4f$ electron energy levels are determined by a combination of the Coulomb interaction among the electrons, the spin-orbit coupling and the crystalline electric field [85].

The transitions from the singly degenerate excited state 5D_0 to the different sublevels within the terminal states 7F_J (from $J = 0$ to 6), correspond to different emission lines depending on the kind of host structure. Kumara et al (2013) studied the emission properties in the $\text{CaAl}_2\text{O}_4:\text{Eu}^{3+}/\text{Eu}^{2+}$, Nd^{3+} nanostructured phosphor [86]. The emission bands they observed which are assigned to the $^5D_0 - ^7F_J$ ($j = 0, 1, 2, 3, 4, 5$ and 6) transitions with excitation 532 nm are as shown in Table 2.2.

Table 2.2: Emission bands in $\text{CaAl}_2\text{O}_4:\text{Eu}^{3+}/\text{Eu}^{2+}$ phosphor with 532 nm excitation due to Eu^{3+} [86].

Transition	Wavelength (nm)
$^5D_0 \rightarrow ^7F_0$	578
$^5D_0 \rightarrow ^7F_1$	591
$^5D_0 \rightarrow ^7F_2$	612
$^5D_0 \rightarrow ^7F_3$	653
$^5D_0 \rightarrow ^7F_4$	702
$^5D_0 \rightarrow ^7F_5$	747
$^5D_0 \rightarrow ^7F_6$	811

The magnetic dipole and electric quadrupole transitions are forbidden for $J' = 0 \rightarrow J = 0$ and Judd– Ofelt theory cannot explain the observation of $^5D_0 \rightarrow ^7F_0$ fluorescence [86]. In $\text{SrAl}_2\text{O}_4:\text{Eu}^{3+}$ the transitions within Eu^{3+} may give sharp luminescence lines between 580 and 720 nm [87]. Roy et al (1997) fabricated $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Eu}$ (1 and 2at%) powder and thin films by sol-gel processes from the organic precursors. They observed that the samples activated with 2 at% Eu showed emission concentrated in the 590 nm orange line due to the $^5D_0 \rightarrow ^7F_1$ (magnetic dipole) and the 610 nm red line corresponding to the $^5D_0 \rightarrow ^7F_2$ (electric dipole) transition of Eu^{3+} though relatively weak [88].

References

- [1] G. Blasse, B. Grabmaier, *Luminescent Materials*, 1994.
- [2] N.L. Hom, *PhD Thesis*, Saga University (Japan), 2010.
- [3] A. Kitai, *Luminescent Materials and Applications*, John Wiley & Sons, Ltd, 2008.
- [4] S. Chawla, *Nanotechnol. Electronics and Photovoltaics* **8** (2013) 96.
- [5] R. Ropp, *Luminescence and the Solid State*, Elsevier, 2004.
- [6] R. Cees, *Luminescence*, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2008.
- [7] J. M. Ngaruiya, S. Nieuwoudt, O. M. Ntwaeaborwa, J. J. Terblans, H. C. Swart, *Mater. Lett.* **62** (2008) 3192.
- [8] M.A. Carpenter, C.J. Howard, M.J. Andrew, R.E.A. McKnight, Y. Liu, R.L. Withers, *J. Appl. Phys.* **107** (2010) 013505 1.
- [9] S.H.M. Poort, W.P. Blokpoel, G. Blasse, *Chem. Mater.* **7** (1995) 1547.
- [10] D. Ravichandran, S.T. Johnson, S. Erdei, R. Roy, W.B. White, *Displays*. **19** (1999) 197.
- [11] J.G. Park, A.N. Cormack, *J. Solid State Chem.* **121** (1996) 278.
- [12] H. Ryu, K.S. Bartwal, *Cryst. Res. Technol.* **44** (2009) 69.
- [13] <http://www.jcrystal.com> [Accessed 12/10/ 2015]
- [14] J.W. Anthony, R.A. Bideaux, K.W. Bladh, M.C. Nichols, "Tridymite", *Handbook of Mineralogy*, 2001.
- [15] L.W. Zhang, L. Wang, Y.F. Zhu, *Adv. Funct. Mater.* **17** (2007) 3781.
- [16] A.H. Wako, F.B. Dejene, H.C. Swart, *J. Rare Earths*. **32** (2014) 806.
- [17] H.F. Brito, M.C.F.C. Felinto, J. Hölsä, T. Laamanen, M. Lastusaari, M. Malkamäki, et al., *Opt. Mater. Express*. **2** (2012) 420.
- [18] R. Stefani, L.C.V. Rodrigues, C.A.A. Carvalho, M.C.F.C. Felinto, H.F. Brito, M. Lastusaari, et al., *Opt. Mater. (Amst)*. **31** (2009) 1815.
- [19] R.D. Shannon, *Acta Cryst. A*. **32** (1976) 751.
- [20] K. Fukuda, K. Fukushima, *J. Solid State Chem.* **178** (2005) 2709.
- [21] S. Ito, S. Banno, K. Suzuki, M. Inagaki, *Z Phys. Chem.* **105** (1977) 178.
- [22] A. Nag, T.R.N. Kutty, *Mater. Res. Bull.* **39** (2004) 331.

- [23] F. Clabau, X. Rocquefelte, S. Jobic, P. Deniard, M. Whangbo, a Garcia, et al., *Chem. Mater.* **17** (2005) 3904.
- [24] R. Zhang, G. Han, L. Zhang, B. Yang, *Mater. Chem. Phys.* **113** (2009) 255.
- [25] T. Katsumata, K. Sasajima, T. Nabaie, S. Komuro, T. Morikawa, *J. Am. Ceram. Soc.* **81** (2005) 413.
- [26] P.D. Nsimama, *PhD Thesis*, University of the Free State, 2010.
- [27] P. Goel, R. Mittal, N. Choudhury, S.L. Chaplot, *J. Physics. Condens. Matter.* **22** (2010) 065401.
- [28] C.C. Chiang, M.S. Tsai, M.H. Hon, *J. Electrochem. Soc.* **154** (2007) 326.
- [29] Y. Xu, W.Y. Ching, *Phys. Rev. B.* **59** (1999) 530.
- [30] R. Kolesov, K. Xia, R. Reuter, R. Stöhr, A. Zappe, J. Meijer, et al., *Nat. Commun.* **3** (2012) 1029.
- [31] R.M. Hanson, *J. Appl. Cryst.* **43** (2010) 1250.
- [32] E. Popovici, M. Morar, L. Muresan, R. Grecu, L. Barbu-tudoran, E. Indrea, *J. Optoelectron. Adv. Mater.* **1** (2009) 1000.
- [33] M. Luisa, E. Caponetti, D. Chillura, S. Enzo, G. Ibba, *Opt. Mater. (Amst).* **31** (2008) 261.
- [34] Y. Huh, Y. Cho, Y.R. Do, *Bull. Korean Chem. Soc.* **23** (2002) 1435.
- [35] K. Ohno, T. Abe, *J. Electrochem. Soc.* **196** (1986) 638.
- [36] S. Geller, E. A. Wood, *Acta Cryst.* **9** (1956) 563.
- [37] W. Ching, Y.N. Xu, *Phys. Rev. B.* **59** (1999) 12815.
- [38] J. Rowland, *PhD Thesis*, University of Florida, 2010.
- [39] M. Zulkimi, A. Zakaria, J. Hassan, *Int. J. Res. Applied, Nat. Soc. Sci.* **2** (2014) 85.
- [40] H. Yamane, M. Shimada, B.A. Hunter, *J. Solid State Chem.* **141** (1998) 466.
- [41] Y. Rabinovitch, O.K. Moune, D. Tétard, M.D. Faucher, *J. Phys. Chem. A.* **108** (2004) 8244.
- [42] H. Yamane, T. Nagasawa, Y. Murakami, T. Kamata, D. Shindo, M. Shimada, et al., *Mater. Res. Bull.* **33** (1998) 845.
- [43] Boundless. "Crystal Field Theory." Boundless Chemistry. [Online] at <https://www.boundless.com/chemistry/textbooks> Retrieved 27 Feb. 2015
- [44] P. Dorenbos, *Phys. Rev. B.* **62** (2000) 640.

- [45] B. Henderson, R.H. Bartram, *Cambridge University Press*, 1992.
- [46] J. H. Van Vleck, *J. Phys. Chem.* **41** (1937) 67.
- [47] P. Dorenbos, *J. Phys. Condens. Matter.* **15** (2003) 575.
- [48] P. Dorenbos, *J. Alloys Compd.* **341** (2002) 156.
- [49] S. Zhou, Z. Fu, J. Zhang, S. Zhang, *J. Lumin.* **118** (2006) 179.
- [50] C.W. Thiel, Y. Sun, R.L. Cone, *J. Mod. Opt.* **49** (2002) 2399.
- [51] E.L. Coetsee, *Master's Thesis*, University of the Free State, 2006.
- [52] Q. Li, L. Gao, D. Yan, *Mater. Chem. Phys.* **64** (2000) 41.
- [53] L.I.U. Chun-jia, Y.U. Rui-min, X.U. Zhi-wei, C.A.I. Jing, Y.A.N. Xing-huang, L.U.O. Xue-tao, et al., *Trans. Nonferrous Met. Soc. China.* **17** (2007) 1093.
- [54] G. Xia, S. Zhou, J. Zhang, J. Xu, *J. Cryst. Growth.* **279** (2005) 357.
- [55] S. V Eliseeva, J.C.G. Bünzli, *Chem. Soc. Rev.* **39** (2010) 189.
- [56] P. Atkins,; J. de Paula, *Atkins' Physical Chemistry*, Oxford University Press, 2002.
- [57] C.Cohen Tannoudji; B.Diu; F.Laloe, *Quantum mechanics*, Wiley, 1999
- [58] L. L. Lohr, *Coord. Chem. Rev.* **8** (1972) 241.
- [59] B.M. Walsh, *Adv. Spectroscopy Lasers Sens.* (2006) 403.
- [60] B.R. Judd, *Phys. Rev.* **127** (1962) 750.
- [61] J.S. Garcia', L.E. Bausia', D. Jaque, *An Introduction to the Optical Spectroscopy*, John Wiley & Sons, Ltd, 2005.
- [62] http://en.wikipedia.org/wiki/Selection_rule (accessed Feb 2015).
- [63] http://faculty.gvsu.edu/majumdak/public_html/OnlineMaterials/ModPhys/QM/Quantum3d_part2.htm [Accessed 12/10/2015]
- [64] J. Teller, *Proc. R. Soc. A* **161** (1937) 220.
- [65] Y.K. Sharma, S.C. Mathur, D.C. Dube, S.P. Tandon, *J. Mater. Sci. Lett.* **14** (1995) 71.
- [66] K. Madhukumar, K.R. Babu, K.C.A. Prasad, J. James, T. Elias, V. Padmanabhan, et al., *Bull. Mater. Sci.* **29** (2006) 119.
- [67] X.W. Sun, H.S. Kwok, *Appl. Phys. A.* **69** (1999) 39.
- [68] S.T.S. Dlamini, H.C. Swart, J.J. Terblans, O.M. Ntwaeaborwa, *Solid State Sci.* **23** (2013) 65.

- [69] M. Nazaraov, *J. Phys. Sci.* **4** (2005) 347.
- [70] T. Kobayashi, T. Sekine, N. Hirotsuki, *Optical Materials* **31** (2009) 886.
- [71] J. Krupa, N.A. Kulagin, *NATO Science Series, II, Math., Phys. and Chem.*, **126** (2003) 166.
- [72] S. Galajev, *Master's Thesis*, University of Tartu (Estonia), 2008.
- [73] Y. Lin, Z. Zhang, Z. Tang, J. Zhang, Z. Zhang, B. Lu, *Mat. Chem. and Phys.*, **70** (2001) 156.
- [74] B. Cheng, H. Liu, M. Fang, Y. Xiao, S. Lei, L. Zhang, *Chem. Commun. (Camb)*. (2009) 944.
- [75] B. C. Cheng, M. Fang and L. D. Zhang, *China Patent*, **8** (2005) 10040647.
- [76] C. N. Xu, H. Yamada, X. S. Wang and X. G. Zheng, *Appl. Phys. Lett.*, **84** (2004) 3040.
- [77] Z. L. Fu, S. L. Zhou and S. Y. Zhang, *J. Phys. Chem. B*, **109** (2005) 14396.
- [78] A.H. Wako, B.F. Dejene, H.C. Swart, *Phys. B Condens. Matter*. **439** (2014) 153.
- [79] Y. Sun, L. Qi, M. Lee, B.I. Lee, W.D. Samuels, G.J. Exarhos, *J. Lumin.* **109** (2004) 85.
- [80] S. Tanaka, I. Ozaki, T. Kunimoto, K. Ohmi, H. Kobayashi, *J. Lumin.* **87–89** (2000) 1250.
- [81] G.S. Ofelt, *J. Chem. Phys.* **37** (1962) 51127.
- [82] S. Ram, S.K. Sinha, *J. Solid State Chem.* **66** (1987) 225.
- [83] A.F. Kirby, F.S. Richardson, *J. Phys. Chem.* **87** (1983) 2557.
- [84] G. Nishimura, T. Kushida, *Phys. Rev. B* **37** (1988) 9075.
- [85] M. Dejneka, E. Snitzer, R.E. Riman, *J. Lumin.* **65** (1995) 227.
- [86] K. Kumar, A. Singh, S. Rai, *Spectrochim. Acta Part A*. **102** (2013) 212.
- [87] V. Kityk, J. Wasylak, D. Dorosz, J. Kucharski, *Optics & Laser Tech.* **33** (2001) 157.
- [88] R. Roy, A. Chakhovskoi, S. Erdei, C.E. Hunt, W.B. White, D. Ravichandran, *J. Lumin.* **71** (1997) 291.

Chapter 3

Investigation Techniques of Phosphors

3.1. Synthesis Methods

3.1.1. Solution-Combustion Method

The solution – combustion method is an important chemical route for the synthesis and processing of advanced ceramics (structural and functional), catalysts, composites, alloys, inter-metallics and nanomaterials [1]. The method has generated more interest in the field of nanomaterials such as luminescent materials (phosphors) and other ceramic materials, because fine particle sizes, multi-component, crystalline and homogenous materials can be achieved at relatively low temperature and less time [2].

In this technique (3-8) a saturated aqueous solution of the desired metal salts and a suitable organic fuel is made to boil, until the mixture ignites and a self-sustaining and rather fast combustion reaction occurs, resulting in a dry, usually crystalline, fine oxide powder. To form a mixed oxide, a mixture containing the desired metal ions, in the form of, for instance, water soluble nitrate salts, a fuel such as urea, glycine or ethylene glycol can be used. Usually redox reactions such as this are exothermic in nature and often lead to explosion if not controlled, but in this technique the combustion of metal nitrates-urea mixtures usually occurs as a self-propagating and non-explosive exothermic reaction. The large amounts of gases formed can result in the appearance of a flame, which can reach temperatures in excess of 1000 °C.

A schematic diagram showing the synthesis of SrAl_2O_4 : Eu, Dy phosphors via combustion method is given in figure 3.1. The energy released from the exothermic reaction between the nitrates and the fuel, which is usually ignited at a temperature much lower than the actual phase transformation temperature, can rapidly heat the system to a high temperature and sustain it long enough, even in the absence of an external heat source, for the synthesis to occur [9].

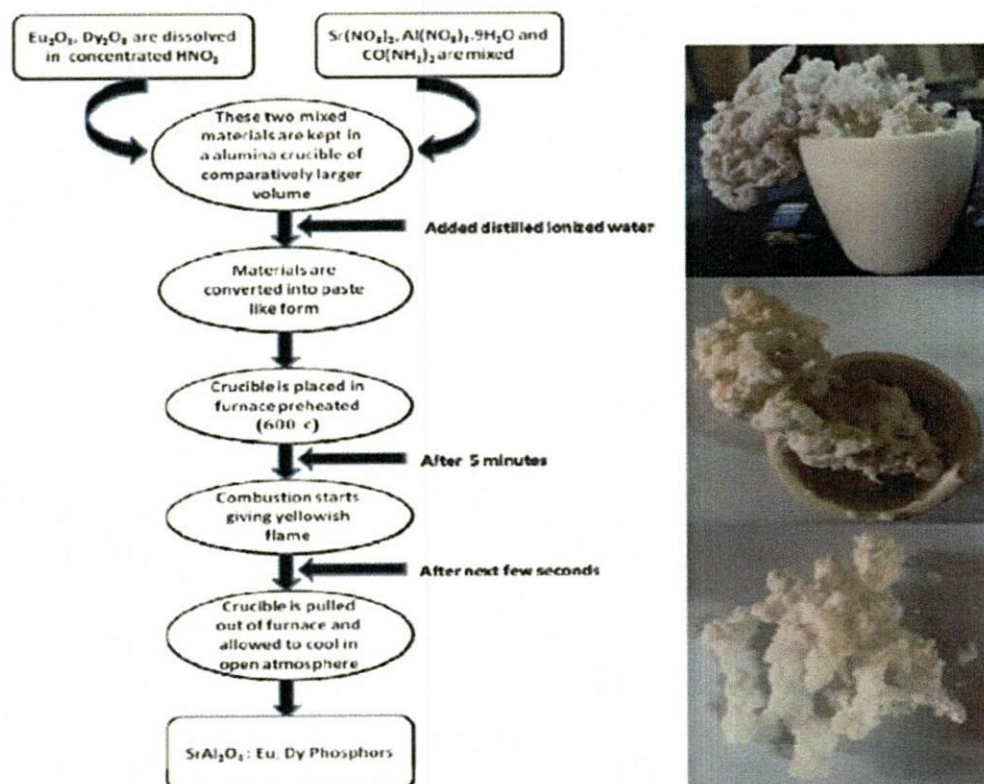


Figure 3.1: Schematic diagram showing synthesis of $\text{SrAl}_2\text{O}_4:\text{Eu, Dy}$ phosphors via combustion method [10].

The luminescent materials (phosphors) prepared by this method have low density, fluffy texture and ultra fine particles. As more gases are released, either agglomerates are not formed or disintegrated into fine particles [11].

In recent years, with the development of the synthesis technologies on materials, several chemical methods have been applied to prepare luminescence powders [12], 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 [13]. 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 [14].

3.1.2. Pulsed Laser Deposition

Pulsed laser deposition (PLD) is a thin film growth technique in which the photon energy of a laser characterized by pulse duration and laser frequency interacts with a bulk (target) material [15, 16].

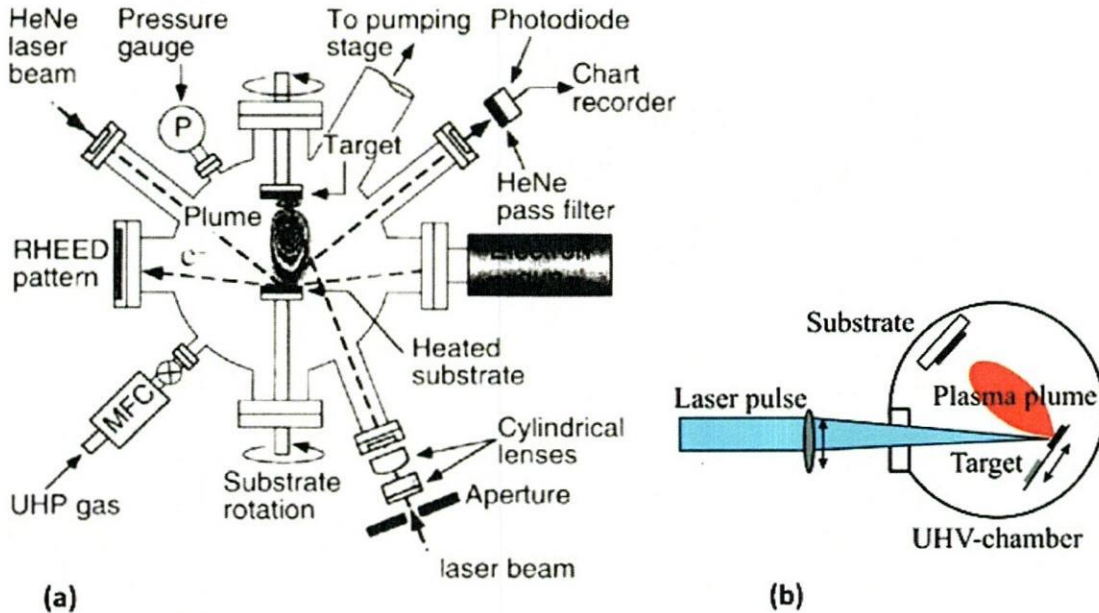


Figure 3.2: (a) and (b); Schematic diagram of a pulsed laser deposition system [17, 18].

The working mechanism of PLD is shown in figures 3.2 (a) and (b). A laser beam is directed and focused onto the surface of a target (solid or liquid) in a chamber and ejects (ablates) material. Ablation of materials occurs above a certain threshold power density, and the ejected, partially ionized material forms a luminous ablation plume. The threshold power density required to create such plasma depends on the absorption properties of the target material, the laser wavelength, and pulse duration. The removed material is directed towards a substrate where it re-condenses to form a film. The growth kinetic of such films depends on the material flux, repetition rate, growth temperature, substrate material, pressure, and background gas (vacuum, reactive).

The laser material interaction during ablation and deposition processes that takes place within a localised interaction volume at, and close to, the surface of the target is shown in figure 3.3;

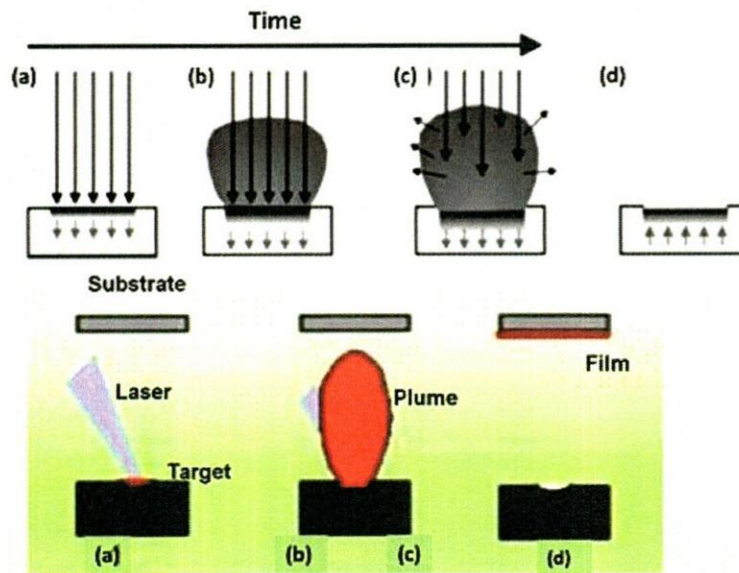


Figure 3.3: Schematic illustrating the PLA process [19]; (a) Initial absorption of laser radiation, melting and vaporization begin. (b) Melt front propagates into the solid, vaporization continues and laser-plume interactions starts. (c) Absorption of incident laser radiation by the plume and plasma formation. (d) Melt front recedes leading to eventual re-solidification

The target will absorb the incoming laser energy which causes extremely fast heating of a significant volume of target material. The fast and strong heating of the target surface by the intense laser beam (typically up to temperatures of more than 5000 K within a few ns, corresponding to a heating rate of about 10^{12} K/s) ensures that all target components irrespective of their partial binding energies evaporate at the same time [18]. This introduces high amplitude stress waves in the solid target and may cause phase transitions. Material will start to boil off forming a high-temperature plasma and expand into the gas phase, which then adiabatically expands in a direction perpendicular to the target surface [17] [18]. Ablation of the material begins on a picoseconds timescale. Thus, unless one is working with high frequency laser pulses, the ensuing plume will be irradiated by the later part of the incident laser pulse. This radiation will, in many cases, be absorbed by the plume, leading to reduction of the light intensity incident on the target and excitation and ionisation of species in the plume. Plasma formation and subsequent optical emission will result [19].

To use PLD for thin film growth has advantages for a number of reasons [20];

- ✓ The flexibility in wavelength and power density allows ablating almost any material or combination of materials.
- ✓ The laser is not part of the vacuum system. Therefore, a considerable degree of freedom in the ablation geometry is possible.

- ✓ The use of a pulsed laser beam enables a precise control over the growth rate.
- ✓ The congruent transfer of the composition can be achieved for most ablated material or materials combinations.
- ✓ Moderation of the kinetic energy of evaporated species to control the growth properties and growth modes of a film.

There are also disadvantages to perform PLD. Some of them are of a technical nature; some are intrinsic to the ablation process and the electromagnetic interaction between photons and matter [14];

- ✓ The large kinetic energy of some plume species causes re-sputtering and similar defects in the substrate surface and growing film.
- ✓ An inhomogeneous energy distribution in the laser beam profile gives rise to an inhomogeneous energy profile and angular energy distribution in the laser plume.
- ✓ Light elements like oxygen or lithium have different expansion velocities and angular distributions in a plume as compared to heavier elements. Therefore, an additional source to supplement these elements to obtain the desired film composition is required, e.g., adequate background gas or an adapted target composition.
- ✓ Due to the high laser energies involved, macroscopic and microscopic particles from the target can be ejected which can be detrimental to the desired properties of films and multi-layers.

There are different types of pulsed lasers used for the ablation of solid materials. Currently Nd:YAG and excimer nano-second (ns) lasers are the most common lasers for PLD systems. Nd:YAG lasers are relatively inexpensive, require little maintenance, there is hardly any divergence of the laser beam, and they can be easily incorporated into small commercial ablation systems. In addition, the beam profile at the base frequency is in most cases close to a Gaussian or a super-Gaussian distribution. Excimer lasers are based on halogen gas-filled laser cavities rather than solid-state crystals. Handling issues demand greater care and laser devices are rather bulky. However, excimer lasers have much bigger power output and typically provide a better defined beam profile [20].

In this study after initial characterization, the powders were pressed into a pellet and used as a target for laser deposition. The pellet was heated at 200 °C for 2 hrs in an oven to expel moisture that may be present and make it hard and strong for use as a target for laser ablation. The target was then loaded on to a rotatable carousel inside the PLD chamber. The carousel raster and rotates the target to prevent constant ablation by the laser beam from the same spot on the target. Silicon (100) wafers of approximately 1 cm² were used as substrates. The wafers were first

cleaned in ultrasonic bath of acetone, ethanol and distilled water in that sequence then blow-dried with clean dry N₂ gas and placed on a fixed substrate holder in the PLD chamber perpendicular to the target at a fixed distance of 4.5 cm from the target. The chamber was then pumped down to vacuum of about 3.0×10^{-6} Mbar. The target was ablated in and then under varying working atmospheres of vacuum, argon and oxygen. Different ambient pressures were used for the gases; 10, 20, and 30 mTorr each for 30, 45 and 60 minutes at substrate temperatures of 100, 200 and 300 °C using a Q-switched Spectra-Physics Quanta Ray 266 nm Nd:YAG nanosecond (ns) pulsed laser operating at 15 Hz with energy and frequency fixed at 45mJ/pulse (fluence of 0.2 Jcm⁻²) and 10Hz, respectively.

3.2. Characterization Methods for Phosphors

In this research work, the phosphor powders and thin films were characterized using Scanning Electron Microscopy (SEM), Energy Dispersive x-ray Spectroscopy (EDS), X-ray Diffraction (XRD), Photoluminescence spectroscopy (PL), UV-VIS spectroscopy and Thermoluminescence spectroscopy (TL). The theory of these characterization techniques are covered in this chapter. It also gives the experimental set-up and layout of the methods used for characterization.

3.2.1. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is used to study the topographical and morphological structures of specimens at very high magnifications which can go to more than 30 000 X. During SEM analysis, a beam of energetically well-defined and highly focused electrons is scanned across a sample. The SEM consists of an electron optical column mounted on a vacuum chamber with electron gun placed on top of the column [14], as illustrated in figure 3.4. The microscope electron gun consists of tungsten or lanthanum hexaboride (LaB₆) filament source or a field emission electron gun which is used to generate electrons, when the applied current causes resistance heating which generates the electrons [21]. It is pumped using turbo and ion pumps to maintain the highest possible vacuum [22].

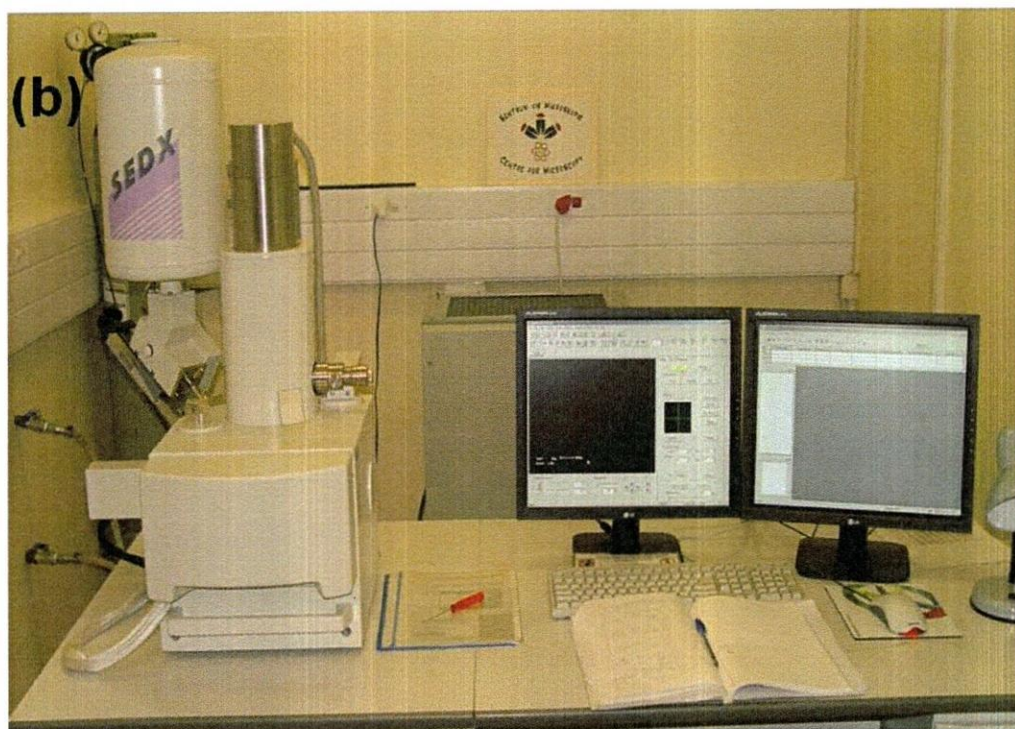
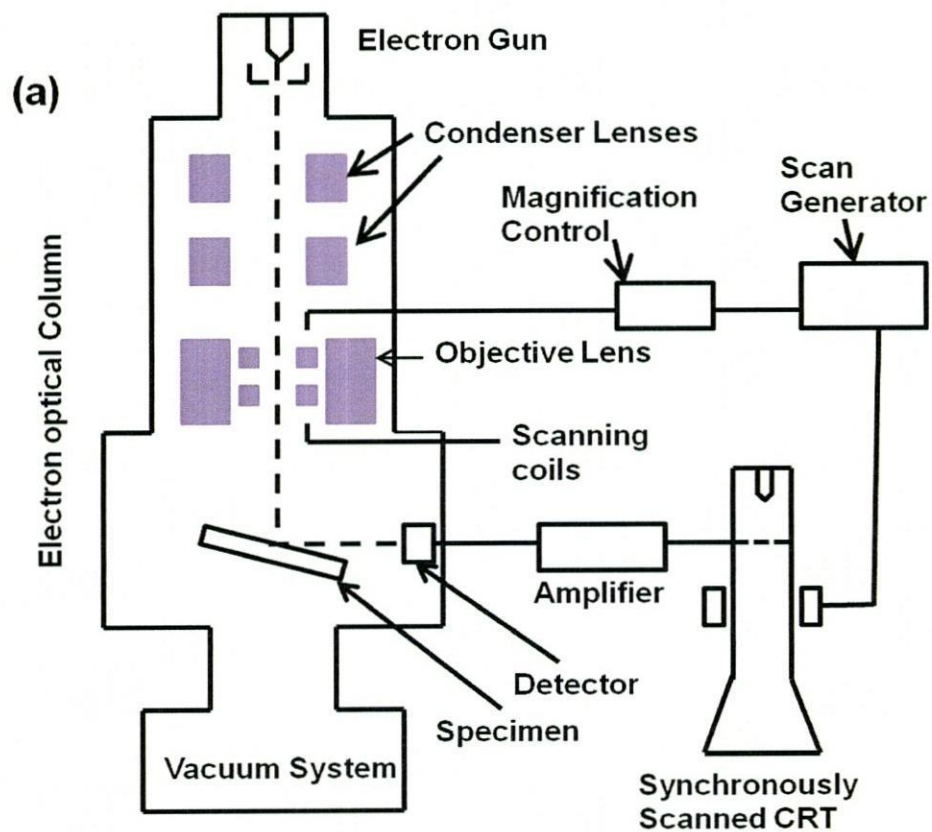


Figure 3.4: (a) Schematic Diagram of a SEM [21]. (b) SEM system at the Centre for Microscopy at UFS

The technique can provide information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample [23].

The SEM is also capable of performing analyses of selected point locations or areas on the sample [24]. If the system is equipped with energy dispersive x-ray spectrometer (EDS), it can also provide information about chemical composition of the material [25].

The basic principle of the system is that, when a high energy electron beam impinges on the sample surface it generates a splash of electrons with kinetic energies much lower than the primary incident electrons called secondary electrons [22]. Depending on the nature of the sample, these can include secondary electrons (electrons from the sample itself), backscattered electrons (beam electrons from the filament that bounce off nuclei of atoms in the sample) and X-rays [14] as shown in figure 3.5.

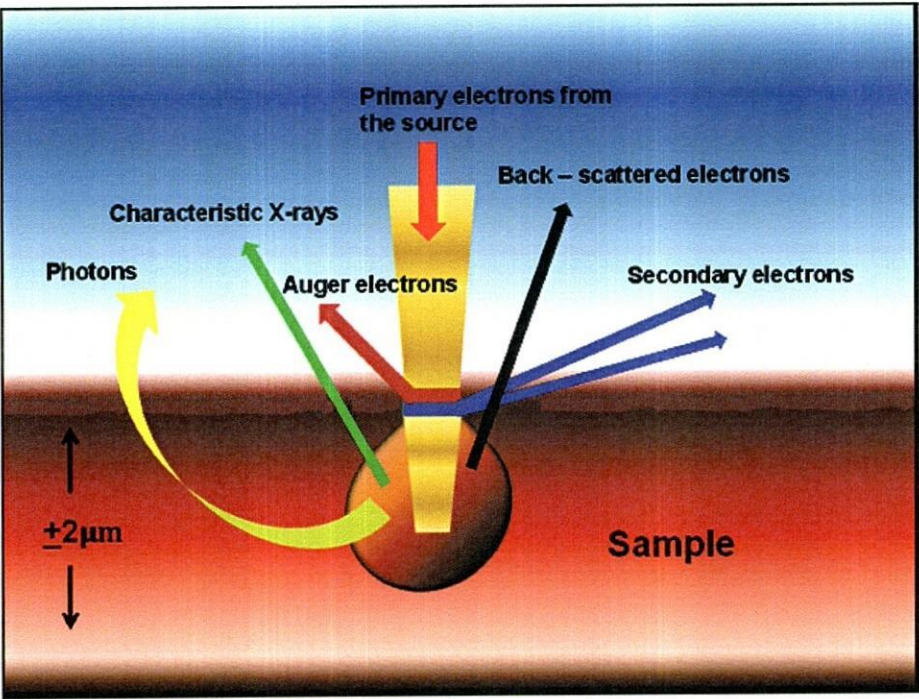


Figure 3.5: Electrons produced in SEM [26].

An image of the sample surface is constructed by measuring the secondary electron intensity as a function of the primary beam position. The SEM has many advantages over traditional microscopes. It has a large depth of field, which allows more of a specimen to be in focus at one time. The SEM also has much higher resolution, so closely spaced specimens can be magnified at much higher levels. Because the SEM uses electromagnetic lenses, the researcher has much more control in the degree of magnification. All of these advantages, as well as the actual

strikingly clear images, make the scanning electron microscope one of the most useful instruments in research today [25].

In this research a highly advanced JSM-7800F field emission Scanning Electron Microscope (SEM) coupled with an Energy Dispersive X-ray Spectrometer (EDS) shown in figure 3.6 below was also used. The JSM-7800F has superb resolution and stability for imaging and analysis which makes it possible to: [27]

- observe the finest structural morphology of nanomaterials at 1,000,000X magnification with sub-1 nm resolution
- collect large area EBSD maps at low magnifications without distortion
- Perform low kV imaging and analysis of highly magnetic samples.
- Image very thin, electron transparent samples with sub 0.8 nm resolution using an optional retractable STEM detector.



Figure 3.6: JSM-7800F field emission Scanning Electron Microscope (SEM) [27].

The JSM-7800F uniquely combines an in-lens field emission gun with an aperture angle control lens (ACL), optimizing large probe currents (up to 200 nA) for operation at the smallest probe diameter. The new super hybrid lens design allows high resolution imaging of (0.8 nm (15 kV)) of any type of specimen. The SEM excels at low accelerating voltage X-ray spectroscopy and Cathodoluminescence (CL), combining large beam currents with a small interaction volume and dramatically increasing analytical resolution to the sub 100nm scale. Beam deceleration in GB

Mode provides charge balance and extreme high resolution imaging of surfaces and nonconductive samples by effectively reducing effects of lens aberrations.

The JSM-7800F is suitable for a wide variety of applications, from cryo-microscopy to electron beam lithography. It accommodates multiple analytical attachments, including EDS, WDS, STEM, BSE, CL, EBIC, and an IR camera and stage navigation camera. The SEM comes with a choice of three stage sizes and three specimen exchange airlock sizes. It can also be equipped with tensile, heating, and cooling stages for in situ experiments. The system can be configured for low vacuum operation for imaging non-conductive samples [27].

3.2.2. Energy Dispersive x-ray Spectroscopy (EDS)

The surface chemical or elemental composition of the synthesized powders grown in this research study was determined by EDS spectroscopy. (EDS or EDX) is a chemical microanalysis technique used in conjunction with scanning electron microscopy (SEM). The EDS technique detects X-rays emitted from the sample during bombardment by an electron beam to characterize the elemental composition of the analyzed volume. Features or phases as small as 1 μm or less can be analyzed [28]. Information about the chemical composition of the sample is obtained by measuring the intensity distribution and energy of the signal generated by a focussed electron beam impinging on the sample. The source of the electron is the electron gun of a scanning electron microscope. The incident beam of electrons interacts with core electrons of the sample's atoms transferring sufficient energy to it, thereby ejecting it from the target atom. This results in the creation of a hole within the atom's electronic structure.

An electron from an outer, higher energy shell then occupies the hole releasing excess energy in the form of an X-ray photon. As a result of electronic transitions which occur between the outer and inner core levels a characteristic X-ray is emitted when the ionized atom 'relaxes' to a lower energy state by the transition of an outer-shell electron to the vacancy in the core shell which provide a quantitative and qualitative elemental composition of the sample [29]. Due to a well defined nature of the various atomic energy levels, it is clear that the energies and associated wavelengths of the set of x-rays will have characteristic values for each of the atomic species present in a sample [29] as shown in figure 3.7.

A characteristic X-ray is usually emitted when the ionized atom 'relaxes' to a lower energy state by the transition of an outer-shell electron to the vacancy in the core shell. The X-ray is called

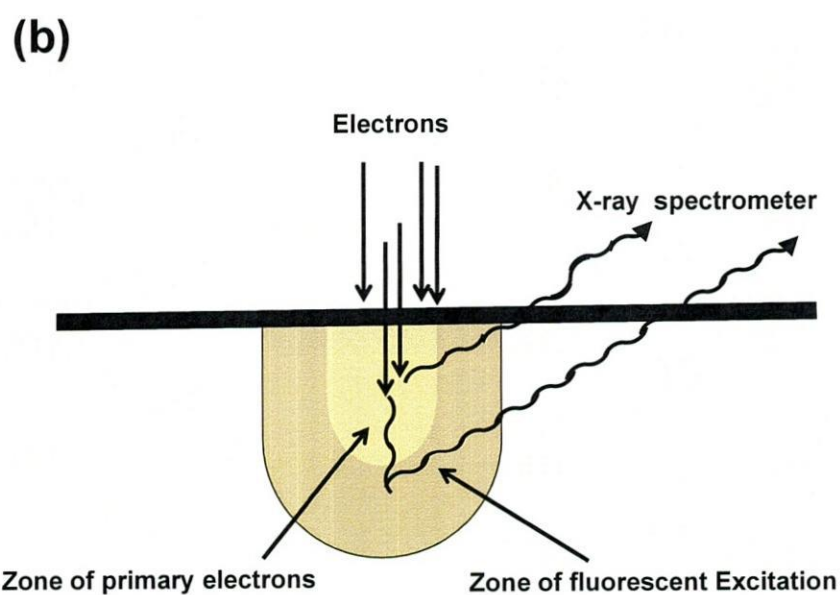
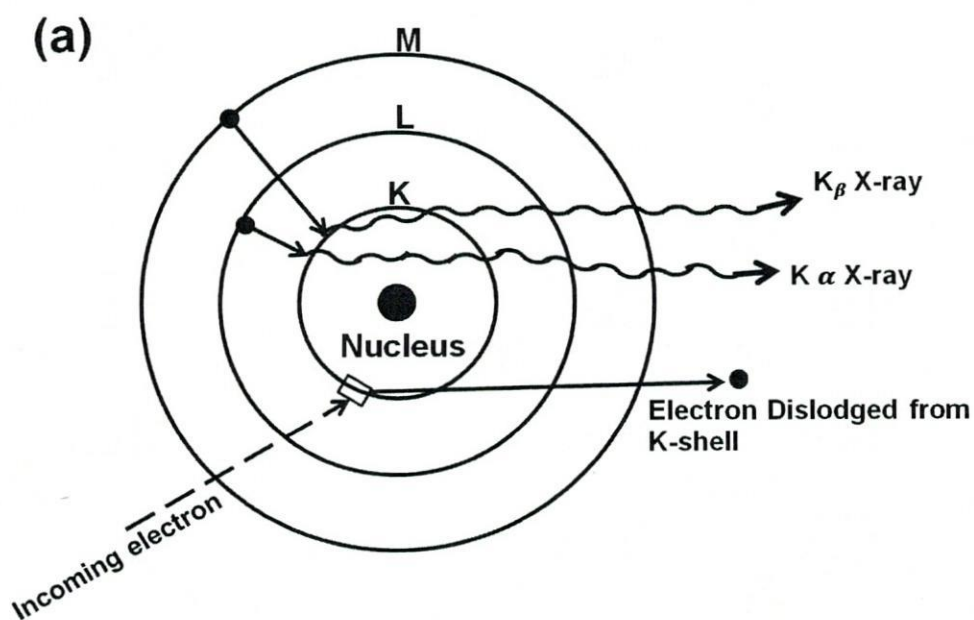


Figure 3.7: Characteristic x-ray radiation (a) electrons beam interacts with core electrons (b) X-rays emitted during EDS analysis [30].

characteristic because its energy equals the energy difference between the two levels involved in the transition and this difference is characteristic of the material.

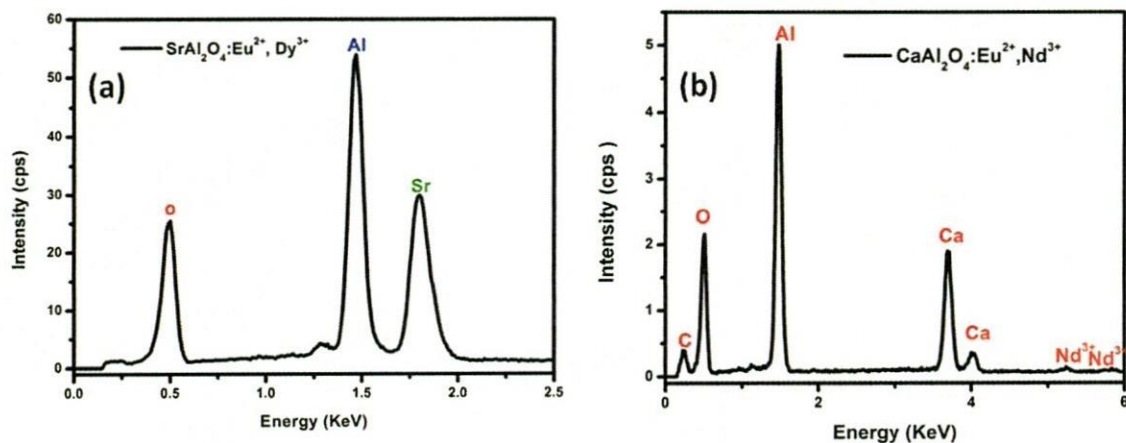


Figure 3.8: EDS spectrum of (a) $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ and (b) $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$.

From the output of an EDS analysis we obtain an EDS spectrum, see figure 3.8. The EDS spectrum shows the frequency in counts of X-rays received for each energy level. The spectrum normally plots the peaks corresponding to the energy levels for which the most X-rays have been received. Each of these peaks corresponds to a specific atom, and therefore characteristic of a specific element. The intensity of a peak in the spectrum correlates with the concentration of the element in the sample [31].

3.2.3. Transmission Electron Microscope (TEM)

Transmission Electron Microscopy (TEM) is an imaging technique whereby a beam of electrons is transmitted through a thin solid or diluted sample/specimen and then an image is formed through the interaction of the electrons with the sample. The image is then enlarged and focused on to a fluorescent screen or photographic film, or to be detected by a sensor such as a CCD camera. Compared to the light microscopes TEMs have significantly higher resolution, because of the small de Broglie wavelength of electrons. This makes the system capable to view fine details in animal and plants cells or other materials down to near atomic levels. It can investigate the size, morphology (shape) and arrangement of the particles which make up the sample/specimen on the scale of atomic diameters [32]. It can be used to study structures of crystals including features like dislocations and grain boundaries. In semiconductors, TEM can be used to study the growth of films, their composition and imperfections/defects, and also to analyze the morphology/shape, quality, size and density of quantum wells, dots, nanowires and nano-rods. Therefore TEM is a valuable analysis technique applied in a wide range of scientific

fields, such as in medical (virology and cancer research), environmental (pollution), biological/physical sciences and material sciences (semiconductors and phosphor) research. Preparation of materials for TEM analysis requires samples with very small dimensions about a few hundred nano-metres in thickness (less than 200 nm) [33]. Powder samples are finely milled and then dispersed in ethanol. A drop is then placed onto a porous circular metal support grid generally copper (figure 3.8 (b)).

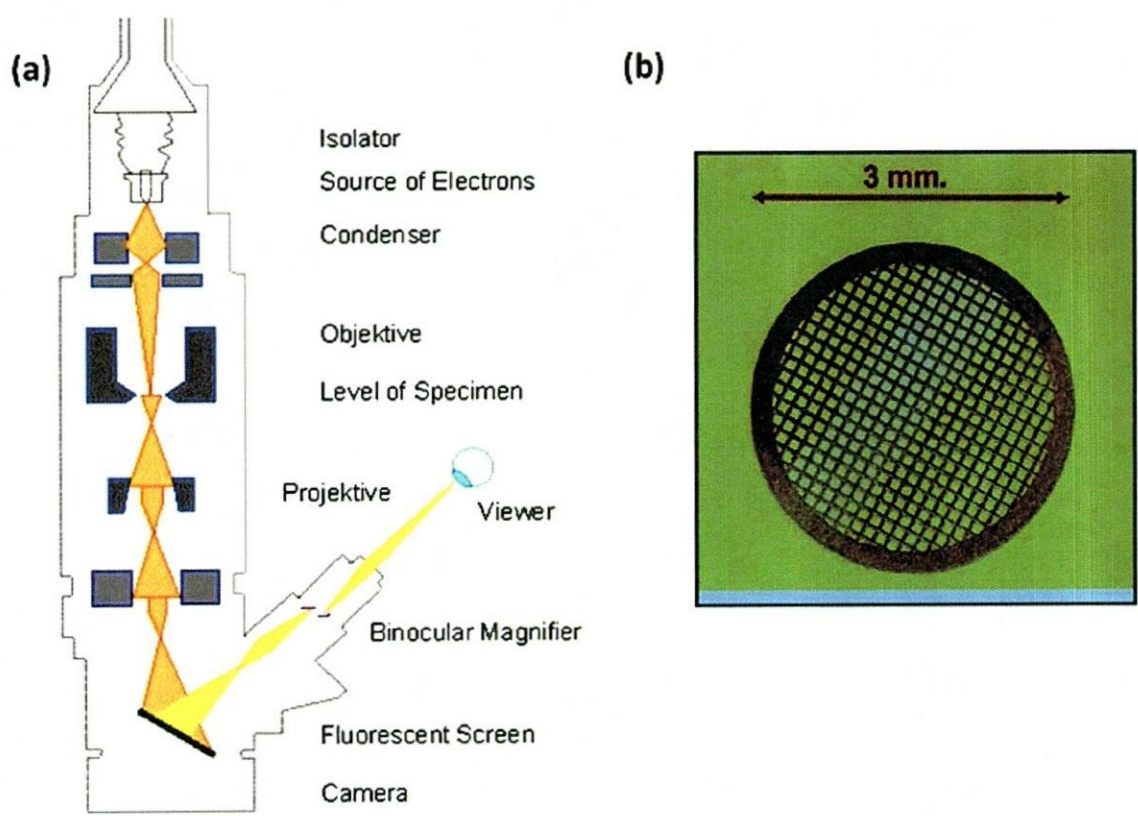


Figure 3.9: (a) Schematic diagram of TEM and (b) TEM sample support mesh “grid”, with ultramicrotomy sections [34].

The suspension is normally a volatile solvent such as ethanol, ensuring that the solvent rapidly evaporates allowing a sample that can be quickly analyzed. In material science/metallurgy the specimens tend to be naturally resistant to vacuum and must be prepared as a thin foil, or etched so that some portion of the specimen is thin enough for the beam to penetrate [35]. Figure 3.9 (a) shows a schematic diagram of the layout of a typical TEM and Figure 3.9(b) shows the sample holders that are used in TEMs.

The operation of the TEM requires an ultra high vacuum (UHV) and a high accelerating voltage (300 kV) than in an SEM. The electrons emitted by a source are focused and magnified by a set of magnetic lenses. The image that is formed is either shown on a fluorescent screen or on a

monitor and it is printed on photographic film. The resolution power is usually determined by the technique with which the preparation was achieved and the quality of the lens system. Today's transmission electron microscopes offer resolutions up to 0.1 nm at 300 kV and probe diameters up to 0.34 nm.

TEM exploits three different interactions of electron beam-specimen; unscattered electrons (transmitted beam), elastically scattered electrons (diffracted beam) and inelastically scattered electrons. Different types of images are obtained in TEM, using the apertures properly as well as the different types of electrons. As a result, diffraction patterns are shown because of the scattered electrons. If the unscattered beam is selected, we obtain the Bright Field Image. Dark Field Images are attained if diffracted beams are selected by the objective aperture [6].



Figure 3.10: The PHILIPS CM 100 model Transmission Electron Microscope.

3.2.4. Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) is a form of scanning probe microscopy (SPM) where a small probe scans across the sample surface to obtain information about the sample's surface roughness [36]. One advantage of AFM over other microscopy techniques is that it can make three dimensional measurements of a sample surface [37]. Also it can be operated not only in an

ultrahigh vacuum but also at ambient conditions or even in liquids [38]. A schematic layout of the atomic force microscopy is shown in figure 3.11.

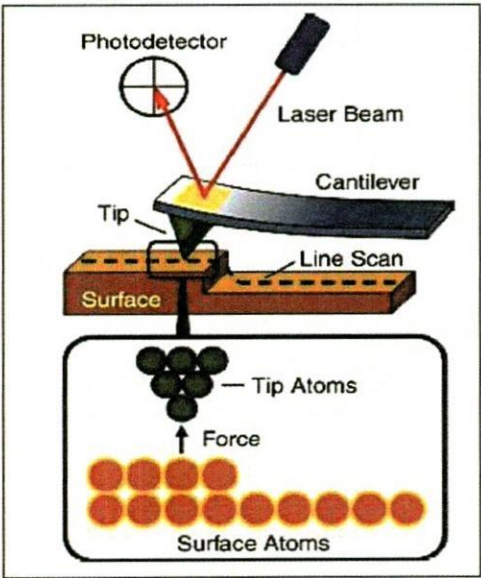


Figure 3.11: A schematic diagram of the atomic force microscopy [39]

The AFM uses a probe with a very sharp silicon tip less than 10 nm in diameter at the end of a cantilever spring. The probe is attached to a piezoelectric scanner tube, which scans the probe across a selected area of the sample surface. Interatomic forces between the probe tip and the sample surface causes the cantilever to deflect as the sample's surface topography changes. During the scanning process, the force between the tip and the surface is determined by the deflection of the cantilever. The deflection of the cantilever is controlled by using the optical lever technique. A beam from a laser diode is focused onto the end of the cantilever and the position of the reflected beam is monitored by a position sensitive detector (PSD) [40].

A laser light reflected from the back of the cantilever measures the deflection of the cantilever. A topographic image of the sample is obtained by plotting the deflection of the cantilever versus its position on the sample. This information is fed back to a computer, which generates a map of topography or other properties of interest. Areas as large as about 100 μm square to less than 100 nm square can be imaged [36]. AFM can be operated in three modes; **contact mode** with the tip touching the sample, or **tapping mode** where the tip taps across the surface, or **non-contact mode** when the tip interaction with the sample is minimal [41].

In the current study the AFM images were recorded using Shimadzu SPM-9600 model shown in figure 3.12.

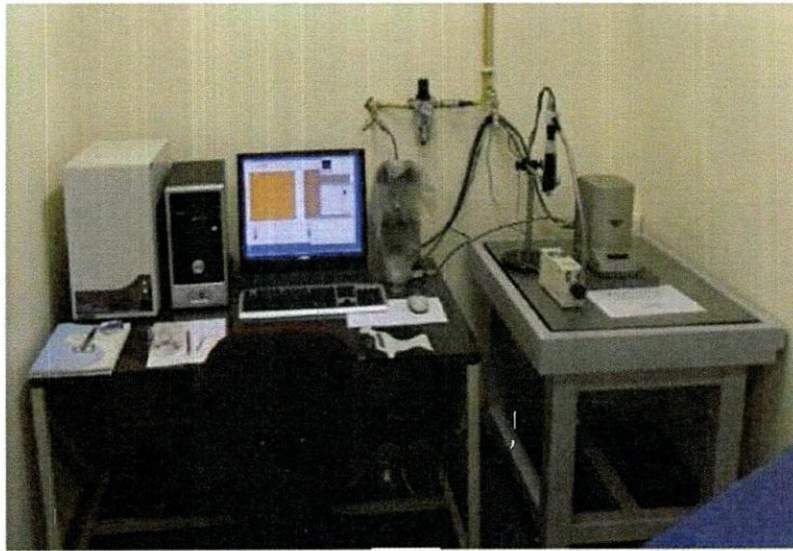


Figure 3.12: Atomic Force Microscopy Shimadzu SPM-9600 model at the University of the Free State.

3.2.5. X-ray Diffraction (XRD)

X-ray diffraction (XRD) is an efficient analytical non-destructive technique used to investigate structural properties of crystalline materials. It is also used for phase identification, determination of grain size, composition of solid solution, lattice constants, and degree of crystallinity in a mixture of amorphous and crystalline substances [42].

An amorphous sample consists of atoms arranged in a random way for example glasses. A sample is said to be crystalline if the atoms are arranged in such a way that their lattice positions are exactly periodic.

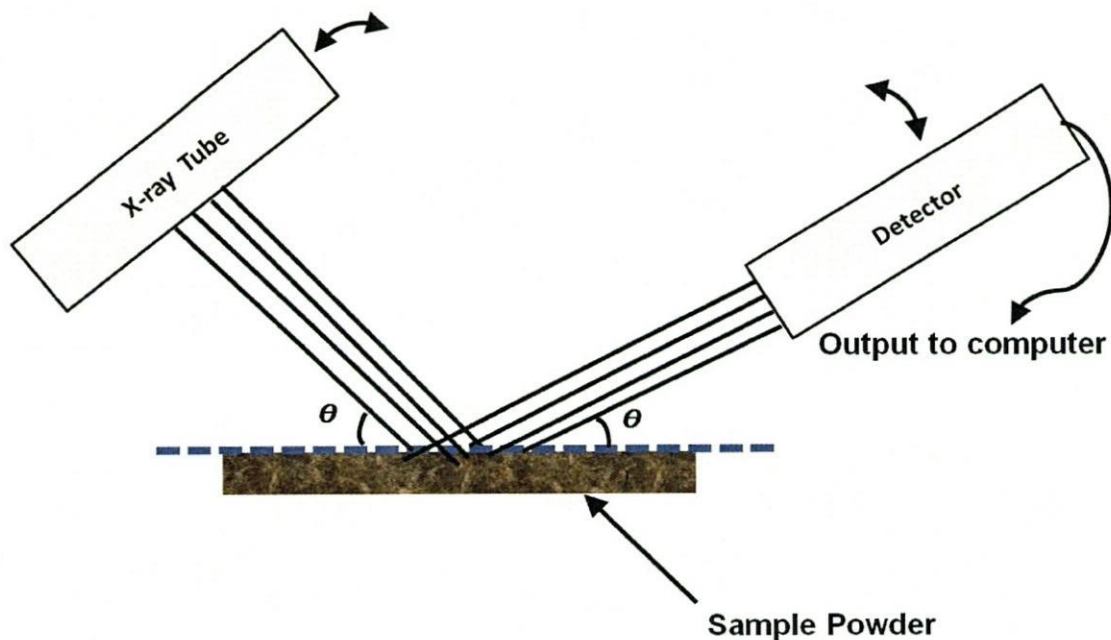


Figure 3.13: An x-ray powder diffractometer [33].

Crystalline materials include ceramics, metals, electronic materials, organics and polymers. The X-ray diffractometer fall into two broad classes viz; single crystals and powder. The powder diffractometer, figure 3.13 is routinely used for phase identification and quantitative phase analysis [43]. X-ray diffractometer consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. X-rays are produced in the X-ray tube. Such a tube is illustrated in figure 3.14. It consists of an evacuated chamber with a tungsten filament at one end of the tube, called the cathode, and a metal target at the other end, called an anode.

Electrical current is run through the tungsten filament, causing it to glow and emit electrons. A large voltage difference (measured in kilovolts) is placed between the cathode and the anode, causing the electrons to move at high velocity from the filament to the anode target.

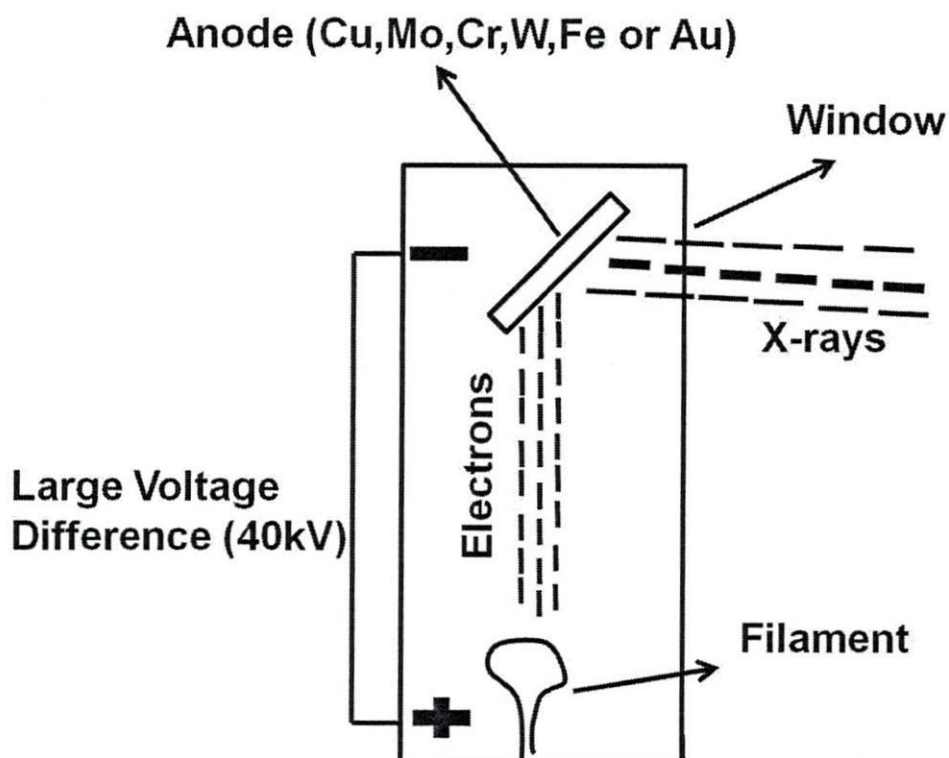


Figure 3.14: Schematic diagram of an X-ray tube [45].

Upon striking the atoms in the target, the electrons dislodge inner shell electrons resulting in outer shell electrons having to jump to a lower energy shell to replace the dislodged electrons [44]. These electronic transitions results in the generation of X-rays. The X-rays then move through a window in the X-ray tube producing characteristic X-ray spectra which can be used to provide information on the internal arrangement of atoms in crystals or the structure of internal body parts. These X-ray spectra consist of several components and the most common are $K\alpha$ and $K\beta$ as shown in figure 3.15 [45].

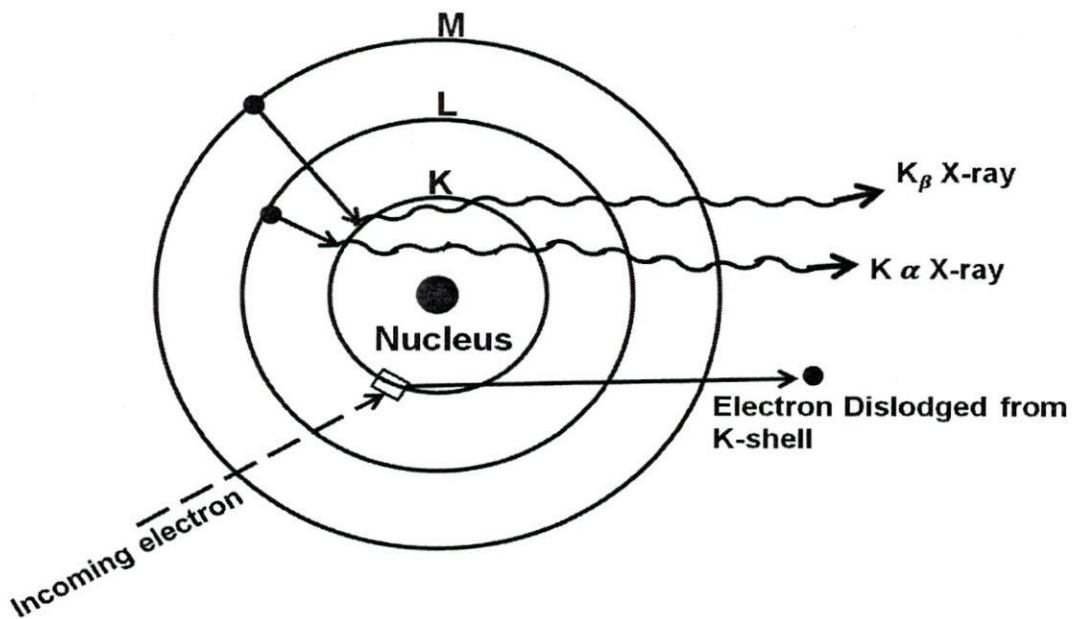


Figure 3.15: Characteristic X-ray Radiation [33]

The target materials that are usually used are Cu, Fe, Mo and Cr. Each of these has specific characteristic wavelengths [44] as shown in table 3.1.

Table 3.1: Characteristic wavelengths of target materials [33].

Element	K α Wavelength (λ) Å
Mo	0.7107
Cu	1.5418
Co	1.7902
Cr	2.2909

3.2.3.1. Continuous and Characteristic X-ray Spectra

When the target material of the X-ray tube is bombarded with electrons accelerated from the cathode filament, two types of X-ray spectra are produced. The first is called the **continuous spectra**. The continuous spectra consist of a range of wavelengths of X-rays with minimum

wavelength and intensity (measured in counts per second) dependent on the target material and the voltage across the X-ray tube. The minimum wavelength decreases and the intensity increases as voltage increases as shown in figure 3.16.

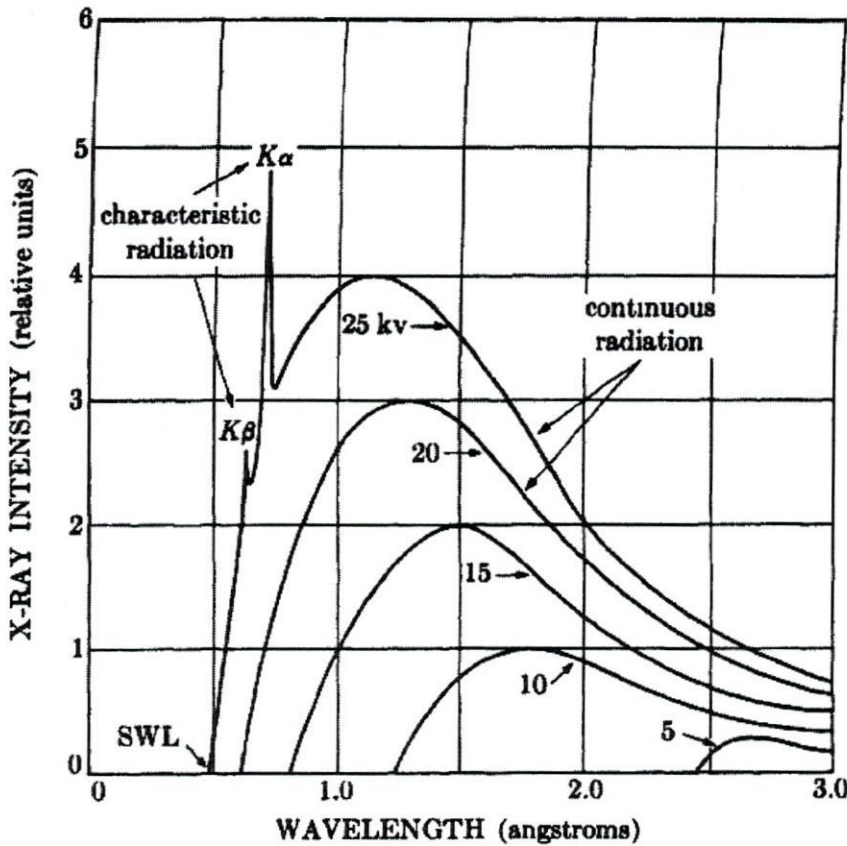


Figure 3.16: The continuous X-ray spectra [45].

The second type of spectra, called the *characteristic spectra*, is produced at high voltage as a result of specific electronic transitions that take place within individual atoms of the target material. This is easiest to see using the simple Bohr model of the atom. In such a model, the nucleus of the atom containing the protons and neutrons is surrounded by shells of electrons. The innermost shell, called the K- shell, is surrounded by the L- and M - shells. When the energy of the electrons accelerated toward the target becomes high enough to dislodge K- shell electrons, electrons from the L - and M - shells move in to take the place of those dislodged. Each of these electronic transitions produces an X-ray with a wavelength that depends on the exact structure of the atom being bombarded. A transition from the L – shell, to the K- shell produces a $K\alpha$ X-ray, while the transition from an M - shell to the K- shell produces a $K\beta$ Xray. These characteristic X-rays have a much higher intensity than those produced by the continuous spectra, with $K\alpha$ X-rays having higher intensity than $K\beta$ X-rays see figure 3.17. The important

point here is that the wavelength of these characteristic x-rays is different for each atom in the periodic table (of course only those elements with higher atomic number have L- and M - shell electrons that can undergo transitions to produce X-rays).

A filter is generally used to filter out the lower intensity $K\beta$ X-rays. For commonly used target materials in X-ray tubes, the X-rays have the well-known experimentally determined wavelengths shown in table 3.1.

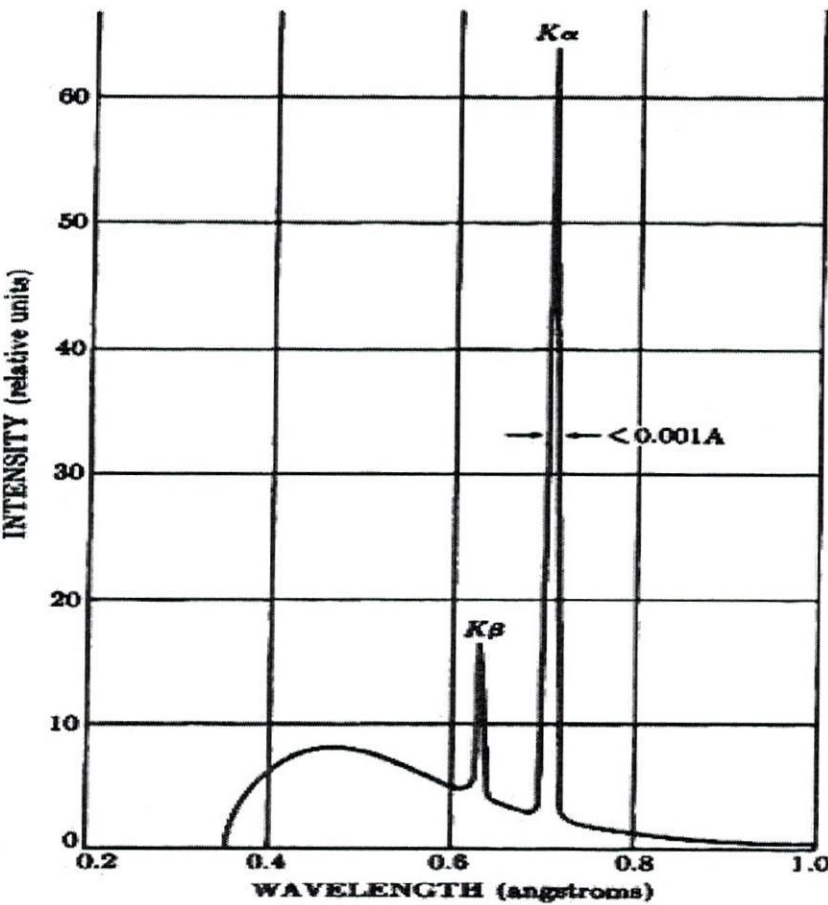


Figure 3.17: Intensity of characteristic $K\alpha$ X-rays and $K\beta$ X-rays [45].

3.2.3.2. Interference

A beam of X-rays consists of a bundle of separate waves which can interact with one another. Such interaction is termed *interference*. Interference of waves can be either *constructive* or *destructive*.

3.2.3.3. Crystal Lattice

A crystal lattice is a regular three-dimensional distribution (cubic, rhombic, etc.) of atoms in space. These are arranged so that they form a series of parallel planes separated from one another by a distance d (figure 3.18), which varies according to the nature of the material. For any crystal, planes exist in a number of different orientations - each with its own specific d -spacing.

3.2.3.4. Bragg's Law

The atoms in crystals interact with X-rays in such a way as to produce interference. The interaction can be thought of as if the atoms in a crystal structure reflect the waves. But, because a crystal structure consists of an orderly arrangement of atoms, the reflections occur from the atomic planes. Consider a beam of monochromatic X-rays entering a crystal with one of its planes oriented at an angle of θ to the incoming beam. Figure 3.18 shows two such X-rays, where the spacing between the atomic planes occurs over the distance, d .

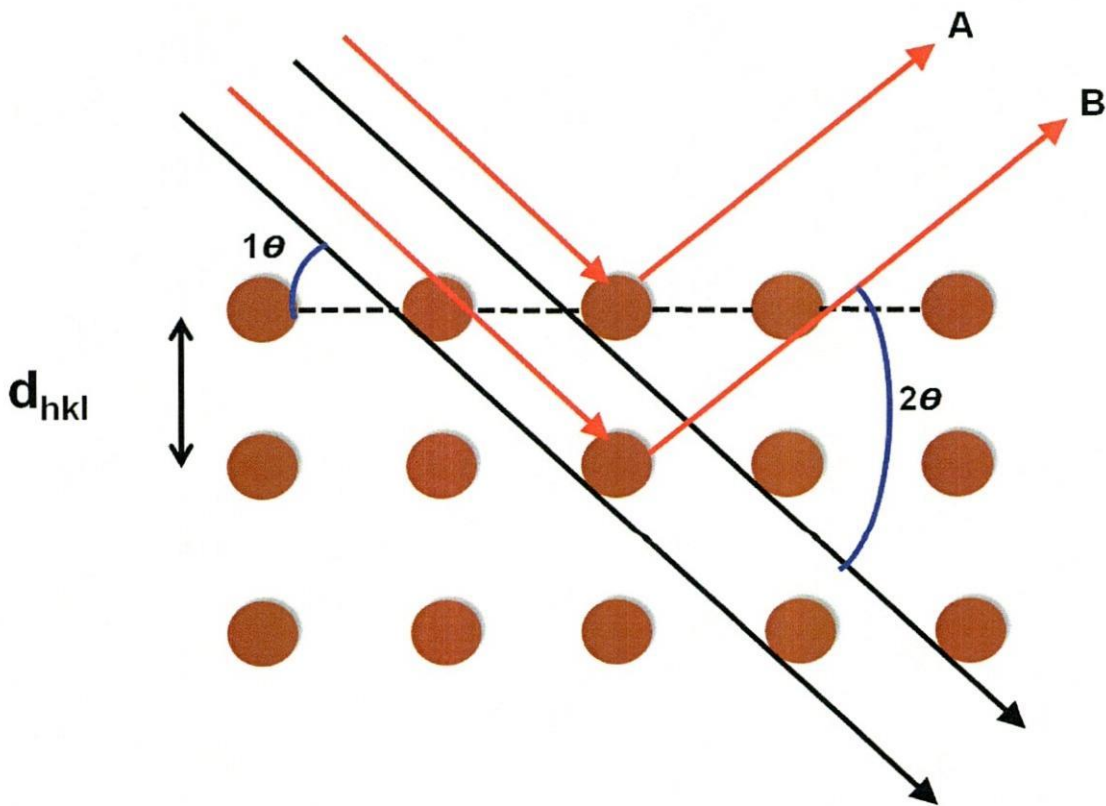


Figure 3.18: Monochromatic X-rays entering a crystal [46].

Ray A reflects off of the upper atomic plane at an angle θ equal to its angle of incidence. Similarly, Ray B reflects off the lower atomic plane at the same angle θ . While Ray B is in the crystal, however, it travels a distance of $2a$ farther than Ray A. If this distance $2a$ is equal to an integral number of wavelengths ($n\lambda$), then Rays A and B will be in phase on their exit from the crystal and constructive interference will occur. If the distance $2a$ is not an integral number of wavelengths, then destructive interference will occur and the waves will not be as strong as when they entered the crystal. Thus, the condition for constructive interference to occur is

$$n\lambda = 2a \dots\dots\dots 3.1$$

But, from trigonometry, we can figure out what the distance $2a$ is in terms of the spacing, d , between the atomic planes.

$$a = d \sin \theta \dots\dots\dots 3.2$$

$$\text{or } 2a = 2 d \sin \theta \dots\dots\dots 3.3$$

$$\text{thus, } n\lambda = 2d \sin \theta \dots\dots\dots 3.4$$

This is known as **Bragg's Law** for X-ray diffraction.

What it says is that if we know the wavelength, λ , of the X-rays going in to the crystal, and we can measure the angle θ of the diffracted X-rays coming out of the crystal, then we know the spacing (referred to as *d-spacing*) between the atomic planes.

$$d = n\lambda / 2 \sin \theta \dots\dots\dots 3.5$$

3.2.6. Photoluminescence Spectroscopy (PL)

Luminescence refers to the emission of light by a material through any process other than blackbody radiation [47]. **Photoluminescence** is luminescence by which electromagnetic radiation, i.e. photons, are used to excite a material, usually by use of ultraviolet light. Excitation occurs when light is directed onto a sample and it gets absorbed and imparts excess energy into the material. This excess energy can be released by the sample through the emissions of light [48], a process

called luminescence. When the luminescence is accompanied by photo-excitation it is called photoluminescence (figure 3.19).

Photoluminescence Spectroscopy is a contactless, nondestructive method of probing the electronic structure of materials. In PL one measures physical and chemical properties of materials by using photons to induce excited electronic states in the material system and analyzing the optical emission as these states relax. Typically, light is directed onto the sample for excitation, and the emitted luminescence is collected by a lens and passed through an optical spectrometer onto a photon detector. See figures 3.20 (a, b and c).

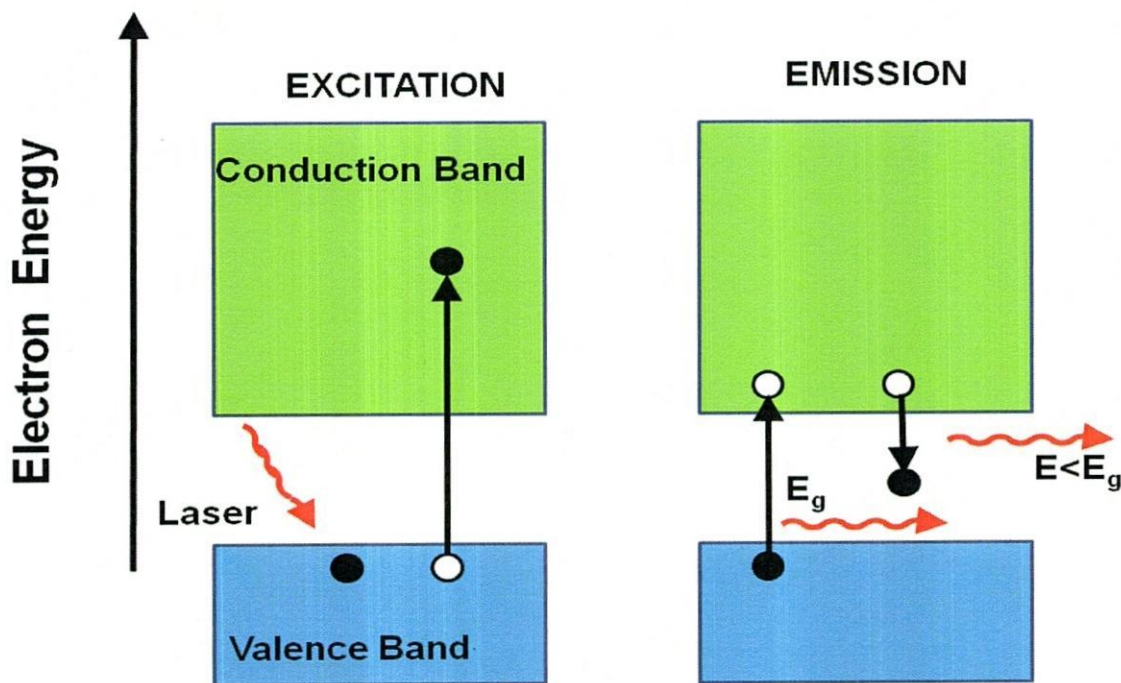


Figure 3.19: Excitation and Emission processes

The spectral distribution and time dependence of the emission are related to electronic transition probabilities within the sample, and can be used to provide qualitative and, sometimes, quantitative information about chemical composition, structure, impurities, kinetic process and energy transfer. Sensitivity is one of the strengths of the PL technique, allowing very small quantities (nanograms) or low concentrations (parts-per-trillion) of material to be analyzed. Precise quantitative concentration determinations are difficult unless conditions can be carefully controlled, and many applications of PL are primarily qualitative.

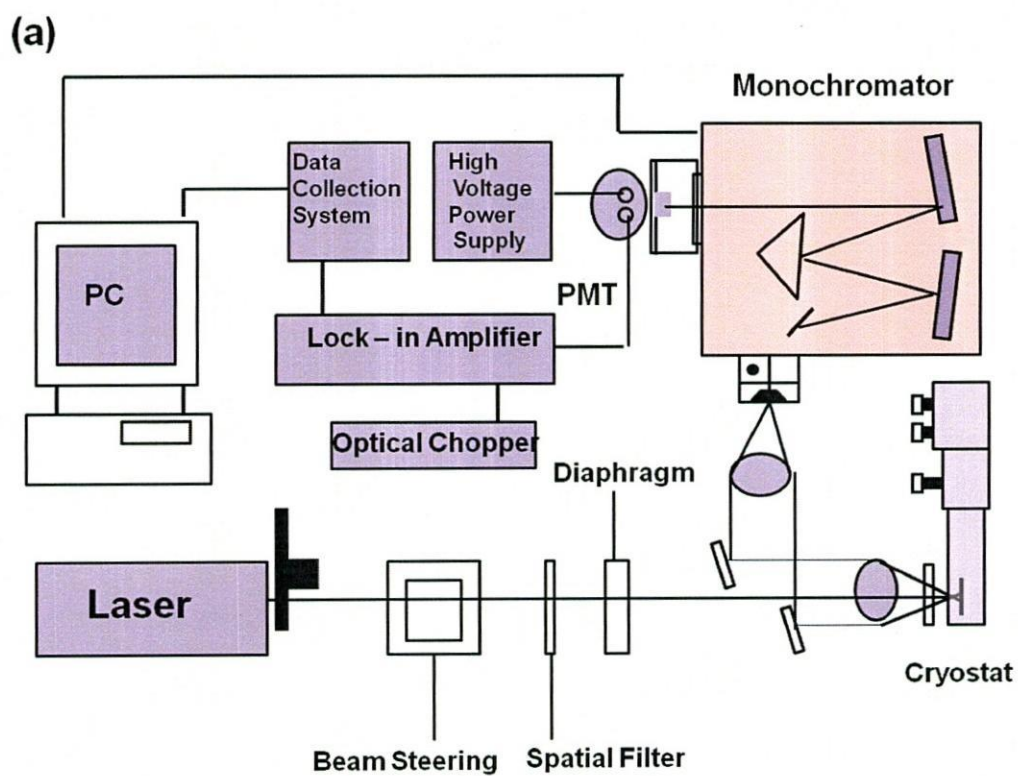


Figure 3.20: (a) Schematic diagram of the PL system (b) PL system used to investigate the luminescent properties of phosphors.

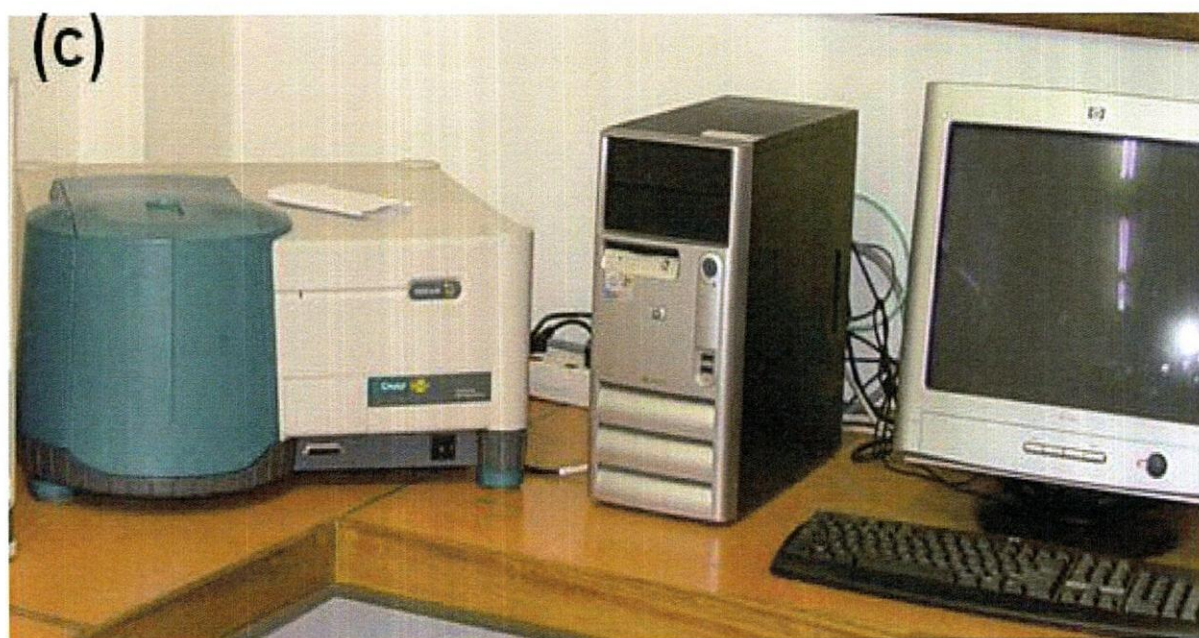


Figure 3.20: (c) Cary Eclipse fluorescence spectrophotometer.

In PL, a material gains energy by absorbing photon at some wavelength by promoting an electron from a low to a higher energy level. This may be described as making a transition from the ground state to an excited state of an atom or molecule, or from the valence band to the conduction band of a semiconductor crystal or polymer (electron-hole creation). The system then undergoes a non-radiative internal relaxation involving interaction with crystalline or molecular vibrational and rotational modes, and the excited electron moves to a more stable excited level, such as the bottom of the conduction band or the lowest vibrational molecular state. After a characteristic lifetime in the excited state, electron will return to the ground state.

In luminescent materials some or all of the energy released during this final transition is in the form of light, in which case the relaxation is called radiative. The wavelength of the emitted light is longer than that of the incident light. It should be noted that depending on the characteristic life-time of emission, fast PL with life-time of sub microsecond is also called “fluorescence”, whereas slow ones, 4 to 10 s, are referred to as “phosphorescence” [49].

In this study in addition to the carry eclipse, two other models of PL spectrometers were used; F-7000 FL Spectrophotometer and a 325 nm He-Cd Laser. In the 325 nm He-Cd, a laser beam is focused on to a sample via optical lenses, mirrors and then the chopper that ensures the light beam is sent in packets as illustrated in figure 3.21. To ensure that only the light beam from the

sample is sent through the photomultiplier tube detector, the glass GG 385 was used to block the laser beam [14].

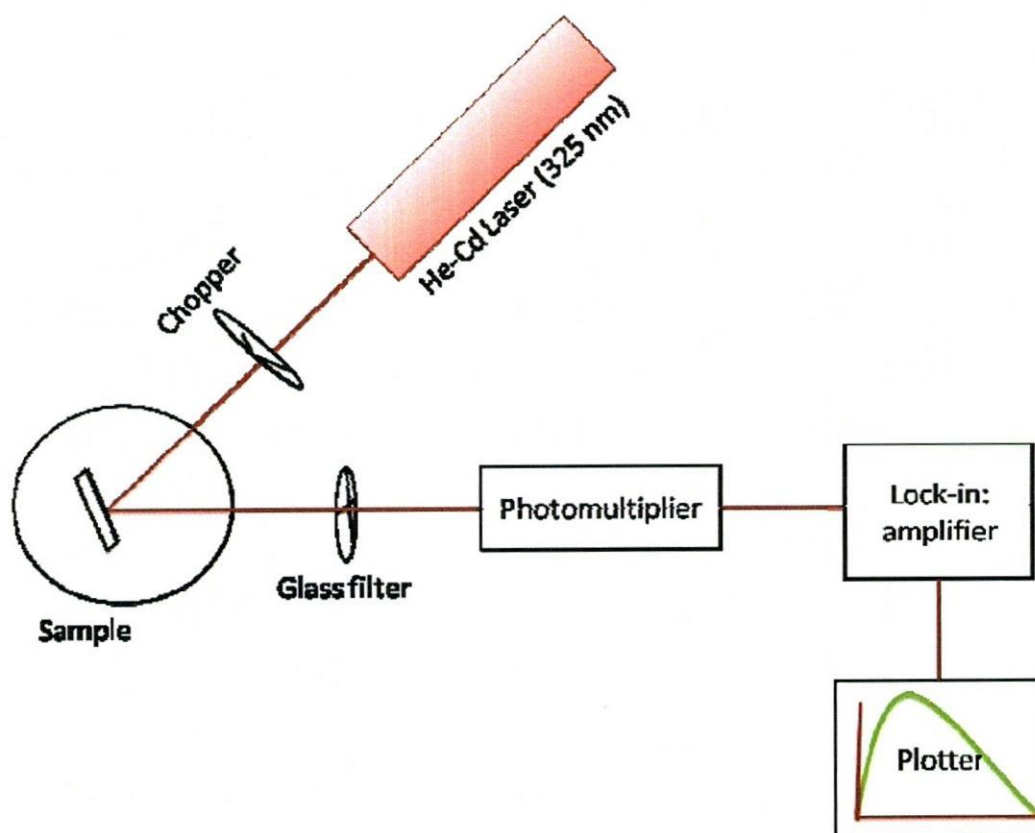


Figure 3.21: Schematic representation of the 325 nm He-Cd laser PL [14].

3.2.7. Ultraviolet –Visible (UV-VIS) Spectroscopy

When radiation is incident onto a sample (solid/liquid) it may be partly absorbed (%A), partly scattered or reflected (%R) and partly transmitted (%T). The absorbed radiation does the work of exciting the electrons within the band gap from the ground state to the excited state. In UV-VIS spectroscopy the amount of radiation absorbed (%A), reflected (%R) or %T is measured as a function of wavelength (λ) from which important qualitative and quantitative deductions can be made about the sample. A spectrophotometer is an instrument used to register the different amounts, %R, %T or %A of the radiation at each wavelength by scanning the Ultraviolet-Visible-Near-Infrared (UV-Vis-NIR) wavelength range and record the spectrum. Figure 3.22 shows a schematic diagram with the main elements of a simple single-beam spectrophotometer.

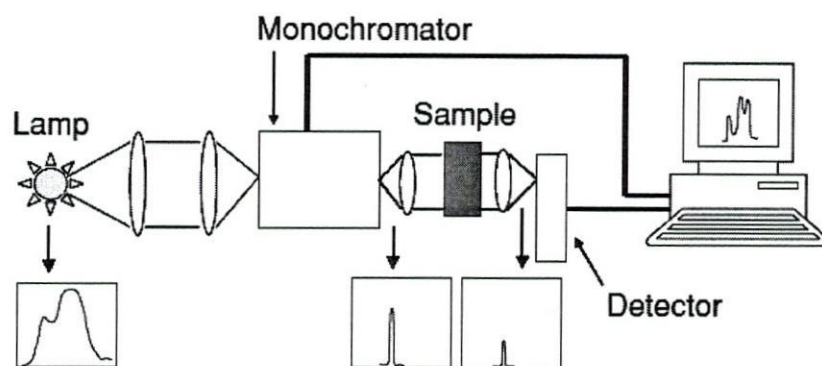


Figure 3.22: Schematic diagram of a single-beam spectrophotometer [50]

The basic elements are: (i) a light source (usually a deuterium lamp for the UV spectral range and a tungsten lamp for the VIS and IR spectral ranges) that is focused on the entrance to (ii) a monochromator, which is used to select a single frequency (wavelength) from all of those provided by the lamp source and to scan over a desired frequency range; (iii) a sample holder, followed by (iv) a light detector (usually a photomultiplier for the UV–VIS range and a SPb cell for the IR range) to measure the intensity of each monochromatic beam after traversing the sample; and finally (v) a computer, to display and record the absorption spectrum

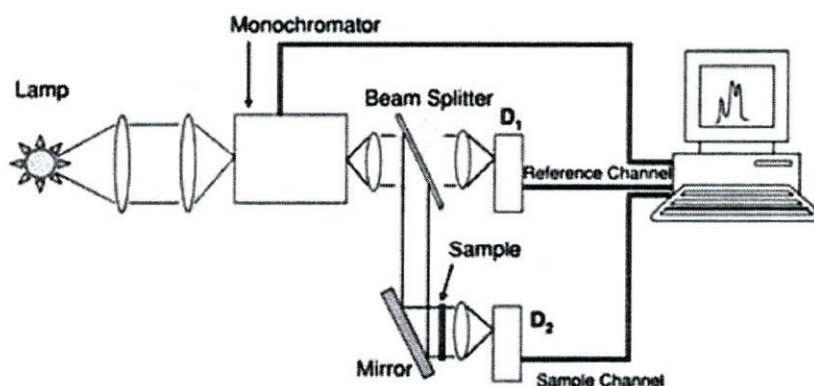


Figure 3.23: Schematic diagram of a double-beam spectrophotometer [50].

Single-beam spectrophotometers pose some challenges due to the spectra being affected by spectral and temporal variations in the illumination intensity. The spectral variations are due to the combined effects of the lamp spectrum and the monochromator response, while the temporal variations occur because of lamp stability. These problems can be overcome by use of double-beam spectrophotometers. Figure 3.23 shows a schematic diagram of the main components of

such spectrophotometers. The illuminating beam is split into two beams of equal intensity by a beam splitter, which is directed toward two different channels; a reference channel and a sample channel. The outgoing intensities correspond respectively to I_0 and I , which are detected by two similar detectors, D1 and D2. As a consequence, the spectral and temporal intensity variations of the illuminating beam affect both the reference and sample beams in the same way, and these effects are minimized in the resulting absorption spectrum. The system can still be improved if a unique detector is used instead of the two detectors, D1 and D2. In such a way, the errors introduced by the usual unequal spectral responses of these detectors are also eliminated. This can be achieved by introducing fast rotating mirrors so that the intensities I_0 and I can be always sent to the same detector [50].

In this project a Perkin Elmer Scan-Lambda 950 UV-Vis spectrophotometer (LAMBDA™ 950) was used to record the absorbance characteristics of samples in reflectance mode. Figure 3.24 illustrates the anatomy of the LAMBDA™ 950 spectrophotometer.

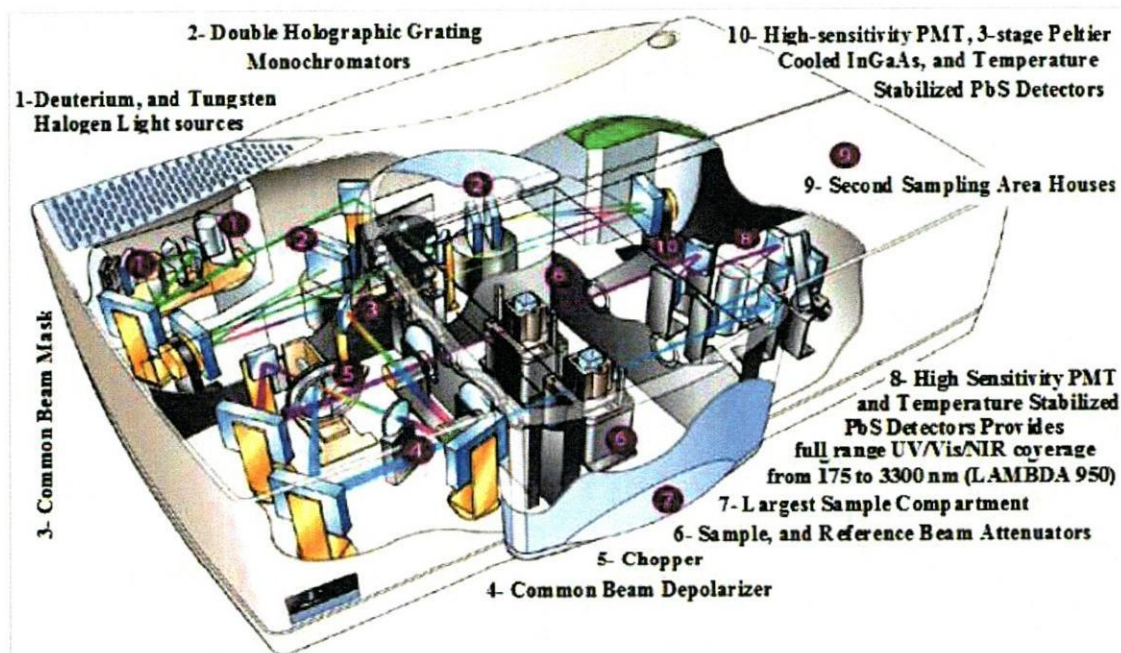


Figure 3.24: Diagram showing the insides of a Perkin Elmer Scan-Lambda 950 UV-Vis spectrophotometer (LAMBDA™ 950) [51].

Reflectance measurements are made using either an integrating sphere or a specular reflectance accessory. Integrating spheres are used for samples with a significant diffuse reflectance component such as powders, and other ‘rough’ materials. The sphere’s internal surface is made of the polymer Spectralon, which offers levels of diffuse reflectance approaching 100%.

Samples are placed at the back of the sphere, and the light is reflected back off the sample, and then, it is collected by the sphere [51].

3.2.8. X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is also referred to as Electron Spectroscopy for Chemical Analysis (ESCA). It is a surface technique mainly employed to obtain information about the chemical states of surfaces of materials such evaluation of valence states, bonding environments and the molecular and atomic composition of surface layers. Today, XPS can be used for elemental analysis, imaging, depth profile and thin-films [51].

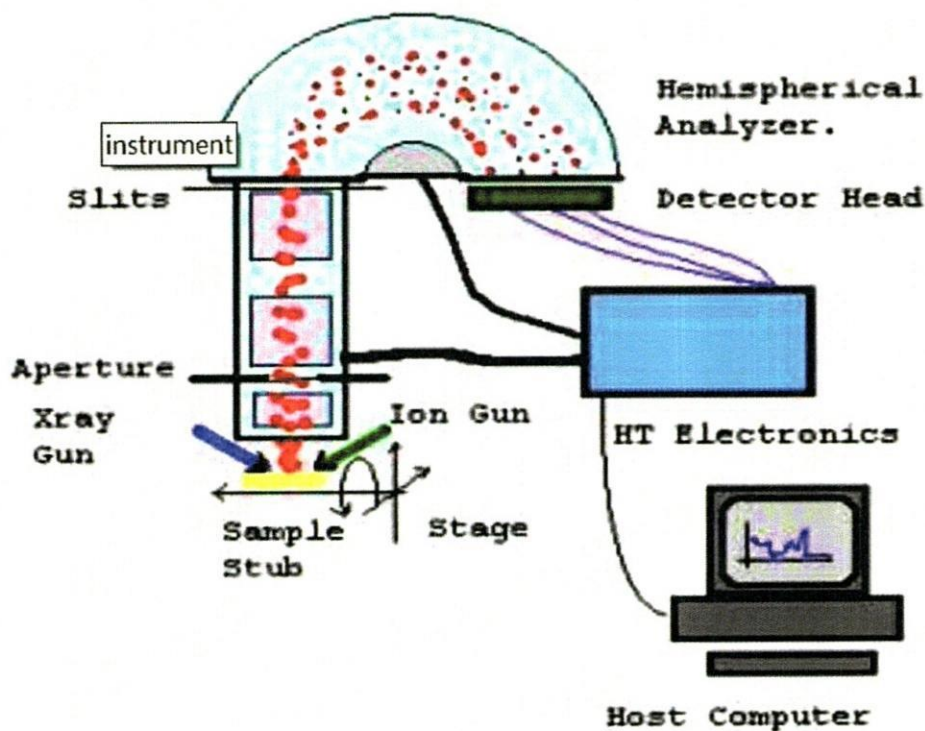


Figure 3.25: Schematic outline for an XPS Instrument [53]

XPS is based on the photoelectric effect where a photon was used to impinge upon as surface and eject electrons from it. XPS utilizes photo-ionization and analysis of the kinetic energy

distribution of the emitted photoelectrons to study the composition and electronic state of the surface region of a sample [39].

During the XPS analysis, energetic x-ray photons incident on a sample surface in vacuum ejects electrons (photoelectrons) from the K-shell level of an atom. Mostly $\text{AlK}\alpha$ (1486.6eV) or $\text{MgK}\alpha$ (1253.6eV) are the preferred photon energies [52].

Photoelectrons are collected and analyzed giving a spectrum of emission intensity versus electron binding energy. Figure 3.25 shows a schematic layout of an XPS.

The binding energies of the photoelectrons are characteristic of the element from which they are emitted. The peaks at particular energies indicate the presence of a specific element in the sample under study while the intensity of the peaks is related to the concentration of the element within the sampled region. In this research the PHI 5000 XPS Versa probe (monochromatic $\text{AlK}\alpha$ lines) system shown in figure 3.26 was used for recording the binding energies (E_b) of electrons within the samples.

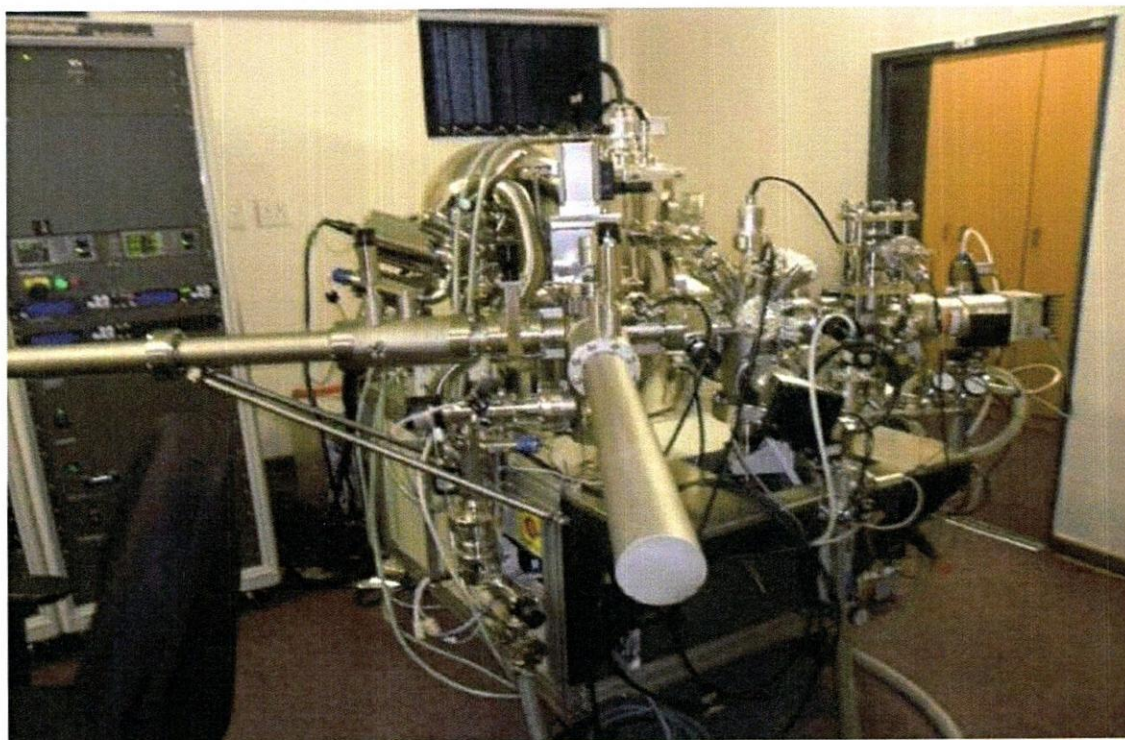


Figure 3.26: The PHI 5000 XPS Versaprobe at the University of the Free State.

3.2.9. Thermoluminescence (TL) Spectroscopy

When a phosphor with deep traps is excited for a while at rather low temperatures and then heated, it shows an increased after-glow called thermally stimulated luminescence due to the

recombination of electrons thermally reactivated from the deep traps. This emission is also called thermoluminescence, and the temperature dependence of the emission intensity is called the glow curve, which is a good means to measure the depth (i.e., the activation energy of traps) [48]. The measurement of a glow curve of a phosphor sample proceeds as follows.

1. The sample is cooled to a low temperature (liquid nitrogen is often used as coolant).
2. The sample is excited by UV light until the traps are filled with electrons or holes.
3. The excitation is terminated, and the temperature of the sample is raised at a constant rate, $dT/dt=\beta$, while the intensity is recorded.
4. The temperature dependence of fluorescence is then measured under a constant UV excitation, which is used to calibrate the effect of temperature quenching on the thermoluminescence intensity.

3.2.6.1. The TL Spectrometer

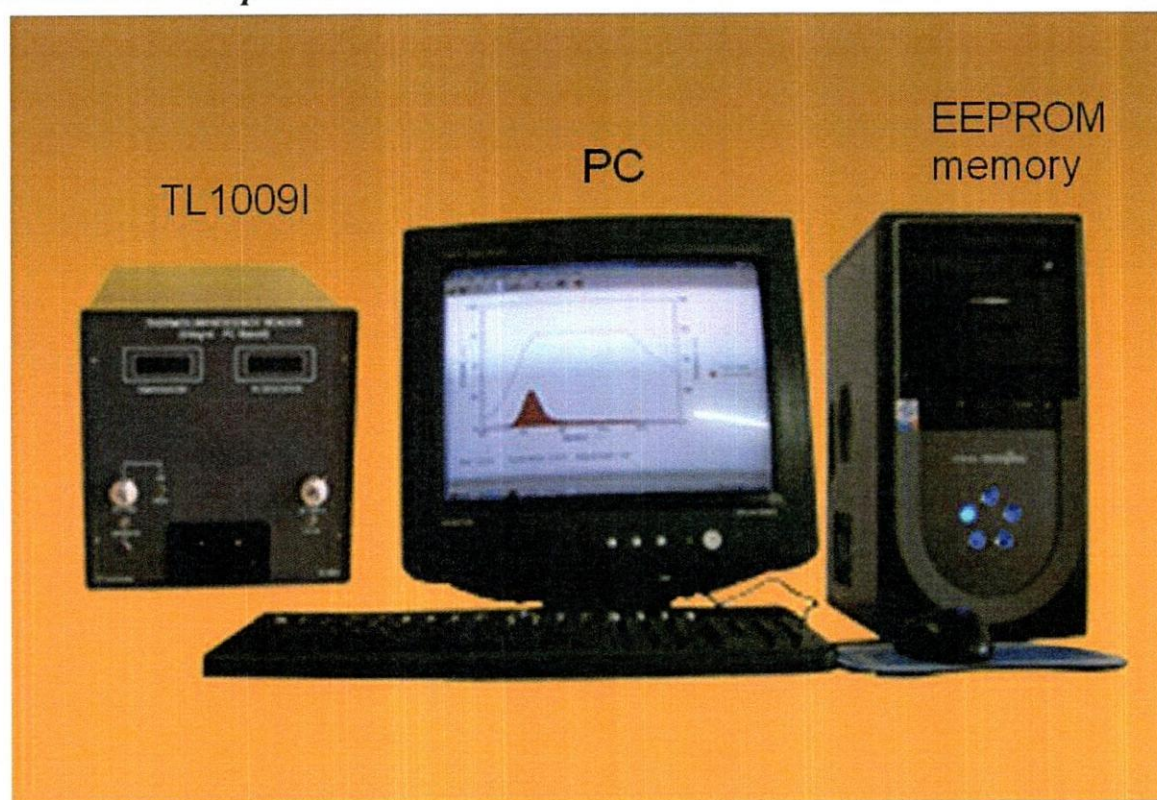


Figure 3.27: Thermoluminescence Reader Type TL1009I [54].

The TSL glow curves in this study were obtained by Thermoluminescence Reader Type TL1009I (Figure. 3.27) with PMT type 9924 designed and offered by M/s Nucleonix Systems Pvt. Ltd., India interfaced to a PC where the TL signals were analyzed. It is a versatile controller

based unit, facilitating the user to subject the TL sample under study to the desired heating profile, to record the digitized TL glow curve.

This unit stores both integral value and digitized glow curve into EEPROM memory.

It records the data in 200 channels, temperature, TL intensity & Run time values.

Entire electronics including PMT, HV bias, Temperature controller circuit, Heater transformer heater strip, sample drawer assembly, data acquisition electronics is all integrated into a single enclosure. The block diagram of the experimental setup of thermoluminescence (TL) is shown in figure 3.28.

The user interface to the unit is through a powerful software GUI, coded in VB which runs on Windows platform. This system essentially works as a PC controlled TLD reader with command buttons and dropdown menus defined for various functions. Built-in serial port in the unit facilitates the user to connect it to a PC for GUI and to achieve full functionality [54].

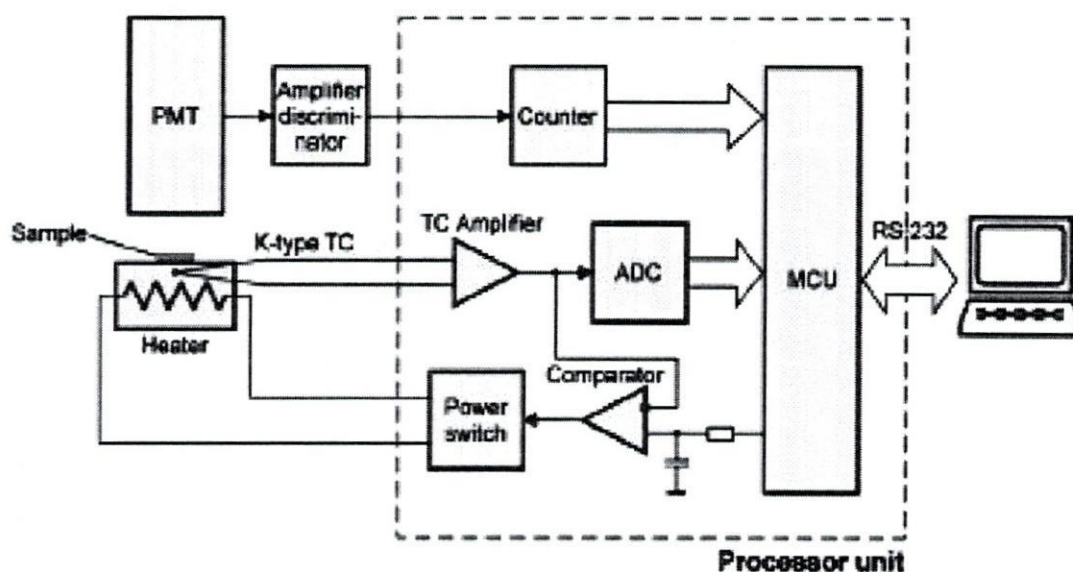


Figure 3.28: A block diagram of the experimental thermoluminescence (TL) setup.

Some TL studies in this research were carried out using a Risø model TL/OSL-DA-20 Luminescence Reader [55] shown in figure 3.29. As compared to the TL1009I whose irradiation source is mostly ultraviolet (UV) and manually operated. The Risø TL/OSL-DA-20 Luminescence Reader is designed for automated measurement of thermally and optically stimulated luminescence. The luminescence is detected by a photomultiplier (E<I 9235QA). Transmission filters consisting of Hoya U-340, Schott BG39 and Corning 7-59 are used to discriminate between the luminescence and scattering stimulating light. This limits the transmission band for the luminescence to 300 – 400 nm. Samples for both thermal and optical

stimulation are placed on a 48 – sample carousel which can be rotated in position under the photomultiplier.



Figure 3.29: A Risø model TL/OSL-DA-20 Luminescence Reader [55].

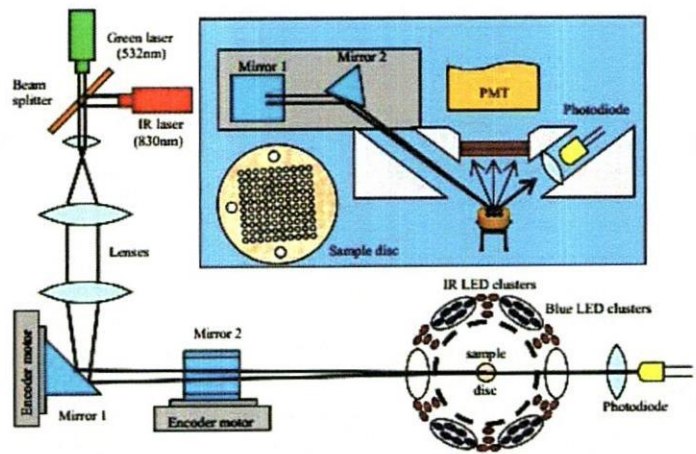


Figure 3.30: A Schematic diagram of the single grain OSL attachment [55].

The heating element located underneath the photomultiplier heats the sample and also lifts the sample to the measurement position. Samples can be heated up to 700 °C at rates from 0.1 to 10 °C/s. If necessary, the sample chamber can be flushed with nitrogen to improve thermal condition between sample disk and the heater and to prevent oxidation of the heating systems at

high temperature. Optical stimulation is done using clusters of light-emitting diodes (870 nm infrared and 470 nm blue LEDs). 532 nm and 830 nm laser stimulation source are optional. The LEDs can be operated at constant intensity for continuous-wave optical stimulation. LM-OSL can be operated if the intensity of the LEDs are pulsed, then time-resolved spectra may be measured. Samples are excited using beta irradiation using a detachable beta irradiator fixed above the sample carousel. The irradiation source is a 1.48 GBq $^{90}\text{Sr}/^{90}\text{Y}$ beta source which emits beta particles with a maximum energy of 2.27 MeV. Optional sources are a 10.7 MBq ^{241}Am foil alpha source and a Varian VF-50J X-ray tube [55]. The schematic diagram of figure 3.30 shows how optical stimulation (OS) is achieved using a laser beam focused by three lenses. The position of the laser spot on the sample is controlled by moving the two mirrors.

References

- [1] K. C. Patil, S.T. Aruna, and T. Mimani, *Sol. State and Mat. Sci.* **6** (2002) 507.
- [2] J.J. Kim, J.H. Kang, D.C. Lee and D.Y. Jeon, *Am. Vac. Soc.* (2003).
- [3] S.S. Manoharan and K.C. Patil, *J. Am. Ceram. Soc.* **141** (1992) 1012.
- [4] M.A. Sekar and K.C. Patil, *J. Mater. Chem.* **2(7)** 1992 739.
- [5] R.G. Chandran and K.C. Patil, *Mater. Res. Bull.* **27** (1992) 147.
- [6] P. Ravindranathan, S. Komameni and R. Roy, *J. Mater. Sci. Lett.* **12** (1993) 369.
- [7] N.A. Dhas and K.C. Patil, *Ceram. Inter.* **20** (1994) 57.
- [8] Y. Zhang and G.C. Stangle, *J. Mater. Res.* **9 (8)** (1994)1997.
- [9] D. A. Furnor, M.R. More and A.M. Segadhes, *Mater. Res. Bull.*, **31(10)** (1996)1243.
- [10] D. S. Kshatri, A. Khare, P. Jha, *Chalcogenide Letters*, **10(3)**, (2013) 121
- [11] N. Suriyamurthy and B.S. Panigrahi, *J. Lumin.* **128** (2008) 1809
- [12] G.A. Hirata, F. Raamos, R.Garcia, E.J. Bosze, J.M. Kittrick, et al. *J. Phys. Stat. Sol.(a)*, **188** (2001) 179.
- [13] Z. Qiu, Y. Zhou, M. Lu, A. Zhang and Q. Ma, *Acta Mat. a* **55** (2007) 2615.
- [14] B. M. Mothudi, *PhD Thesis*, University of the Free State, 2009.
- [15] P. R. Willmott, J.R. Huber, *Rev. Mod. Phys.* **72**, (2000) 315.
- [16] X. Yang, Y. Tang, M. Yu, Q. Qin, *Thin Solid Films* **187** (2000) 358,
- [17] J.C. Miller, R.F. and Haglund, *Laser Ablation and Desorption*, **30** (1998) 671
- [18] H. Krebs, M. Weisheit and J. Faupel et al, *Advances in Solid State Physics SE – 36*, **43** (2003) 505
- [19] M. N. R. Ashfold, F. Claeysens, G. M. Fuge and S. J. Henley, *Chem. Soc. Rev.*, **33** (2004) 23
- [20] C. W. Schneider and T. Lippert, *chapt 5. Laser Ablation and Thin Film Deposition*, 2011, 89

- [21] R. W. Kelsall, I. W Hamley, M. Geoghegan, Nanoscale Science and Technology, Wiley, 2005.
- [22] M.S. Dhlamini, *PhD Thesis*, University of the Free State, 2008.
- [23] http://serc.carleton.edu/research_education/geochemsheets/techniques/SEM.html [Accessed 12/10/2015]
- [24] M.P. Sylvia, *MSc Thesis*, University of the Free State, 2009.
- [25] J. Schweitzer, Electrons in Scanning electron microscopy, <http://www.purdue.edu> [Accessed 12/10/2015]
- [26] <http://www.vcbio.science.ru.nl/en/fesem/info/principe/> [Accessed 12/10/2015]
- [27] <http://www.jeol.co.jp/en/products/detail/JSM-7800F.html> [Accessed 12/10/2015]
- [28] Description of EDS Technique <http://mee-inc.com/index.html> [Accessed 12/10/2015].
- [29] B. G. Yacobi, D. B. Holt and L.L. Kazmerski Microanalysis of Solids, New York, Plenum Press, 1994.
- [30] A.H. Wako, *MSc Thesis*, University of the Free State, 2011.
- [31] <http://etd.uovs.ac.za/ETD-db/theses/available/etd-02192007-101454/unrestricted/CoetseeE.pdf>. [Accessed 12/10/2015].
- [32] Z.L. Wang, Y. Liu, Z. Zhang, Handbook of nanophase and nanostructured materials, 4th edition, New York, 2003.
- [33] W.A. I. Tabaza, *PhD thesis*, University of the Free State, 2014.
- [34] M.M Biggs, *M.Sc Thesis*, University of the Free State, 2009.
- [35] M.S. Dhlaminis, *M.Sc Thesis*, University of the Free State, 2008.
- [36] L D Hanke, Handbook of Analytical Methods for Materials: Materials Evaluation and Engineering, Inc, 763, 449-8870 (2009).
- [37] <http://www.nanoscience.gatech.edu/zwang/research/afm.html> [Accessed 12/10/2015].
- [38] A Vilalta-Clement and K Gloystein, Physics of Advanced Materials Winter School (2008).
- [39] P.A Moleme, *M.Sc Thesis*, University of the Free State, 2011.
- [40] N. Jalili, K. Laxminarayana, Mechatronics **14** (2004) 907.
- [41] http://www.novascan.com/education/non_contact_mode_afm.php. [Accessed 12/10/2015].
- [42] G. Cao, Nano Structures and Nano Materials, Synthesis, Properties and Applications, 6th edition, Imperial College Press, London, UK, 2004.
- [43] F. A. Settle, Handbook of Instrumental Techniques for Analytical Chemistry, Prentice

- Hall PTR, USA, 339.
- [44] http://serc.carleton.edu/research_education/geochemsheets/techniques/XRD.html
[Accessed 12/10/2015].
 - [45] B. D. Cullity, Elements of X-ray Diffraction, *Addison-Wesley*, (1956)
 - [46] <http://www.doitpoms.ac.uk/tlplib/xray-diffraction/bragg.php> [Accessed 12/10/2015]
 - [47] C. Colvard, C.R. Brundle, C.A. Evans Jr., and S. Wilson, Buitenvorth- Heineman Stoneham, MA, Encyclopaedia of Materials Characterization 1992, 373.
 - [48] S. Shionoya, W.M. Yen, Phosphors Handbook, CRC Press, USA, 1998, 95.
 - [49] G. Cao, University of Washington, USA, 346.
 - [50] J. G. Sol'e, L.E. Baus'a and D. Jaque. An Introduction to the Optical spectroscopy of Inorganic Solids 2005, 33.
 - [51] S. K Shaat, PhD Thesis, University of the Free State, 2013.
 - [52] <http://www.uksaf.org/tech/xps.html> [Accessed 12/10/2015].
 - [53] http://www.casaxps.com/help_manual/XPSInformation/XPSInstr.htm. [Accessed 12/10/2015].
 - [54] <http://www.nucleonix.com/cancer/ch22.html>. Accessed 12/10/2015].
 - [55] <http://eqdb.nrf.ac.za/equipment/other/ris%C3%B8-national-laboratory-tlosl-da-20-luminescence-reader> [Accessed 12/10/2015].

Chapter 4

Thermoluminescence of beta-irradiated $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$, Dy^{3+} phosphors

4.1. Introduction

When an insulator, a semiconductor or a phosphor with deep traps is exposed to ionizing radiation for a while at rather low temperatures, it absorbs energy from the radiation and gets excited. When the temperature of the material is raised, it shows an increased after-glow called thermally stimulated luminescence (TSL) due to the recombination of electrons thermally reactivated from the deep traps and the energy is converted to luminescence and released in the form of visible light. This phenomenon is known as thermoluminescence (TL) [1]. The heat only acts as a stimulant whereas the ionizing radiation plays the role of an exciting agent. During the process of irradiating a material with α -rays, β -rays, UV-rays, χ -rays, or γ -rays, part of the irradiation energy is used to transfer electrons to traps [2]. Some of these electrons are trapped and locate themselves at a depth (E) below the conduction band. The trap levels or centers play a significant role in energy storage for persistent photoluminescent and thermoluminescent phosphors. This radiation energy stored in the form of trapped electrons is released by raising the temperature of the material and the released energy is converted to luminescence. This trapping process followed by the release of the stored energy in thermoluminescent materials is widely applied in radiology such as in ionizing radiation dosimeters. All phosphorescent materials have a minimum temperature; but many have a minimum triggering temperature below normal temperatures and are not normally thought of as thermoluminescent materials [3]. By cooling a TL material and reheating it again does not make it emit light. It should first be exposed to the radiation and then heated for it to emit light again. The storage capacity of a TL material makes it in principle suitable for dosimetric applications [4]. Materials that exhibit TSL include glasses, ceramics, plastics and some organic solids.

In order to obtain information about luminescence process of phosphors and to apply them in various fields, the knowledge of defects or traps and their location in the band gap of materials is very important. TL measurement is a very important and convenient method of investigating and providing information concerning the nature of traps and trapping levels in crystals. The

glow curve which is a representation of the temperature dependence of the emission intensity is a good means to measure the trap depth (i.e., the activation energy of traps) [5]. During TL measurements the irradiating source is cut off and the thermally stimulated luminescence recorded while gradually increasing the temperature. Various parameters of the trapping process such as activation energy (E), amount of trap depth (n_0), trapping rates, etc are then deduced by analysing the shape and position of the obtained TL glow curve [6]. When a TL glow curve having several overlapping peaks is obtained deconvolution is carried out in order to isolate one of the glow peaks from the others to enable the calculation of these parameters. The term peak shape method is reserved in the TL literature for such methods, although there are other methods for finding activation energy, (E) which are also based on the glow-peak shape (i.e. curve fitting methods) [7, 8]. The work by Chen [9] is a reference point in the derivation of the peak shape methods.

$\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ has been studied by many researchers on its use as luminescent material. Nevertheless, there are few reports dealing with its use as a TL material. In this paper we report the TL behaviour of as-prepared $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ synthesised by solution-combustion method at initiating temperature of 500 °C to find out its suitability in various TL applications. In particular it is concerned with the dosimetric analysis of the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ TL glow curves such as the dose response. Also kinetic analyses were carried out using variable heating rate method and the peak shape method to study the energy levels and the discrete trapping and recombination centres within the phosphor material.

4.2. Experimental

4.2.1. Synthesis

$\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor was synthesized using the solution - combustion method. The starting raw materials used in the experiment included various proportions of analytical pure grade $\text{Sr}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Dy}(\text{NO}_3)_3$, and urea ($\text{CO}(\text{NH}_2)_2$). The raw materials were weighed according to the chemical composition of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$, dissolved in 10 ml of de-ionized water and thoroughly mixed using a magnetic stirrer for 15 minutes without heating to obtain a uniform saturated aqueous solution.

The solutions were then poured into China crucibles and placed one at a time in a muffle furnace pre-heated at 500 °C. The mixture ignited and a fast, self-sustaining combustion reaction took off. At first, the solution boiled losing all the water in the form of steam followed by decomposition letting off large amounts of gases (oxides of carbon, nitrogen and ammonia). The mixture then frothed and swelled enormously forming foam, then spontaneous ignition and smoldering occurred which gradually led to an explosion which ruptured the foam with a flame

that glowed to incandescence. The product of combustion was a voluminous white $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} foam. The foam was taken out of the muffle furnace, cooled then milled resulting in a dry, and usually crystalline, fine white oxide powders. The whole combustion process took about 5 minutes. The powders were stored in transparent glass sample bottles for characterization.

4.2.2 Characterization

Thermoluminescence measurements were made on $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} phosphor. The samples were prepared into discs of 5 mm in diameter and 1 mm thick. A β -source based on the ^{90}Sr isotope was used for thermoluminescence excitation prior to heating. The radiation dose rate at the location of the samples was 10.75 Gy per minute. TL measurements were made in a nitrogen atmosphere using a Risø model TL/OSL-DA-20 Luminescence Reader. The TL was detected by an Electron Tubes Ltd model 9235QB photomultiplier through a BG-39 band-pass filter (transmission band 340–620 nm FWHM). Samples were heated from 30 to 150 or 200 °C at various heating rates and doses.

4.3. Results and Discussion

4.3.1. Dose response

To check the dose dependence effect on the peak positions, the samples were irradiated at different doses between 26 Gy and 185 Gy at a constant linear heating rate of 1 °C s⁻¹. Figure 4.1 shows the effect of variation in the TL intensity with different irradiation exposure time. The total TL signal and glow curve peaks show in all cases a linear response and the degree of linearity increases with the energy of the incident *beta* radiation and the temperature T_{max} of the TL peak.

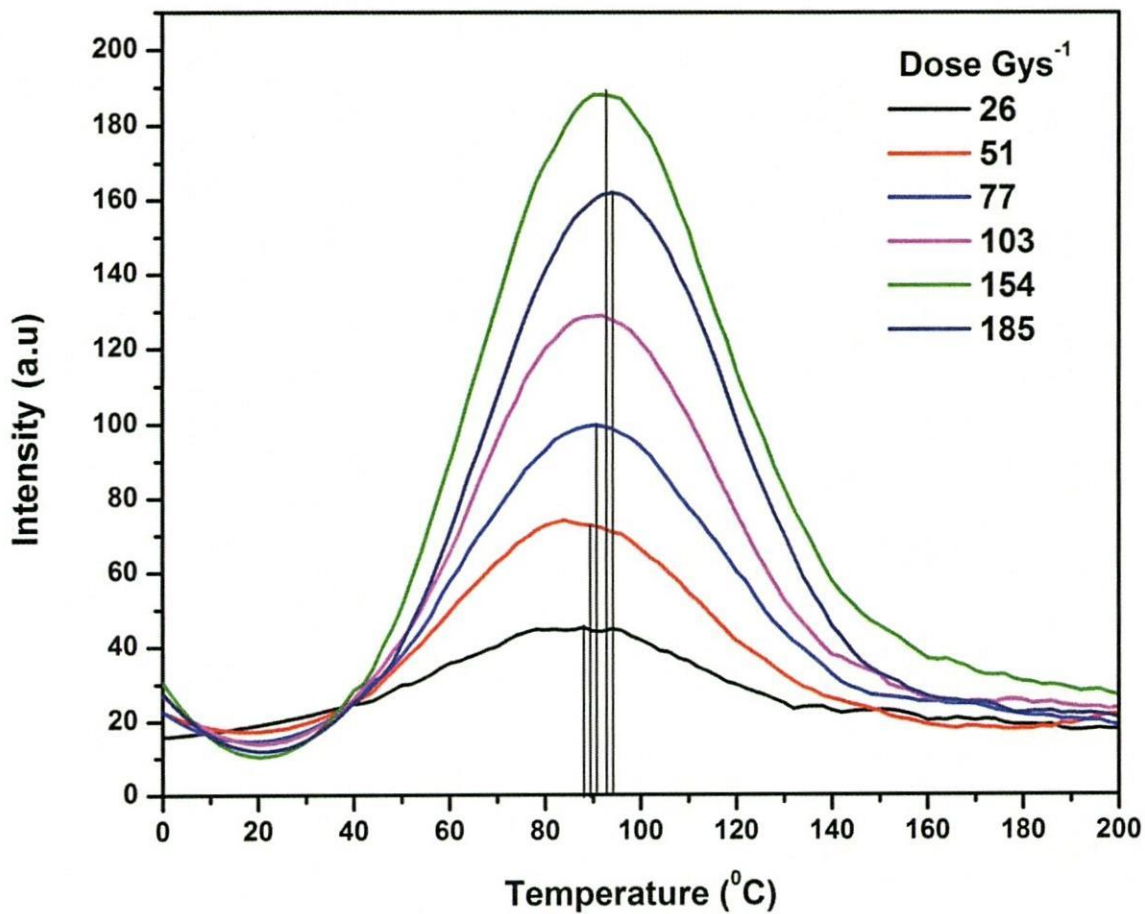


Figure 4.1: TL glow curve of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor showing effect of irradiation doses on TL intensity.

From figure 4.2 it is clearly seen that the dose responses of peaks first increase linearly up to 154 Gy ($I_{\text{max}} = 188$ a.u) with a slope of 1.1 after which the intensity starts to saturate at higher doses. The glow curve intensity (I) during heating is found to be proportional to the concentration (n_0) of the trapped charge carriers [10]. The increase in TL intensity can be attributed to the increase in luminescence centre with irradiation dose. The higher concentration of defects that generate non-radiative states within the band gap is responsible for decrease in TL the intensity after saturation. In TL theory [8], the peak temperatures of glow peaks are expected to be influenced only by changes in the heating rate. But on the contrary, as seen in figure 4.2, the position of the peak temperature T_{max} is observed to continuously shift towards the higher temperature from 86-95 °C with increased radiation dosage levels. This might also be attributed to the population of the trap centers and luminescence centers. This result indicates that the peaks in the glow curve of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ between RT and 200 °C should have first-order kinetics.

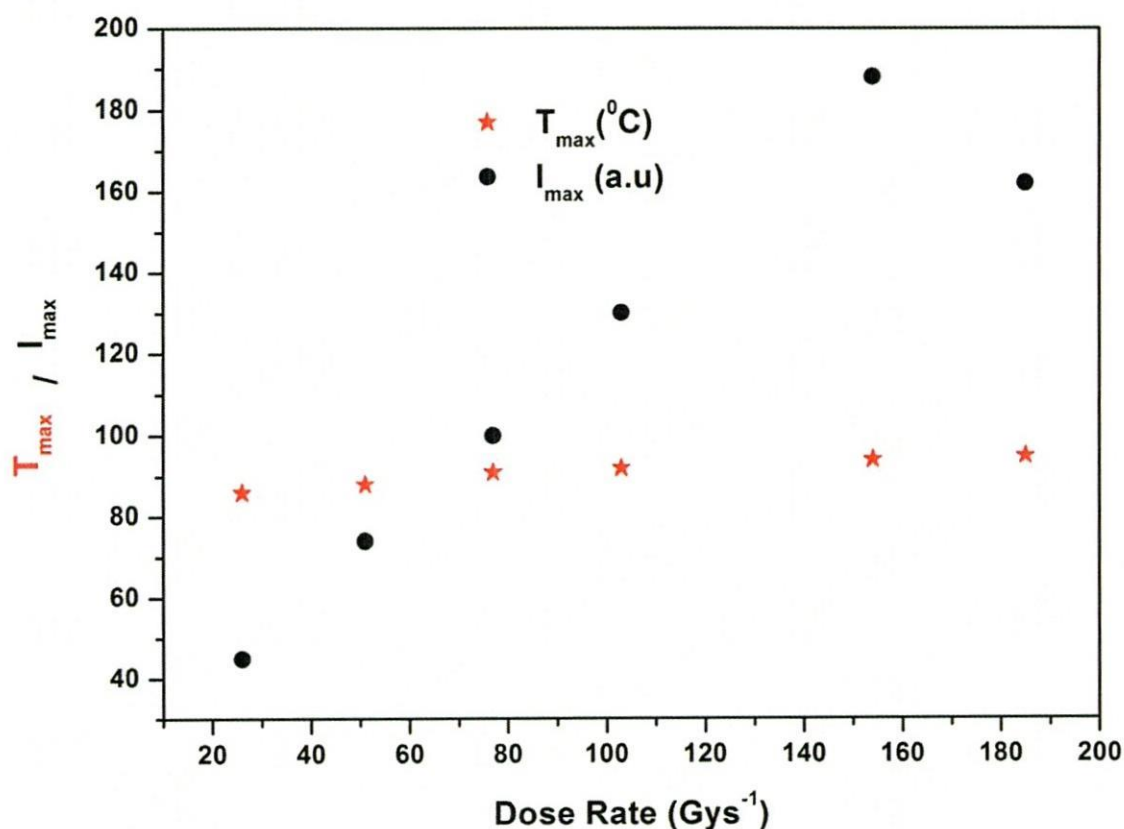


Figure 4.2: Variation of $T_{\max}$ and $I_{\max}$ with irradiation doses on TL glow curve of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} phosphor.

4.3.2. Variable heating rates

This method was used to determine the kinetic parameters in this investigation. The behavior of the glow curve was monitored as the heating rate increased from $0.6\text{ }^{\circ}\text{C}^{-1}$ to $5\text{ }^{\circ}\text{C}^{-1}$. The normalized glow curves of figure 4.3 (a) shows the effect of these heating rates. The peak TL intensity ($I_{\max}$) of the phosphor exponentially decreased with an increase in heating rate (from $I_{\max} = 350$ to 230 a.u.) as shown in figure 4.3 (b). The maximum intensity ($I_{\max}$) of the peak at the low-temperature side was about 350 a.u. at a heating rate of $0.6\text{ }^{\circ}\text{C}/\text{sec}$. However from figure. 4.3 (c) the peak temperatures ($T_{\max}$) of the glow curves are seen to exponentially shift to the higher temperature side from 72 to $95\text{ }^{\circ}\text{C}$ with increased heating rate. The higher the peak temperature the deeper trap depth [11]. Glow curve peaks at higher temperature are a result of deeper traps which have higher activation energy E_T . Hence, larger heat energy is required to free charge carriers from the deep traps.

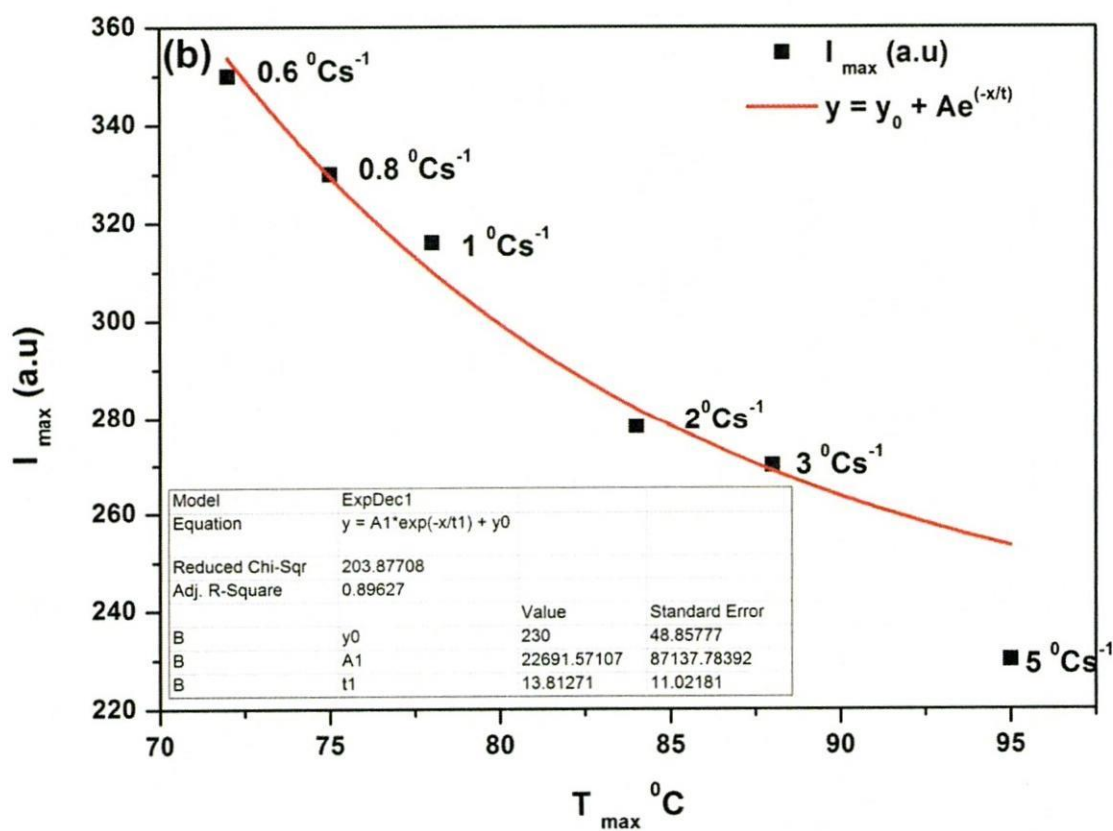
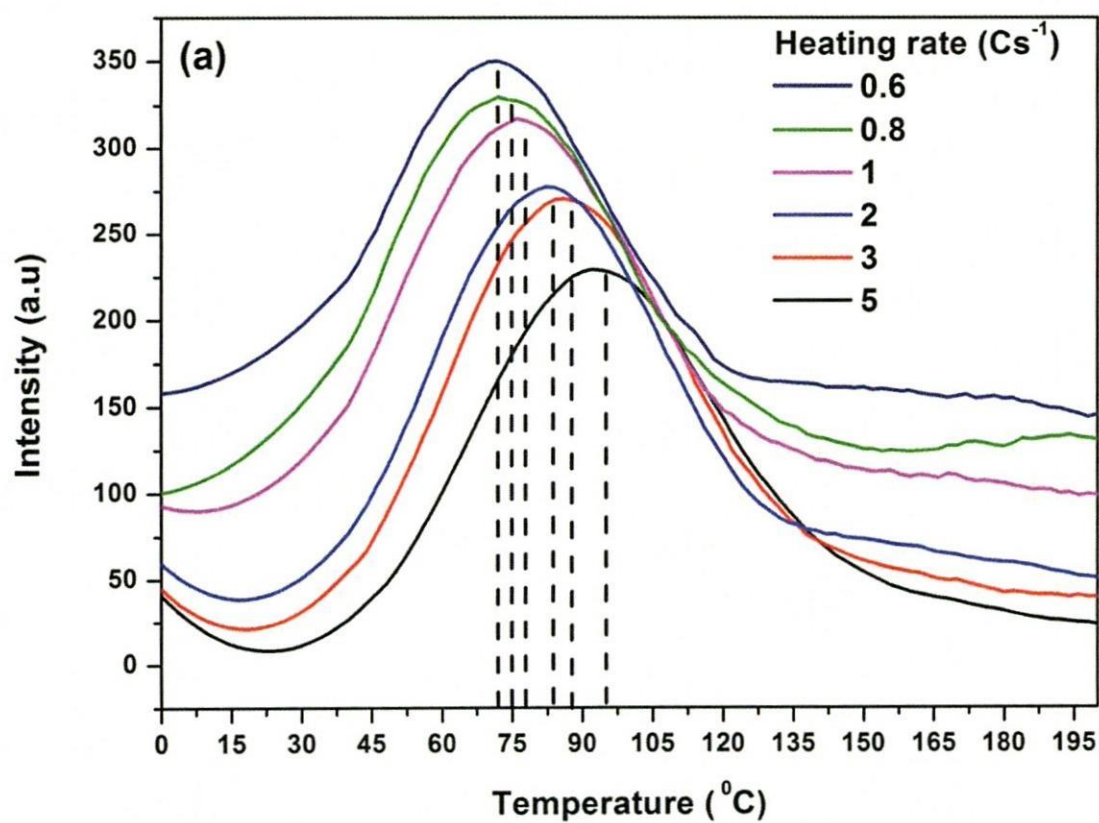


Figure 4.3: (a) and (b); Variation of $T_{\max}$ and $I_{\max}$ with heating rate on TL glow curve of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor.

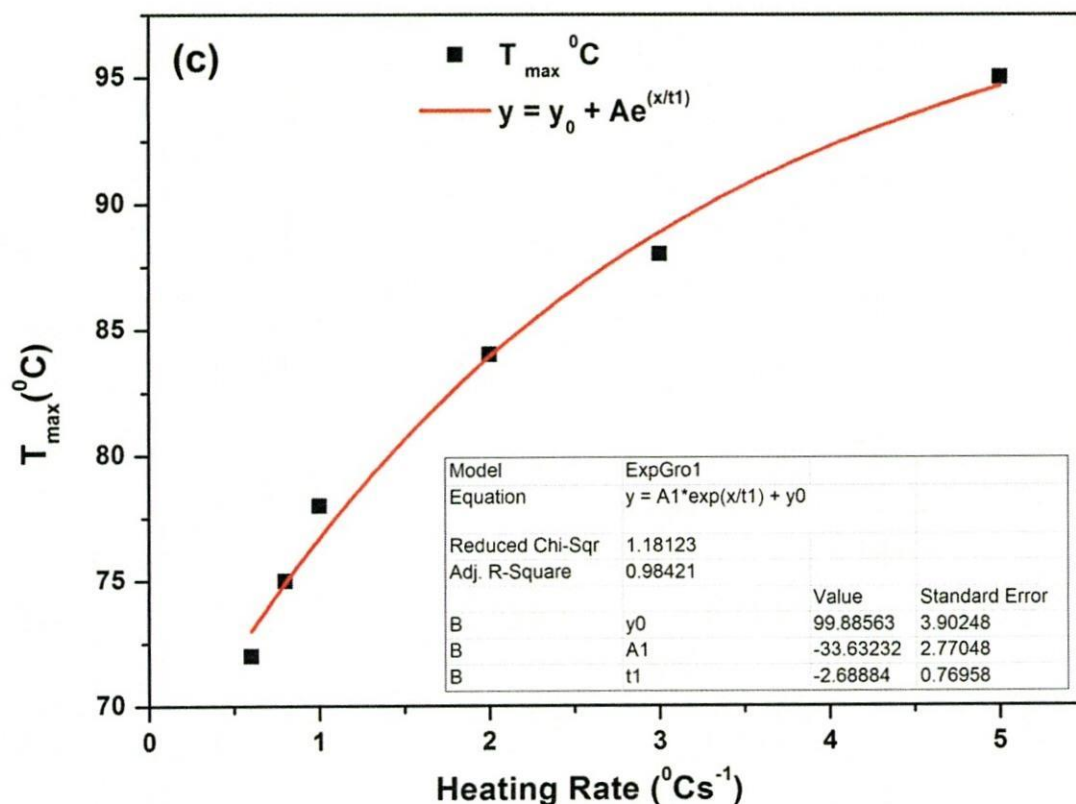


Figure 4.3: (c); Variation of $T_{\max}$ with heating rate on TL glow curve of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor.

The trap depths were calculated by the Hoogenstraaten method, which relates the TL peak temperature and heating rate [12]. The depth of each trap was determined using the following equation:

$$\ln\left(\frac{T_{\max}^2}{\beta}\right) = \left(\frac{E}{k}\right)\frac{1}{T_{\max}} + \ln\left(\frac{E}{sk}\right) \dots \dots \dots 4.1$$

where β is the heating rate, $T_{\max}$ is the peak temperature of the glow curve, E is the trap depth, k is the Boltzmann constant, and s is a frequency factor or “escape frequency” of the trapped charge carriers. A plot of $\ln\left(\frac{T_{\max}^2}{\beta}\right)$ versus $\frac{1}{T_{\max}}$ gives a linear relation with slope $\left(\frac{E}{k}\right)$ as shown in figure 4.4 The solid line through the data points gives the line of best fit for equation 4.1 and inset is a table of the fitting parameters.

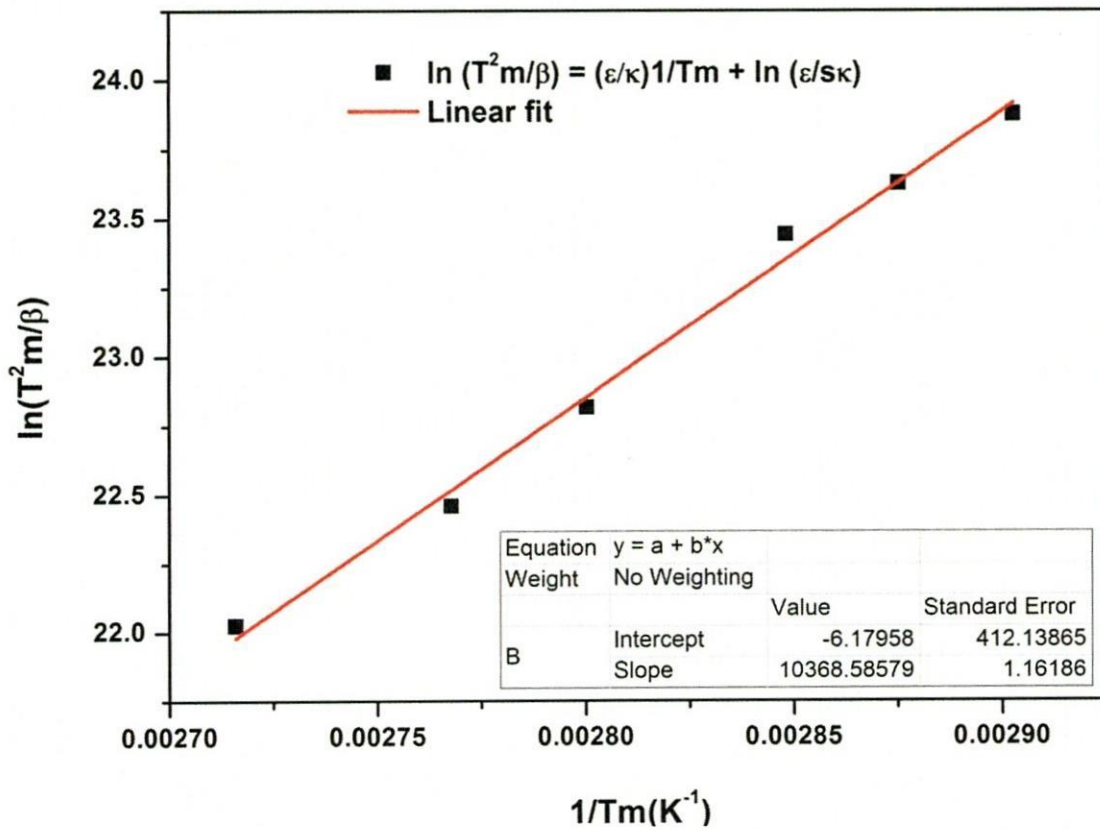


Figure 4.4: A plot of $\ln\left(\frac{T_{max}^2}{\beta}\right)$ versus $\frac{1}{T_{max}}$

Hence it is possible to obtain the trap depth or thermal activation energy (E) from the slope of the straight line. In this investigation, the frequency factor (s) is found to be $5 \times 10^6 \text{ s}^{-1}$ and the trap depth due to Dy^{3+} ion substitution is $0.89 \pm 0.0001 \text{ eV}$, which agrees with the theoretical value reported and shows a positive correlation between the trapping depth and the 4f-5d transition energy of Dy^{3+} [13,14,15].

The mechanism of electron trapping by rare earth ions can be explained using the model by Dorenbos [14]. The Eu^{2+} ($4f^7$) ground energy state is 3.2 eV below the bottom of the conduction band and the Dy^{2+} ($4f^{10}$) ground state is at about 0.9 eV below. On exposure to photons of sufficient energy from β -irradiation, the electron from Eu^{2+} is optically excited. When the material is thermally activated through the TL process, the 5d electron is excited to the conduction band forming Eu^{3+} . The electron is then trapped by Dy^{3+} to form Dy^{2+} [16]. The energy difference between the lowest 5d state and the bottom of the conduction band is 0.017 eV.

The model shows that the ground state of Dy^{2+} is located 0.9 eV below the bottom of the conduction band, which gives a value close to the trap depth of about 1 eV derived from TL

studies by Yamamoto and Matsuzawa [17] and Nag and Kutty [18]. The trapped electron is thermally released and recombines with Eu^{3+} yielding the 5d–4f emission of Eu^{2+} . Or in other words the Eu^{3+} ion releases a hole into the valence band reducing to the divalent Eu^{2+} state again becoming a source of electrons for the surrounding traps thus forming a cycle of continuous excitation. This explains the slow saturation and slow thermal release that brings about the persistent luminescence in phosphors.

4.3.3. Peak-shape method

This method known as “general order kinetics” was proposed by Chen in 1969 [9]. Based on determination of a few relevant parameters on a single glow-peak, it provides a way to avoiding the problem of the unknown order. The parameters necessary for use with the various expressions developed using the peak shape method include the peak maximum temperature T_{max} , the temperatures at half maximum TL intensity $T_1(\frac{1}{2}max)$ and $T_2(\frac{1}{2}max)$ at the low and high temperature side of the glow-peak respectively and half width parameters; $\omega = T_2(\frac{1}{2}max) - T_1(\frac{1}{2}max)$, $\delta = T_2(\frac{1}{2}max) - T_{max}$ and $\tau = T_{max} - T_1(\frac{1}{2}max)$.

According to this method, the kinetic order b of a single peak is easily obtained by means of the Halperin – Braner geometrical factor geometric/symmetry factor of the glow-peak [19, 8];

$$\mu_g = \frac{T_2(\frac{1}{2}max) - T_{max}}{T_2(\frac{1}{2}max) - T_1(\frac{1}{2}max)} = \frac{\delta}{\omega} \dots\dots\dots 4.2$$

Chen (1969) deduced the following expression to determine E_T using the peak shape method:

$$E = c_\alpha \left(\frac{kT_{max}^2}{\alpha} \right) - b_\alpha (2kT_{max}) \dots\dots\dots 4.3$$

Where α stands for τ , δ or ω [9]. The values of c_α and b_α depend on which of these three observed parameters of the peak is used. In the form given by Chen [8, 9], these are;

$$c_\omega = \frac{\omega I_m}{\beta n_0} \dots\dots\dots 4.4$$

$$c_\delta = \frac{\delta I_m}{\beta n_m} \dots\dots\dots 4.5$$

$$c_\tau = \frac{\tau I_m}{\beta(n_0 - n_m)} \dots\dots\dots 4.6$$

$$\text{with } n_m = \int_{t_m}^{\infty} I dt \dots\dots\dots 4.7$$

where I_m is the peak maximum intensity, n_m the high temperature half integral of the glow peak, t_m the time at peak maximum intensity and c_ω , c_δ and c_τ are quantities which describe the kinetic order. Chen [8, 9] evaluated the coefficients c_α and b_α for first and second order kinetics and used an interpolation – extrapolation method to evaluate the values for intermediate order kinetics. His final expressions are;

When τ is used in Eq.4.3;

$$c_{\tau} = 1.15 + 3.0(\mu_g - 0.42) \dots\dots\dots 4.8$$

$$b_{\tau} = 1.58 + 4.2(\mu_g - 0.42) \dots\dots\dots 4.9$$

When δ is used

$$c_{\delta} = 0.976 + 7.3(\mu_g - 0.42), b_{\delta} = 0 \dots\dots\dots 4.10$$

When ω is used

$$c_{\omega} = 2.52 + 10.2(\mu_g - 0.42), b_{\omega} = 1 \dots\dots\dots 4.11$$

Long after glow is influenced by concentration of the traps. Exposure to β -irradiation generates free electrons and hence the larger the amount of traps the more the number of free electrons captured leading to a longer afterglow. The values of different parameters calculated from the glow curves are presented in table 4.1. From table 4.1 and figure 4.5, it can be seen that the calculated values of activation energy lies between 0.49 and 0.55eV. For these glow curves the activation energy with maximum intensity (large trap concentration) using Chen method [20] is calculated to be 0.49 eV. It is well known that a suitable energy level within the host matrix plays a significant role for afterglow luminescence. Shallow traps (with a depth lower than around 0.4 eV [8]) are completely emptied at low temperatures, or the trapped electron can easily return to the excited state and do not actively contribute to luminescence processes at room temperature, thus resulting in short afterglow lifetime.

Table 4.1: Values of different parameters calculated from TL glow curves

Glow curve Temperature			Glow-peak shape parameters				TSL parameters				
$T_1(^{\circ}\text{C})$	$T_m(^{\circ}\text{C})$	$T_2(^{\circ}\text{C})$	τ	δ	ω	μ_g	E_{τ}	E_{ω}	E_{δ}	$E(\text{eV})$	$n_0(\text{cm}^{-3})$
62.91	94.9	125.34	31.99	30.44	62.43	0.48759	0.3749	0.536	0.56281	0.49124	6.65×10^3
64.34	93.75	123.39	29.41	29.64	59.05	0.50195	0.42834	0.59529	0.61538	0.54634	7.48×10^3
63.17	94.35	125.6	31.18	31.25	62.43	0.50056	0.39744	0.55894	0.58182	0.51273	7.78×10^3
64.34	95.23	125.08	30.89	29.85	60.74	0.49144	0.39661	0.56128	0.58597	0.51462	7.9×10^3
62.13	94.43	126.25	32.3	31.82	64.12	0.49626	0.37613	0.53483	0.56017	0.49038	8.43×10^3
Average $E(\text{eV})$										0.51 ± 0.02	

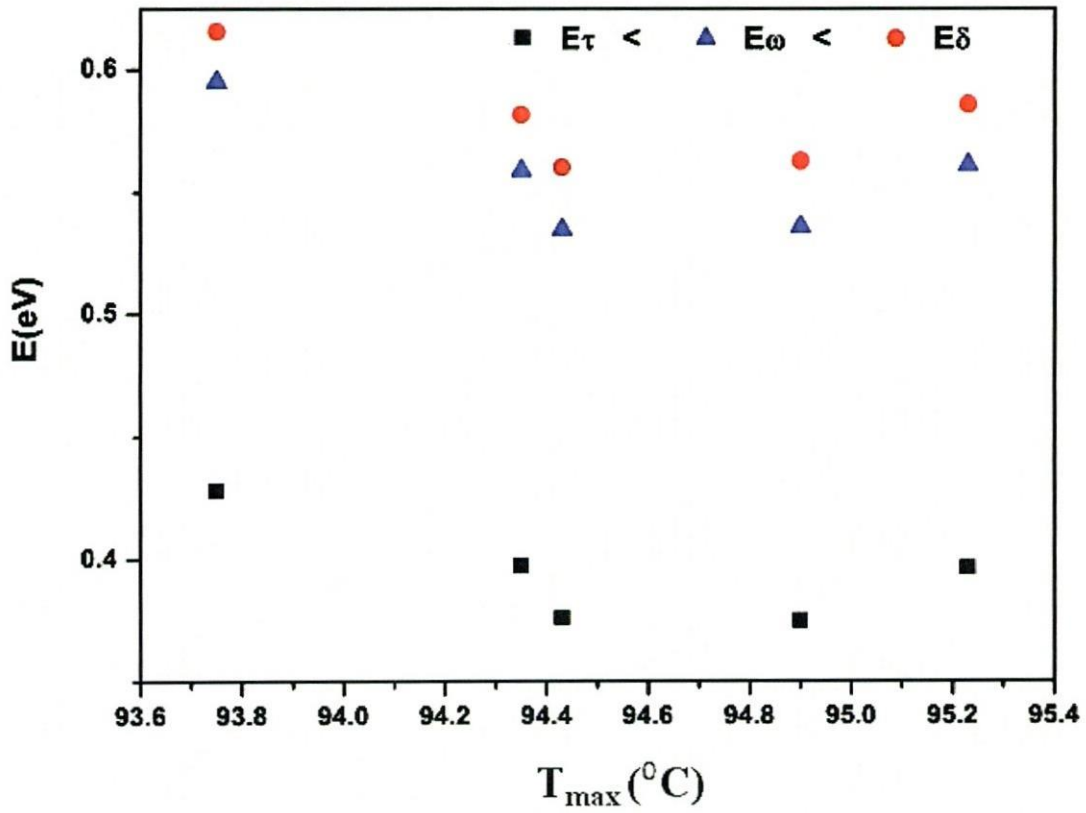


Figure 4.5: A plot of the activation energy E (eV) and $T_{\max}$ ($^{\circ}\text{C}$) for a series of partial heating measurements made on a sample irradiated to 215 Gy and measured at 1°Cs^{-1} .

On the other hand, if the energy level is too deep (very deep traps around 2 eV or deeper [14]), more energy is needed for the electron to return to the excited state level or the deep traps to be emptied than is available at room temperature hence the electron cannot return, and therefore cannot generate persistent luminescence resulting in a poor afterglow property. For persistent luminescence to occur at room temperature, the activation energy of the traps should be between these two limits, a trap depth ≈ 0.65 eV is considered to be optimal [21, 22]. However trap depths of materials with persistence luminescence have been estimated to spread over a wide range from $E(\text{eV}) \approx 0.5$ to ≈ 1.25 eV [23]. The shape factor μ_g , which ranges from 0.48 to 0.50, shows that the kinetics of the obtained glow curves for the as-prepared samples are of first order i.e. the charge gets untrapped very fast [24].

Conclusion

SrAl₂O₄:Eu²⁺, Dy³⁺ phosphor was synthesized using the solution - combustion method. Samples were heated from 30 to 150 or 200 °C at various heating rates and doses. In all cases, the total TL signal and glow curve peaks show a linear response and the degree of linearity increases with the energy of the incident *beta* - radiation and the temperature (T_{max}). At higher doses the intensity starts to saturate due to higher concentration of defects that generate non-radiative states within the band gap. The position of the peak temperature (T_{max}) shifts towards the higher temperature with increased radiation dosage levels. This might also be attributed to the filling of the trap centers. The peak TL intensity (I_{max}) of the glow curves exponentially decreased with an increase in heating rate while the peak temperatures (T_{max}) are seen to exponentially shift to the higher temperature side. The higher peak temperature the deeper the trap depth. The calculated values of activation energy lie between 0.49 and 0.55 eV. The shape factor (μ_g) shows that the kinetics of the obtained glow curves for the as-prepared samples are of first order.

References

- [1] S.W.S. McKeever, Thermoluminescence of Solids, Cambridge University Press, (1988).
- [2] B. Nameeta, D. P. Bisen, R. S. Kher and M. S. K. Khokhar, *Physics Procedia*, **2(2)** (2009) 431.
- [3] <http://uvminerals.org/fms/luminescence> [Accessed 12/10/2015]
- [4] A.J.J. Bos, *Rad. Meas.*, **41** (2007) 45.
- [5] S. Shionoya, W.M. Yen, Phosphors Handbook, CRC Press, USA, (1998) 95.
- [6] S. Basuna, G.F. Imbuschb, D.D. Jiac, W.M. Yenc, *J. Lumin.*, **104** (2003) 283.
- [7] R. Chen, Y. Kirsh, *Pergamon Press* (Oxford), **15** (1981) 167.
- [8] R. Chen, S.W.S. McKeever, *World Scientific*, (Singapore), (1997).
- [9] R. Chen, *J. Appl. Phys.*, **40** (1969) 570.
- [10] J.T. Randall, M.H.F. Wilkins, *P. Roy. Soc. Lond. A*, **184** (1945) 365.
- [11] L. Xingdong, Z. Minjuan, W. Renqin, J. Wuhan, *Univ. of Technology-Mater. Sci. Ed.*, **23** (2008) 654.
- [12] Y. Kojima, K. Aoyagi, T. Yasue, *J. Soc. Inorg. Mater. Japan*, **13** (2006) 228.
- [13] P. Dorenbos, *J. Electrochem. Soc.*, **7** (2005) 152.
- [14] E. Nakazawa, Y. Murazaki, and S. Saito, *J. Appl. Phys*, **100** (2006) 113113.
- [15] T. O. Arellano, R. Meléndrez, P.M. Montero, B. Castañeda, V. Chernov, W.M. Yen, F.M. Barboza, *J. Lumin.*, **128** (2008) 173.
- [16] A.J.J. Bos, R. M. V. Duijvenvoorde, E. V. Kolk, W. Drozdowski, P. Dorenbos, *J. Lumin.*, **131** (2011) 1465.
- [17] H. Yamamoto and T. Matsuzawa, *J. Lumin.*, **287** (1997) 72.
- [18] A. Nag and T. R. N. Kutty, *Mater. Res. Bull.*, **39** (2004) 331.
- [19] S. W. S McKeever, Thermoluminescence of Solids, Cambridge University Press, (1985).
- [20] K. V. Eeckhout, P. F. Smet, D. Poelman, *Materials*, **3** (2010) 2536.
- [21] T. Matsuzawa, Y. Aoki, N. Takeuchi, Y. Murayama, *J. Electrochem. Soc.*, **143** (1996) 2670.
- [22] R. Sakai, T. Katsumata, S. Komuro, T. Morikawa, *J. Lumin.*, **85** (1999) 149.
- [23] M. Mashangva, M. N. Singh, T.B. Singh, *Indian J. Pure & Applied Physics*, **49**, (2011) 583.
- [24] Chen R, *J. Electrochem. Soc.*, **116** (1969) 1254.

Chapter 5

Combustion synthesis, characterization and luminescence properties of barium aluminate phosphor

5.1. Introduction

Rare earth doped aluminates form a group of luminescence materials which exhibit high stability, brightness, and versatile industrial processing characteristics suitable for manufacture of lighting and display devices [1,2]. They exhibit high quantum efficiency in the visible region [3]. The Eu^{2+} doped solid state materials usually show strong broad band luminescence with a short decay time of the order of some tens of nanoseconds [4]. The very short decay time and strong intensity of the luminescence arise from the allowed states of the electronic transitions both in the excitation and emission. The luminescence is very strongly affected by changes in the structure of the host and can range from the ultraviolet to the red region of the electromagnetic spectrum. The high intensity emission of Eu^{2+} finds important industrial applications in, for example, the tricolor low pressure mercury fluorescence lamps.

The discovery of the plasma display panel (PDP) and light-emitting diode (LED) has contributed significantly to comprehensive studies for large-scale flat panel display and lighting devices [5]. Plasma display panels (PDPs), are gaining considerable popularity because of its obvious merits, such as a fast response, a wide viewing angle, large screen, low energy consumption and high scalability [6]. Eu^{2+} and Nd^{3+} -doped alkaline earth aluminate phosphors exhibit afterglow which is visible to the naked eye for longer duration after exposure to a fluorescent light or sunlight. The synthesis of oxide phosphors has been achieved by a variety of methods. The solution-combustion process is very simple, safe, energy saving and takes only a few minutes. The technique makes use of the heat energy from the redox exothermic reaction at a relatively low igniting temperature between metal nitrates and urea as fuel. In the present work, $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Nd}^{3+}$ materials were prepared with different Ba/Al molar ratios and constant Eu^{2+} and Nd^{3+} concentrations. The effects of this on the stability, homogeneity and structure as well as persistence luminescence were presented and discussed based on the analyses of the X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy

(SEM) and transmission electron microscopy (TEM) imaging as well as photoluminescence spectroscopy (PL) studies.

5.2. Experimental

6.2.1 Synthesis

$\text{BaAl}_2\text{O}_4\text{:Eu}^{2+}$, Nd^{3+} phosphors were synthesized using the solution-combustion method under atmospheric pressure without any post treatment. The starting raw materials used in the experiment included various proportions of analytical pure grade $\text{Ba}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Nd}(\text{NO}_3)_3$, and urea ($\text{CO}(\text{NH}_2)_2$). No flux was added. The precursors were prepared with different Ba/Al molar ratios of 0.1:1, 0.4:1, 0.7:1 and 1.4:1, respectively. The doping concentrations of both Eu^{2+} and Nd^{3+} were kept constant at 0.2 mol. %. A minimum amount of distilled water together with excess amount of urea was added and then thoroughly mixed at room temperature using a magnetic stirrer for 15 min without heating to obtain uniform aqueous solutions.

The solutions were introduced into a muffle furnace previously maintained at 500 °C. Dehydration occurred as the solution boiled and decomposed letting off large amounts of gases (CO_2 , NO_2 and NH_4). The mixture then frothed and swelled enormously into foam. Spontaneous ignition and smoldering occurred which gradually led to an explosion rupturing the foam with a flame that glows to incandescence producing white foamy and voluminous $\text{BaAl}_2\text{O}_4\text{:Eu}^{2+}$, Nd^{3+} . The foam was taken out of the muffle furnace, cooled then milled resulting in a dry, usually crystalline, fine white oxide powders of $\text{BaAl}_2\text{O}_4\text{:Eu}^{2+}$, Nd^{3+} . The whole combustion process took about 5 min. The powders were stored in glass sample bottles for characterization.

5.2.2 Characterization

The structure and phase purity of the phosphor samples was checked with a Bruker-AXS D8 Advance X-ray diffractometer (Bruker Corporation of Germany) operating at 40 kV and 4 mA using $\text{Cu K}\alpha=0.15406$ nm. The morphologies of the phosphor powders were obtained by using a Shimadzu Superscan SSX-550 SEM coupled with an energy dispersive X-ray spectrometer (EDS) for elemental composition. For analysis of molecular bonding, binding energy, chemical and valence state of the samples, XPS was done using a PHI 5000 Versa probe - scanning XPS microprobe. Absorption spectra were recorded using a Perkin Elmer Scan-Lambda 950 UV-Vis spectrophotometer. The PL excitation and emission spectra were measured at room temperature using a Cary Eclipse luminescence spectrometer (model LS-55) with a built-in 150 W xenon flash lamp as the excitation source and a grating to select a suitable excitation wavelength.

5.3. Results and Discussion

5.3.1 XRD analysis

Figure 5.1 shows the XRD pattern of different phases of BaAl_2O_4 along with the (hkl) values for the various peaks recorded from the $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Nd}^{3+}$ samples with varying Ba/Al concentrations. Non-stoichiometric Ba/Al molar ratio were selected in order to investigate how the different phases formed by a shortage or excess of Ba ions as compared to Al ions would affect the luminescence properties of the phosphors. The results of X-ray phase analysis of the as-prepared powders at 500 °C revealed that several crystalline phases are formed depending on the ratio of these main components of the host [7]. The patterns could separately be indexed to the various hexagonal systems of the BaAl_2O_4 and the lattice parameters were in agreement with the JCPDS data 072-0387 and 075-0707.

It is observed that the peaks for hexagonal BaAl_2O_4 with space group $P6_322$ began to appear distinctly producing the highest intensity for samples with Ba/Al molar ratio of 0.7:1. Impurity phases including Eu_2O_3 , Ba_3Al_5 , and $\text{Ba}_7\text{Al}_{10}$ could be identified. These impurities are attributed to the unreacted reagents that could be present in the as-prepared phosphor. Line broadening features are characteristics of samples exhibiting smaller particle size, indicating that the phosphor nanocrystallines can be prepared in a far low temperature (about 500 °C).

It is well known that broadening occurs in the diffraction rings as the particle size of the powders decreases. The average crystallite size deduced according to the Scherrer's equation using full-width at the half maximum (FWHM) data [8] was 70 nm.

The crystal structure of BaAl_2O_4 is depicted in figure 5.2(a) and (b). It belongs to the $P6_322$ space group and has a stuff tridymite (hexagonal) structure with lattice parameters $a = 0.5218$ nm and $c = 0.8781$ nm [9]. Usually it consists of two types of tetrahedral rings: trigonal and asymmetrical rings.

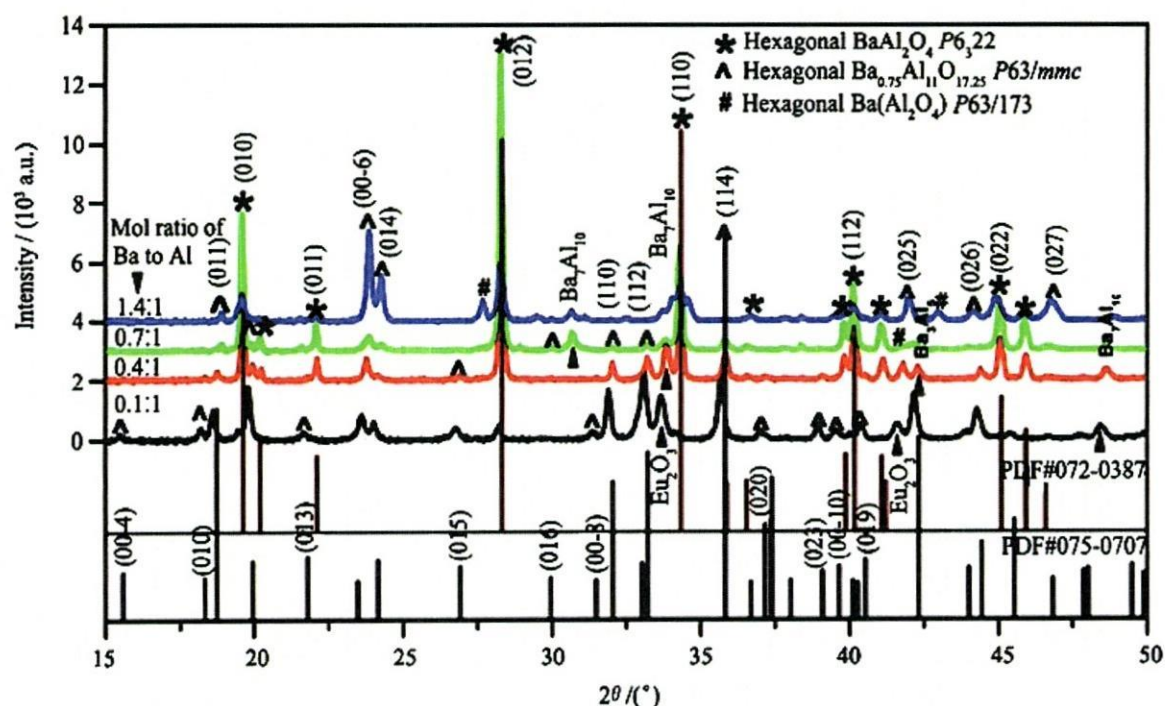


Figure 5.1: Effect of varying Ba:Al molar ratios on the XRD structure of the BaAl₂O₄:Eu²⁺,Nd³⁺ phosphor as compared with JCPDS # 72-0387 and 075-0707 of hexagonal BaAl₂O₄.

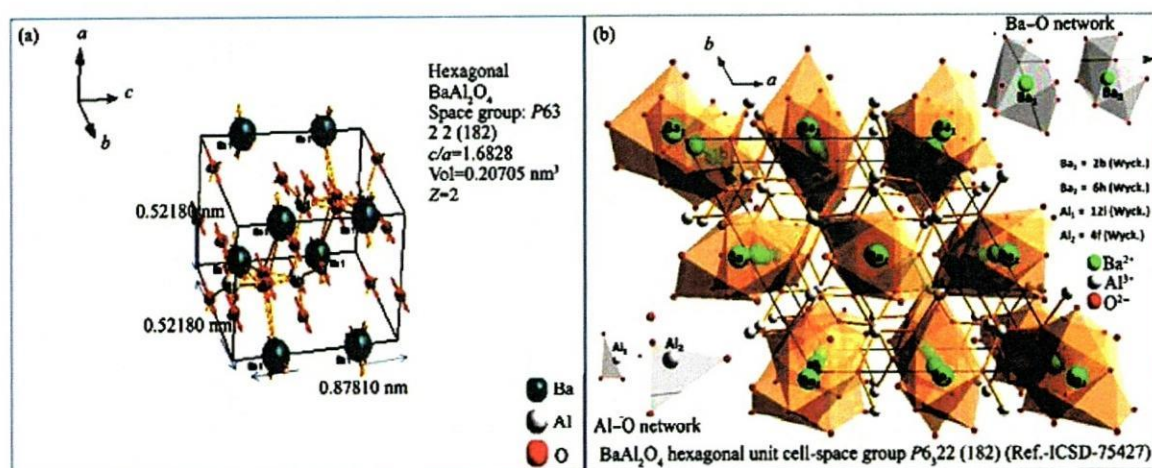


Figure 5.2: The hexagonal crystal structure of BaAl₂O₄ viewed along the (111) direction

The trigonal rings, comprising a quarter of the total number of rings, contain in their centre the Ba atoms. In the asymmetrical rings the Ba atoms are located at the general position (6c) site (figure 5.2(b)).

5.3.2 XPS analysis

Figure 5.3: (a), (b) and (c) shows the fitted XPS spectra of $\text{BaAl}_2\text{O}_4\text{:Eu}^{2+}, \text{Nd}^{3+}$ phosphor powder with a Ba:Al molar ratio of 0.1:1.

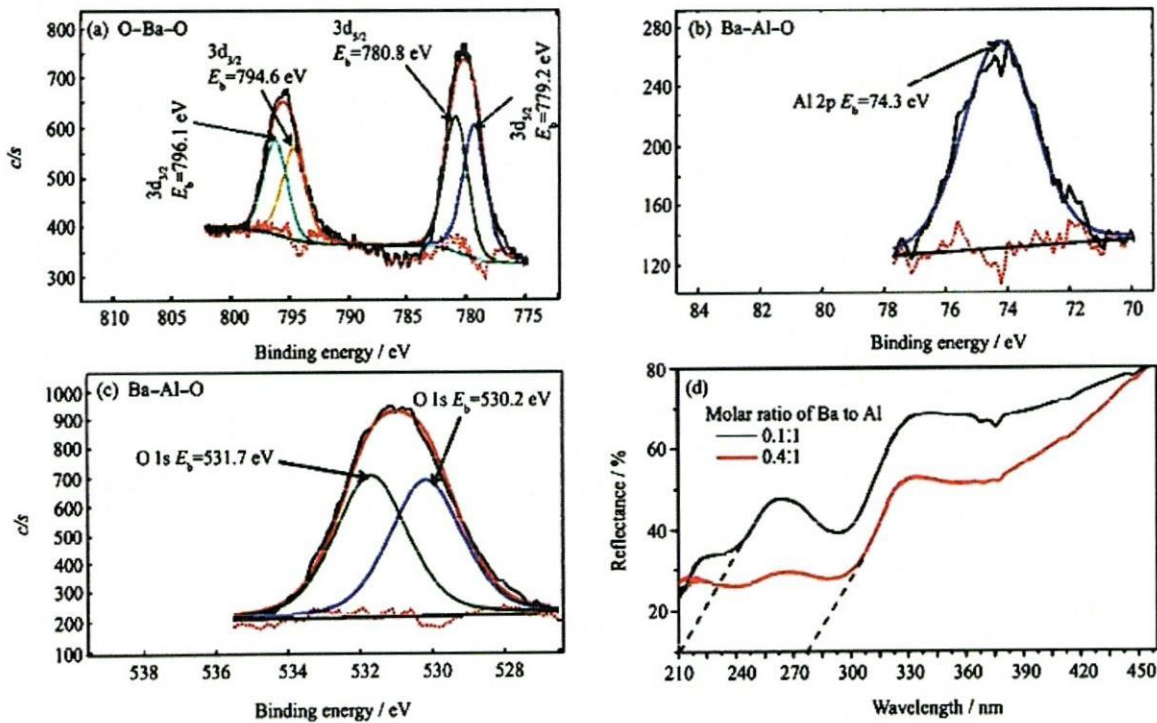


Figure 5.3: Fitted XPS graphs of $\text{BaAl}_2\text{O}_4\text{:Eu}^{2+}, \text{Nd}^{3+}$ sample with Ba/Al molar ratio of 0.1:1 (a)-(c) and UV reflectance spectra for Ba/Al molar ratio of 0.1:1 and 0.4:1, respectively (d)

From figure 5.3 (a) it can be seen that the 3d spectrum for Ba has two peaks of O–Ba–O bonds for the 3d_{5/2} as well as the 3d_{3/2} existing within the $\text{BaAl}_2\text{O}_4\text{:Eu}^{2+}, \text{Nd}^{3+}$ structure at 779.2, 780.8 and 794.6, 796.1 eV, respectively. These two peaks can be attributed to have emanated from the two Ba^{2+} sites of BaAl_2O_4 . A single peak depicted in figure 5.3 (b) presents the Al 2p spectrum with a typical Ba–Al–O bond at 74.3 eV. This could be characteristic of Al species in the AlO_4 tetrahedra [10]. Figure 5.3 (c) shows two fitted peaks of the 1s spectrum for O at 530.2 and 531.7 eV respectively which arise from the Ba–Al–O bonds within the BaAl_2O_4 matrix.

The binding energy (E_b) of O 1s in BaAl_2O_4 has been reported to be at 531.3 and 529.6 eV [10]. The $E_b = 531.3$ eV could be ascribed to the characteristics of O species in the surface hydroxyl (OH) groups from H_2O molecules absorbed by the BaAl_2O_4 material [11] as well. The optical property of a material revealed by its UV reflectance/absorption spectrum tells about the energy separation between the filled valence band and the empty conduction band i.e. the band gap. Optical excitation of electron across the band gap is strongly allowed, producing an abrupt

increase in absorption at the wavelength corresponding to the band gap energy. This feature in the optical spectrum is known as the optical absorption edge [12].

Figure 5.3 (d) presents the diffuse reflectance spectra of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Nd}^{3+}$ samples with Ba/Al molar ratio of 0.1:1 and 0.4:1. It reveals that reflectance decreases with an increase in the Ba:Al molar ratio. The band gaps (E_g) corresponding to the absorption edges of $\lambda=210$ nm and $\lambda=280$ nm are found to be 5.9 and 4.43 eV for samples with Ba/Al molar ratio of 0.1:1 and 0.4:1, respectively, which further reveals that as the Ba:Al molar ratio increased the band gap decreased. Such changes in the host matrix leading to the shift of the band gap width also caused changes in the energy of the Eu^{2+} ion in the transition process [13].

5.3.3 SEM, TEM and EDS analysis

Figure 5.4 shows the micrographs of the as-prepared $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Nd}^{3+}$ material. Figures. 4 (a) and (b) are the representative SEM micrographs taken for Ba/Al molar ratio of 0.4:1 and 0.7:1, respectively. The nanostructures crystallized to form fine, regular hexagonal platelets exhibiting smooth surface and well-developed faces with size around 70 nm calculated from the Scherrer method. The endothermic reactions during the solution-combustion process are characterised by decomposition and removal of nitric oxides and significantly vary depending on the precursor ingredients and the ratio of metal nitrate to urea [14]. Consequently, the surfaces of the samples reveal pores and voids, which may be attributed to these evolved gases during combustion. The presence of hexagonal platelets with well-developed faces seem to dominate the morphology of the samples with Ba/Al molar ratio of 0.7:1 (figure 5.4(b)). Phosphors with regular morphology are well known to improve the packing density, slurry properties and improve the luminescence of phosphor [15]. This explains the high luminescence intensity obtained by the sample with Ba/Al molar ratio of 0.7:1 in the next section. Figure 5.4(c) presents the TEM image taken for Ba/Al molar ratio of 0.1:1. It can be seen that the $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Nd}^{3+}$ nanocrystals exhibit an ideal spherical morphology which is more beneficial at increasing packing densities and brightness than irregularly shaped particles [16]. Furthermore, it reveals that the synthesized grain sizes calculated using Scherrer's formula are in the same range of 45–74 nm of the TEM results. The EDS spectrum of figure 5.4(d) confirms the elemental composition of the phosphors. However the very low concentration of the rare earth dopants was the reason for their tiny peaks in the EDS spectra.

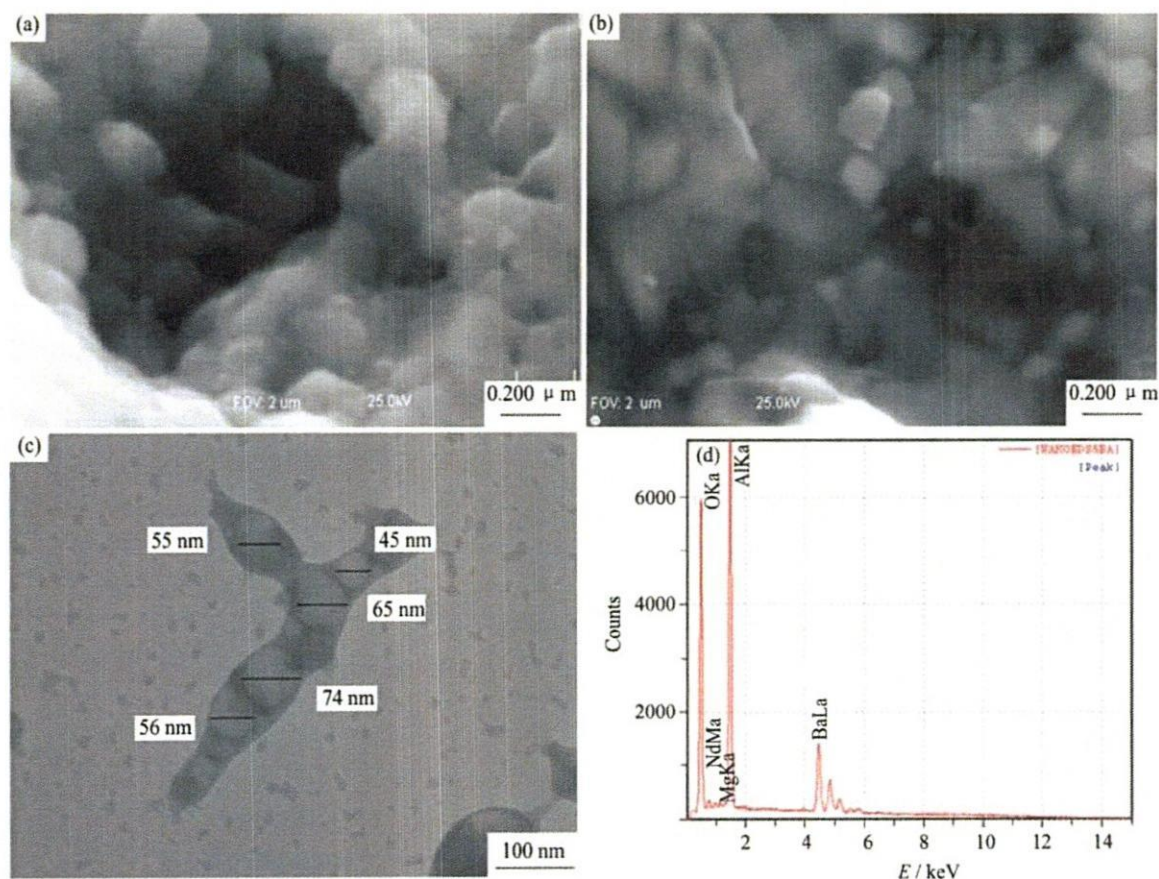


Figure 5.4: SEM images of samples with Ba/Al molar ratios of 0.4:1 and 0.7:1 at 2 μm FOV (a) and (b), TEM micrograph for the 0.1:1 Ba/Al molar ratio on a 100 nm scale bar (c) and the EDS spectra of the $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ phosphor (d).

5.3.4 PL analysis

Figure 5.5 shows the effect of varying the Ba:Al molar ratios on the luminescence characteristics of the $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ phosphor. From figure 5.5(a) there is an excitation peak at around 333 nm in the excitation spectrum ($\lambda_{\text{em}}=500$ nm) which is in conformity with the absorption of the host BaAl_2O_4 as observed in the absorption results earlier in this study. Two maxima curve fits, peaking at 490 and 525 nm, were observed in the luminescence spectra of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ (Figure 5.5(c)) which arise from the two emissions of Eu^{2+} in the two Ba^{2+} sites within in the BaAl_2O_4 structure. These are due to the transitions from the lowest 2D level of the excited $4f^65d^1$ configuration to the ground $^8S_{7/2}$ level of the $4f^7$ configuration of the Eu^{2+} ion [17].

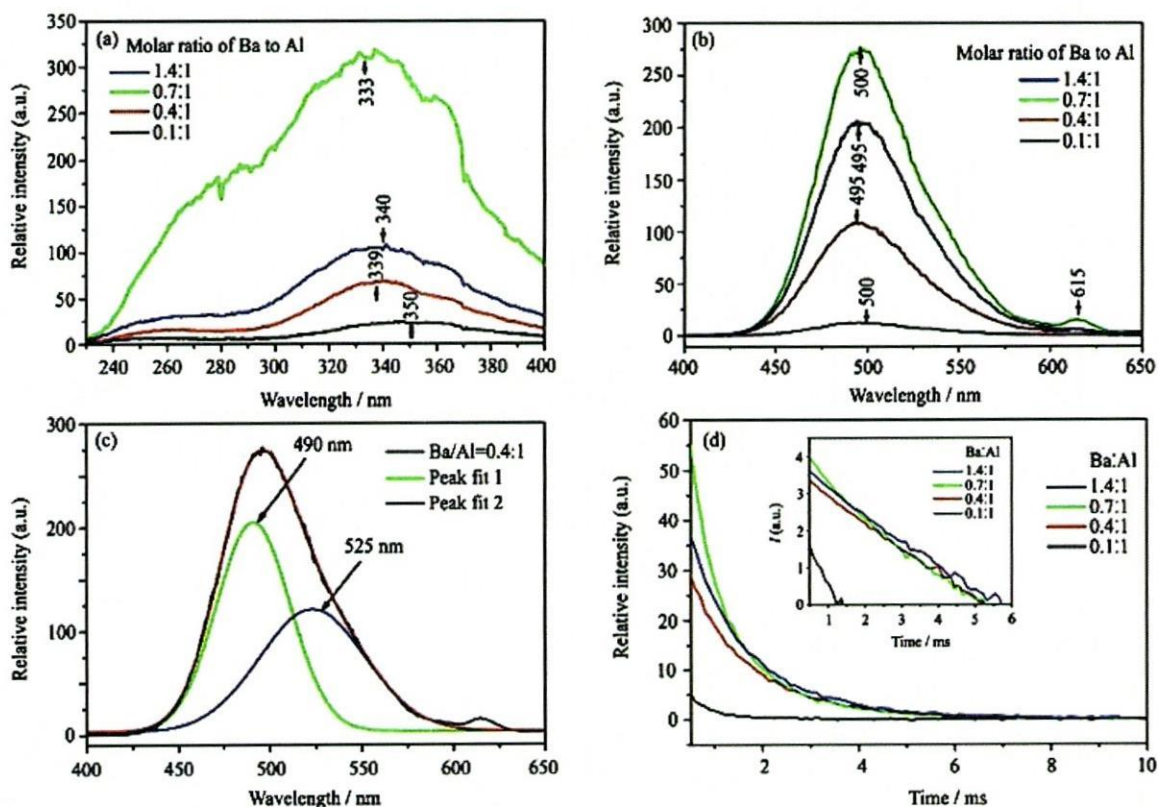


Figure 5.5: Effect of varying Ba/Al molar ratios on the excitation characteristics (a) and the emission spectra (b) of the $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ phosphor, two maxima curve fits peaking at 490 and 525 nm (c), and decay curves of the $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ phosphor (d) (The inset graph shows the natural log of intensity $\ln(I)$ versus time (t) plot for the samples).

The emission intensity at 490 nm was observed to be higher relative to the one at 525 nm (Fig. 5(c)) indicating that the Eu^{2+} ions preferred occupying one of the Ba^{2+} sites. Both Ba^{2+} sites are coordinated with nine oxygen (O) ions and the sites are similar in average size ($d(\text{Ba}-\text{O})_{\text{ave}} = 0.286$ and 0.287 nm). However, the lower symmetry site also has shorter Ba–O distances (0.269 nm) corresponding to those typical of $\text{Eu}^{2+}-\text{O}$ (0.268 nm) [18]. According to the crystal structure, the first Ba^{2+} site (2a) has the multiplicity of two and a site symmetry of $c3$ while the second one (6c) has six and $c1$. It would therefore seem reasonable that this 6c site is filled preferentially.

This is also supported by the higher PL intensity as a result of contribution from six instead of two Eu^{2+} ions [17]. Slight shifts in peak positions can be observed in both the excitation and emission spectra (figure 5(a) and (b)) which may be ascribed to structure changes caused by the variation in the quantity of Ba ions in the host. The changes in the structure shifts the peak position of Eu^{2+} ions since the $4f^6 5d^1 \rightarrow 4f^7$ of Eu^{2+} is parity allowed transition in addition to the oscillation strength which is strongly affected by the crystal field due to the extended nature of

the 5d wave function[19]. The narrow emissions in red region at 615 nm arise from the f-f transitions of the remnant unreduced Eu³⁺ ions.

From the decay curves of figure 5.5(d), the effect of the increase in number of Ba ions is very clear. It can be seen that the Ba/Al=0.7:1 gives higher luminescence intensity in agreement with both the excitation and emission spectra. The inset graph of figure 5.5(d) shows the natural log of intensity ln(I) versus time (t) plot giving a number of straight lines. The decay curves were fitted using the second order exponential decay equation [20]:

$$I = A_1 \exp\left[\frac{-t}{\tau_1}\right] + A_2 \exp\left[\frac{-t}{\tau_2}\right]..... 5.1$$

where I is the phosphorescence intensity, A₁ and A₂ are constants, t is the time after switching off the excitation source, and τ₁ and τ₂ are decay times for the exponential components representing the decay rate for the fast and slow exponential decay components, respectively. The second order exponential decay fit may be attributed to a number of possibilities; (i) variations in the concentration of dopants which arise from their non-uniform distribution in the host matrix, (ii) the probability of non-radiative decays for lanthanide ions at or near the surface could be different from those at larger depths of the particles and (iii) energy transfer from donor to activators [21,22]. We consider parameters with the lowest and highest intensity shown in the inset of figure 5(d) since the parameters in between are too close to each other that accuracy of results could not be guaranteed.

Table 5.1 shows decay times for the fitted curves of all the samples. It shows that the initial luminescence intensity and the decay time of phosphors are greatly affected with the increase in the Ba/Al molar ratios. The result of sample with Ba:Al molar ratio of 0.7:1 shows good agreement with the emission spectrum within the range of experimental errors. The long decay time and strong intensity of the luminescence is due to the allowed nature of the electronic inter configurational transitions both in the excitation and emission which makes this material suitable for plasma display panel PDP applications.

Table 5.1: Decay times for the fitted curves of all the Ba:Al molar ratios

Ba:Al molar ratio	0.1:1	0.4:1	0.7:1	1.4:1
Fast(τ ₁)	0.84±0.15	1.54±0.02	0.46±0.008	0.73±0.04
Slow (τ ₂)	2.8±0.05	0.55±0.04	1.42±0.02	1.61±0.03

5.4 Conclusion

Blue-green emitting $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Nd}^{3+}$ phosphor was synthesised by a solution- combustion method. The influences of the varying quantity of Ba on the structural and luminescent properties of the phosphor were studied. SEM results indicated that the nanostructures crystallized to form fine, regular hexagonal platelets exhibiting smooth surface and well-developed faces. XRD analysis revealed several crystalline phases formed depending on the ratio of the main components (Ba/Al) of the host. XPS results showed that the 3d spectrum for Ba had two peaks of O–Ba–O bonds for $^3d_{3/2}$ and $^3d_{5/2}$ existing within the $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Nd}^{3+}$. The absorption spectra showed the absorption edge at $\lambda=210$ nm and $\lambda=280$ nm for which the corresponding band gaps (E_g) were 5.9 and 4.43 eV respectively. The long decay time and strong luminescence intensity of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Nd}^{3+}$ makes it suitable for PDP applications.

References

- [1] T. Justel, J. Krupa, D. Wiechert, *J. Lumin.*, **93** (2001) 179.
- [2] L. Y. Zhou, J. L. Huang, L. H. Yi, M. L. Gong, J. X. Shi, *J. Rare Earths*, **27** (2009) 54.
- [3] F. C. Palilla, A. K. Levine, M. R. Tomkus, *J. Electrochem. Soc.*, **115** (1968) 642.
- [4] G. Blasse, B.C. Grabmaier, *Berlin: Springer Verlag*, 1994. 232.
- [5] T. Justel, H. Nikol, *Adv. Mater.*, **12** (2000) 527.
- [6] C. H. Kim, H. S. Bae, C. H. Pyun, G. H. Hong, *J. Korean Chem. Soc.*, **5(42)** (1998) 588.
- [7] S. Kimura, E. Bannai, I. Shindo, *Mater. Res. Bull.*, **17(2)**, (1982) 209.
- [8] B. D. Cullity, *MA: Addison-Wesley*, (1997) 102.
- [9] D. Jia, X. Wang, E. Van der Kolk, W. M. Yen, *Opt. Commun.*, **204** (2002) 247.
- [10] L. Zhang, L. Wang, Y. Zhu, *Adv. Func. Mater.*, **17** (2007) 3781.
- [11] M. A. Lephoto, O. M. Ntwaeaborwa, H. C. Swart, J. R. Botha, B. M. Mothudi, *Physica B*, **407(10)** (2012) 1603.
- [12] M. Ziauddin, N. Brahme, D. P. Bisen, R. S. Kher, *Lumin. Appl.*, **3(1)** (2013) 76.
- [13] Z. Ding, Z. N. Yu, D. P. Zhang, W. Xue, W. Y. Wang, *J. Rare Earths*, **27** (2009) 398.
- [14] P. D. Sarkisov, N. V. Popovich, A. G. Zhelnin, *Glass Ceram.*, **60** (2003) 309.
- [15] X. M. Teng, W. D. Zhang, Y. S. Hu, C. L. Zhao, H. Q. He, X. W. Huang, *J. Alloys Compd.*, **458** (2008) 446.
- [16] B. S. Jeon, G. Y. Hong, Y. K. Yoo, J. S. Yo, *J. Electrochem. Soc.*, **148** (2001) 128.
- [17] R. Stefani, L. C. V. Rodrigues, C. A. A. Carvalho, M. C. F. Felinto, H. .F. Brito, M. Lastusaari, J. Hölsä, *Opt. Mater.*, **31** (2009) 1815.
- [18] R. D. Shannon, *Acta Crystallogr. A*, **32** (1976) 751.
- [19] Q. H. Zeng, H. Tanno, K. Egoshi, N. Tanamachi, S. X. Zhang, *Appl. Phys. Lett.*, **88** (2006) 051906.
- [20] R. Sakai, T. Katsumata, S. Komuro, T. Morikawa, *J. Lumin.*, **85** (1999) 149.

- [21] J. W. Stouwdam, F.C. J. M. van Veggel, *Nano Lett.*, **2** (2002) 733.
- [22] N. S. Singh, R. S. Ningthoujam, N. Yaiphaba, R. K. Vasta, S. D. Singh, *Appl. Phys.*, **105** (2009) 064303.

Chapter 6

Characterization of cerium doped yttrium gadolinium aluminate garnet $(Y,Gd)_3Al_5O_{12}:Ce^{3+}$ phosphor thin films fabricated by pulsed laser deposition

6.1. Introduction

Yttrium aluminium garnet (YAG) has proved to be an excellent host material compatible with lanthanides and most trivalent rare earth dopants. YAG are mostly applied in solid state lasers especially the white light emitting diodes (LEDs) by incorporating them with suitable rare earth dopants. YAG activated by trivalent Cerium (Ce^{3+}) has excellent chemical and thermal stability and is also well known for good scintillators [1]. The optical band gap energy for YAG bulk powder is in the order of 6.6 eV comprising of filled O_2 2p orbitals in the valence band and empty 4d orbitals [2].

Yttrium-gadolinium aluminium gallium garnet $(Y,Gd)_3Al_5O_{12}:Ce^{3+}$ is a modified form of $Y_3Al_5O_{12}:Ce^{3+}$ where Ce^{3+} and Gd^{3+} are incorporated into the $Y_3Al_5O_{12}$ lattice such that Gd^{3+} substitutes Y^{3+} in the system $(Y_x Gd_{1-x})_3Al_5O_{12}:Ce^{3+}$. Since the ionic radius of Gd^{3+} is larger than that of Y^{3+} replacing Y^{3+} with Gd^{3+} results in lattice expansion. This way depending on the concentration of Gd^{3+} the host matrix structure can be modified in order to blue-shift or red-shift the emission from the Ce^{3+} . $(Y,Gd)_3Al_5O_{12}:Ce^{3+}$ can efficiently absorb a wide range of excitation wavelengths from ultra-violet (UV) to visible light and it can give out a broad band emission in the spectral range of 510 nm to over 600 nm [3] which makes it suitable for white LED applications. This color shift can be attributed to the fact that the characteristic broad yellow emission band from the $5d^1 - 4f^1$ transitions of Ce^{3+} is highly sensitive to changes in the chemical environment of the host which induces crystal-field effect in the lowest $5d^1$ orbital [4].

Several methods have been used to grow thin films such as Physical Vapour Deposition (PVD) and/or Chemical Vapour Deposition (CVD) [5], Chemical Bath Deposition [6], rf magnetron sputtering [7] pulsed laser deposition (PLD) [8] and epoxide-catalyzed sol-gel methods [9]. However PLD has several advantages over other techniques such as the homogeneous stoichiometric evaporation of the ablated material on to the substrate [5] and good quality thin films can be obtained at low temperatures [10] by varying parameters such as substrate distance, atmosphere and substrate temperature among others. These parameters affect the thickness,

roughness and overall quality of the obtained films which in turn influence the structure and photoluminescence (PL) properties of the $(Y,Gd)_3Al_5O_{12}:Ce^{3+}$ phosphor.

In this study thin films of $(Y,Gd)_3Al_5O_{12}:Ce^{3+}$ were prepared using PLD. The effect of different annealing temperatures on the structure and photoluminescent (PL) properties of the $(Y,Gd)_3Al_5O_{12}:Ce^{3+}$ thin films were investigated.

6.2. Experimental

A Commercial yellow $(Y,Gd)_3Al_5O_{12}:Ce^{3+}$ powder obtained from Phosphor Technology (UK) was pressed into a pellet and used as a target for laser deposition after initial characterization. The pellet was then heated at 200 °C for 2 hrs in a furnace to expel moisture that may be present and make it hard and strong for use as a target for laser ablation. The target was then loaded on to a rotatable carousel inside a PLD chamber. The carousel raster and rotates the target to prevent constant ablation by the laser beam from the same spot on the target.

Silicon (100) wafers of approximately 1 cm² were used as substrates. The wafers were first cleaned in an ultrasonic bath of acetone, ethanol and distilled water in that sequence then blow-dried with clean dry N₂ gas and placed on a fixed substrate holder in the PLD chamber perpendicular to the target at a fixed distance of 4.5 cm from the target. The chamber was then pumped down to vacuum of about 3.0x10⁻⁶ mbar. The target was ablated using a 266 nm Nd:YAG nanosecond (ns) pulsed laser with energy and frequency fixed at 45mJ/pulse (fluence of 0.2 Jcm⁻²) and 10 Hz respectively.

The ablation of the $(Y,Gd)_3Al_5O_{12}:Ce^{3+}$ target was carried out in the PLD chamber with a vacuum pressure of 10⁻⁶ mbar at constant substrate temperature of 200 °C. To investigate the effect of annealing, the as-deposited films were first characterized and then post-annealed in air for 60 minutes at 400 °C, 800 °C and 1000 °C in an XD-1200 NT tube furnace. The room temperature PL excitation and emission fluorescence spectra were recorded using an F-7000 FL Spectrophotometer at scan speed of 60 nm/min at 400 PMT voltage and excitation and emission monochromator slit widths of 5 nm. X-Ray Diffraction (XRD) continuous scans were recorded using a Bruker-AXS D8 Advance X-ray diffractometer operating at 40 kV and 4 mA using Cu Ka = 1.5406 nm from 15° to 65° (2θ), with a scan rate of 0.39° (2θ)/min and step scans with a step size of 0.02° (2θ).

6.3. Results and Discussion

6.3.1. Structure

XRD patterns of the $(Y,Gd)_3Al_5O_{12}:Ce^{3+}$ phosphor powder and thin films that were post-calcined at 400 °C, 800 °C and 1000 °C are shown in figure 6.1(a). Except for impurity peaks the rest fitted well with the powder and the JCPDS card number 072-1315 for the cubic $Y_3Al_5O_{12}$ of space group Ia-3d(230), cell ratios a/b=1.0000 b/c=1.0000 c/a=1.0000 and cell parameters a=12.0160Å. increased FWHM is an indication of peak broadening [11]. From the figure it was observed that XRD peak broadening occurred with an increase in the annealing temperature up to around 700 °C (estimated from the smoothed curve) and then narrowed down as the temperature was increased to 1000 °C. This is also displayed on figure 6.2(a) which shows the comparison of FWHM with annealing temperature.

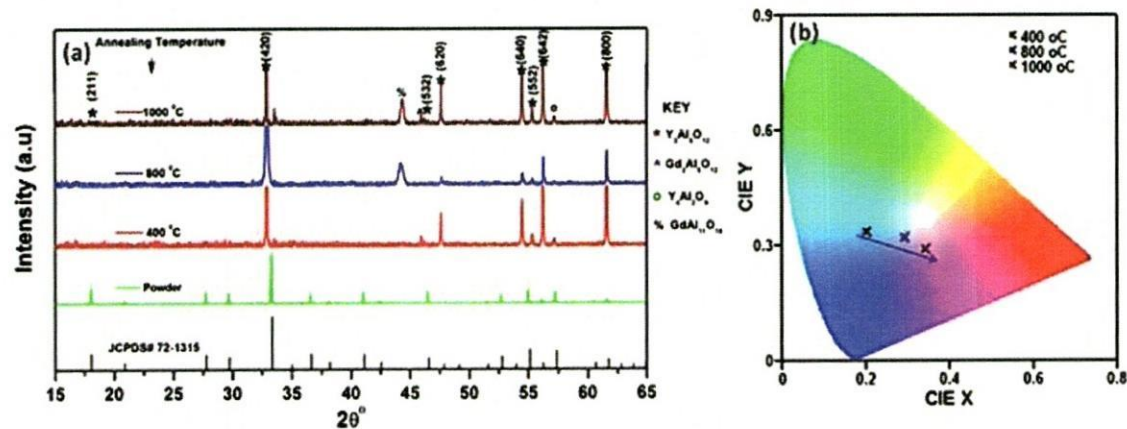


Figure 6.1: (a) XRD patterns of the $(Y,Gd)_3Al_5O_{12}:Ce^{3+}$ phosphor powder and thin films that were deposited in vacuum at 300 °C for 10 minutes and annealed at 400 °C, 800 °C and 1000 °C respectively and (b): CIE color chromaticity as a function of annealing temperature.

The average crystallite sizes calculated for the (420) direction were obtained using Scherrer's equation

$$D = \frac{\kappa \lambda}{\omega \cos \theta} \dots \dots \dots 6.1$$

where D is the mean particle size, κ is a geometric factor, λ is the X-ray wavelength and ω is Full Width at Half Maximum (FWHM).

Figure 6. 2 (a) and (b) also shows how the crystallite size varied with annealing temperature. The crystallite size reduced as the temperature increased up to around 700 °C suggesting improved crystallinity and growth [11] but as annealing temperature increased above 700 °C, the sample was gradually losing crystallinity which could be attributed to phase change that may have introduced impurities. As was also reported by Deng et al (2006) that $Y_3Al_5O_{12}: Gd$ thin films deposited at 700 °C were amorphous, supports this fact [7].

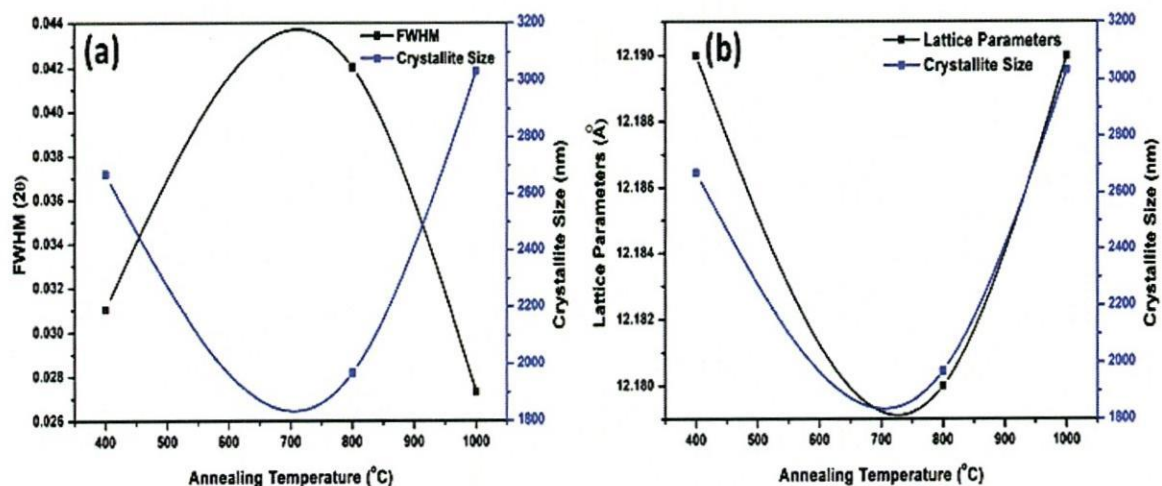


Figure 6.2(a) and (b): FWHM, Crystallite size and Lattice parameter as a function of annealing temperature.

It was also reported elsewhere that the phases; $Y_3Al_5O_{12}$ (cubic) and $YAlO_3$ (perovskite) were stable between room temperature and their melting points of 1970 and 1870 °C respectively but $Y_4Al_2O_9$ was unstable below 1000 °C [12]. Yousif et al (2013) showed that new phases were formed after annealing the $Y_3(Al,Ga)_5O_{12}:Tb^{3+}$ films at temperatures greater than 1073 K [8].

From figure 6.2(b) we observed that the lattice parameters are also influenced by the annealing temperature in a similar manner. It was observed to decrease with increasing temperature up to around 700 °C.

It was also observed that diffraction peaks in the directions; (420), (552), (640) and (642) shift toward smaller angles compared to those of the $(Y-Gd)_3Al_5O_{12}:Ce^{3+}$ commercial powder and the JCPDS card #072-1315 which could be due to the impurities phases; $Gd_3Al_5O_{12}$, $Y_4Al_2O_9$ and $GdAl_{11}O_{18}$ that were formed as the temperature was increased. It has been reported that the phases YAM ($Y_4Al_2O_9$), YAP ($YAlO_3$) and YAG ($Y_3Al_5O_{12}$) are often present in the $Y_2O_3-Al_2O_3$ system even if YAG is prepared stoichiometrically [13]. Therefore, this shift could be due to lattice expansion caused by differences in ionic radius when $Y(r = 0.104 \text{ nm})$ is substituted by $Gd(r = 0.108 \text{ nm})$ from the impurities phases [14] formed during the ablation process.

The crystallization temperature of the samples prepared by solid-state reaction (>1600 °C) is quite higher than the highest annealing temperature of 1000 °C in our experiment. But, during laser ablation, the temperature within the irradiated target volume rises rapidly exceeding the melting/boiling points of the target composition leading to explosive boiling because the laser heating rate significantly exceeds that of thermal diffusion and radiative losses [15].

6.3.2 Photoluminescence

Figures 6.3(a) and (b) show the PL excitation and emission spectra recorded from the $(Y,Gd)_3Al_5O_{12}:Ce^{3+}$ as-prepared powder and thin films annealed at 400 °C, 800 °C and 1000 °C. The PL emission spectra from the powder sample with a maximum at 546 nm is a broad band ranging from 450 nm to 650 nm when excited with 337 nm UV due to the 4f-5d electronic transition of Ce^{3+} attributed to the de-localization of electrons from the lowest 5d level to the crystal field split $4f(^2F_{5/2} / ^2F_{7/2})$ levels of Ce^{3+} .

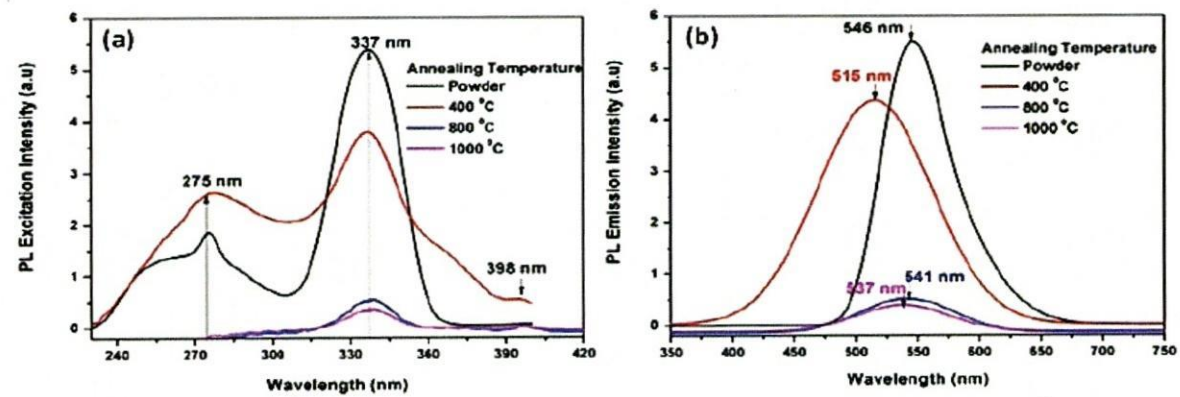


Figure 6.3 (a) and (b): Excitation and emission spectra of the $(Y,Gd)_3Al_5O_{12}:Ce^{3+}$ phosphor powder and thin films that were deposited in vacuum at 200 °C for 10 minutes and annealed at 400 °C, 800 °C and 1000 °C, respectively.

The normalized PL spectra for the annealed samples reveal changes in the peak positions and intensities relative to that of the powder sample. The PL intensity of the samples increased as the annealing temperature was increased from 400 °C to around 700 °C and then decreased with continued increase in the annealing temperature as shown in figure 6.4 (a). Such observation was reported by Yousif et al (2013) who observed that intensity ratio of I_{490nm}/I_{544nm} and I_{625nm}/I_{544nm} for $Y_3(Al,Ga)_5O_{12}:Tb^{3+}$ phosphor, gradually decreased when the annealing temperature was increased from 1073 K (800 °C) to 1473 K (1200 °C) [8]. This can be attributed to stress and cracking that led to the diffusion of Si film at higher temperatures [16]. Also it can be due to the impurity phases, $Gd_3Al_5O_{12}$ and $GdAl_{11}O_{18}$ that are higher in Gd concentration since it is well known that for a phosphor to exhibit the required properties, purity is very important. The PL intensities of the films are generally low in all cases compared to those of the powder of the same chemical composition due to total internal reflection in thin films [17]. However thin films have advantages over the powders in that they possess better thermal stability, better adhesion to the substrate, higher lateral resolution and less out gassing in device applications [8,18]. As

shown in figure 6.3(b) the centers of the emission bands red-shift from 515 to 541 nm as the annealing temperature increased. This red-shift can be explained by an increase in the crystal field effect when the Y^{3+} vacancies are occupied by the larger Gd^{3+} . Since the ionic size of Gd^{3+} is larger than that of Y^{3+} it results in lattice expansion confirmed by the shifting of XRD peaks towards the smaller angles, which correlates with the red-shift of Ce^{3+} emission. The variation of the lowest crystal-field energy level of the 5d1 state is strongly influenced by the electrostatic field in the surrounding host lattice which in turn depends on the crystalline structure of the host $(Y,Gd)_3Al_5O_{12}$ lattice [3].

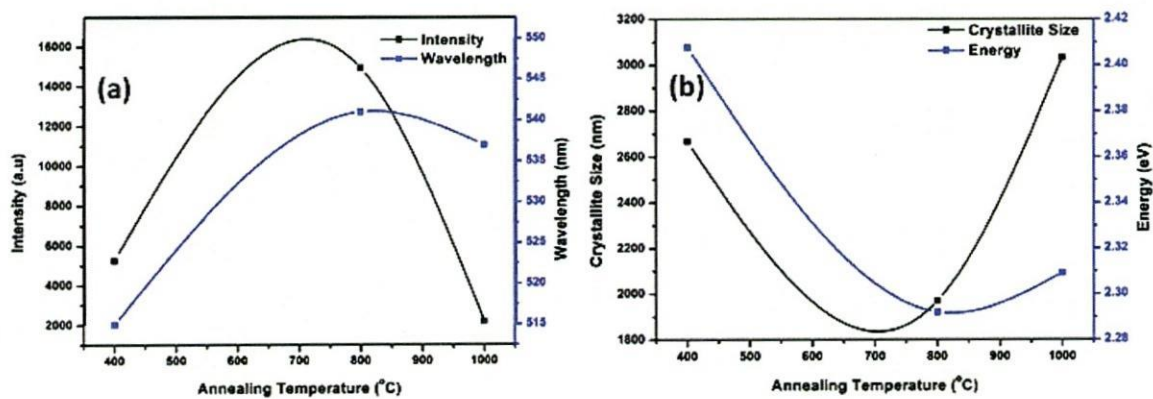


Figure 6.4: (a) PL intensity (a.u), Peak wavelength (nm) and (b) Peak Wavelength and band gap energy as a function of annealing temperature

The CIE chromaticity co-ordinates of PL spectra of all the samples compared with the powder are shown in figure 6.1(b). It is clear that as the annealing temperature increases the co-ordinates shift to red as pointed out by the arrow. This is also supported by the PL spectra wavelength shifts in figure 6.3(b).

Figure 6.4(a) also shows how the PL wavelength peak positions vary as a function of annealing temperature. The wavelength peaks slightly shifted to higher wavelengths (red-shift) from 515 to 541 nm as the annealing temperature was increased from 400 – 800 °C and then blue-shifts to lower wavelengths at temperatures above 800 °C. The optical band gap calculated with respect to the PL peak positions shifted to a lower energy from 2.41 - 2.29 eV with increasing annealing temperature from 400 - 800 °C and then to higher energy 2.29 - 2.31 eV above 800 °C as shown in figure 6.4(b). These changes have been attributed to the morphological dependent properties of the energy band gap [19]. The band gap of the thin film nanophosphors was calculated to be ~2.34 eV, which is generally red shifted in comparison to the band gap (~6.6 eV) of its bulk counterpart. The blue shift in band gap is a clear signature of nanostructure formation and may be attributed to the quantum size effect [20].

Conclusion

In this study thin films of $(Y,Gd)_3Al_5O_{12}:Ce^{3+}$ were prepared using the PLD technique. The effect of varied annealing temperature on the structure and PL properties of the $(Y,Gd)_3Al_5O_{12}:Ce^{3+}$ thin films were investigated. It was found that as the annealing temperature increase broadening of the XRD peaks occurs. Since the ionic size of Gd^{3+} is larger than that of Y^{3+} substitution of Y^{3+} with Gd^{3+} leads to lattice expansion confirmed by the shifting of the XRD peaks towards the lower angles which in turn cause slight shifts in the wavelength of the PL spectra toward red with respect to the annealing temperature which is probably due to a change in the crystal field caused by lattice expansion.

References

- [1] A. Potdevin, G. Chadeyron, V. Briois and R. Mahiou, *Mater. Chem. Phys.*, **130** (2011) 500.
- [2] S. T. S. Dhlamini, H. C. Swart, J. J. Terblans and O. M. Ntwaeaborwa, *Solid State Sci.*, **23** (2013) 6.
- [3] Y. X. Pan, W. Wang, G. K. Liu, S. Skanthakumar, R. Rosenberg, X. Z. Guo and K. K. Li, *J. Alloys Compd.*, **488** (2009) 638.
- [4] A. Yousif, H. C. Swart and O. M. Ntwaeaborwa, *J. Lumin.*, **143** (2013) 201.
- [5] G. A. Hirata, O. A. Lopez, L. E. Shea, J. Y. Yi, T. Cheeks and J. Mckittrick, *J. Vac. Sci. Technol.*, **14** (1996) 1694.
- [6] L. F. Koao, F. B. Dejene and H. C. Swart, *Mater. Sci. Semicond. Process.*, **27** (2014) 33
- [7] Y. Deng, J. D. Fowlkes, P. D. Rack and J. M. Fitz-Gerald, *Opt. Mater. (Amst.)*, **29** (2006) 183.
- [8] A. Yousif, H. C. Swart, O. M. Ntwaeaborwa and E. Coetsee, *Appl. Surf. Sci.*, **270** (2013) 331.
- [9] S. Murai, M. A. Verschuuren, G. Lozano, G. Pirruccio, A. F. Koenderink and J. G. Rivas, *Opt. Soc. Am.*, **2** 1707
- [10] X. W. Sun and H. S. Kwok, *Appl. Phys. A* **69** (1999) S39
- [11] L. I. U. Chun-jia, Y. U. Rui-min, X. Y. Zhi-wei, C. A. I. Jing, Y. A. N. Xing-huang, and L. U. O. Xue-tao, *Trans. Nonferrous Met. Soc. Chin.*, **17** (2007) 1093.
- [12] B. Cockayne, *J. Less-Comm. Met.*, **114** (1985) 199.
- [13] Y. Huh, Y. Cho and Y. R. Do, *Bull. Korean Chem. Soc.*, **23** (2002) 1435.
- [14] S. S. Uysal, A. Ege, M. Ayvacikli, A. Khatab, E. Ekdal, E. J. Popovici, M. Henini and N. Can, *Opt. Mater. (Amst.)*, **34** (2012) 1921.
- [15] M. N. R. Ashfold, F. Claeysens, G. M. Fuge and S. J. Henley, *Chem. Soc. Rev.*, **33** (2004) 23
- [16] A. Yousif, H. C. Swart and O. M. Ntwaeaborwa, *Proc. SAIP*, (2013) 1
- [17] J. Choe, *Mater. Res Innov.*, **6** (2002) 238
- [18] K. T. Hillie, O. M. Ntwaeaborwa and H. C. Swart, *Phys. Status Solidi*, **1** (2004) 2360.
- [19] F. I. Ezema, B. C. Ekwealor and R. U. Osuji, *Turk J Phys*, **30** (2006) 157.
- [20] V. Ankush, G. Sanjeev, K. Ravi, K. C. Amit, C. Ramesh, S. Nafa, H. C. Keun, *J. Alloys Compd.*, **527** (2012) 1.

Chapter 7

Structural and luminescence properties of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} , Nd^{3+} phosphor thin films grown by pulsed laser deposition

7.1. Introduction

Long afterglow or persistent phosphors have the ability of absorbing energy from UV or sunlight and then release it slowly in the dark [1,2]. Inorganic phosphors doped with rare earth elements show broad band emission from blue to red which makes them suitable for a variety of industrial applications, such as luminescent pigments, fluorescent lamps, color display, plasma display panels (PDP), radiation dosimetry and X-ray imaging [3]. The type and duration of emission from a phosphor is affected by a number of parameters such as the type and amount of activators or dopants, the structure of the host lattice, the method of preparation or growth conditions and other post-treatments. These parameters play a significant role in inducing a crystal field effect within the host matrix which in turn influences the emission wavelength, its intensity and lifetime. The main task would therefore be to optimize these factors so as to obtain a phosphor that gives the best performance for the desired application.

Long afterglow or persistent phosphors have the ability of absorbing energy from UV or sunlight and then release it slowly in the dark [1,2]. Inorganic phosphors doped with rare earth elements show broad band emission from blue to red which makes them suitable for a variety of industrial applications, such as luminescent pigments, fluorescent lamps, color display, plasma display panels (PDP), radiation dosimetry and X-ray imaging [3]. The type and duration of emission from a phosphor is affected by a number of parameters such as the type and amount of activators or dopants, the structure of the host lattice, the method of preparation or growth conditions and other post-treatments. These parameters play a significant role in inducing a crystal field effect within the host matrix which in turn influences the emission wavelength, its intensity and lifetime. The main task would therefore be to optimize these factors so as to obtain a phosphor that gives the best performance for the desired application.

Luminescent Eu^{2+} -doped strontium aluminate ($\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$) phosphors have been studied extensively because they exhibit excellent properties such as bright and long-persistent

phosphorescence which glow for many hours and are also safer and chemically stable and free from radioactive radiations as compared with sulfide phosphors like ZnS:Cu [4]. Persistent luminescence and intensity can be enhanced by co-doping $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ with other rare earth elements [5]. Most of the research mainly focused on the trivalent dysprosium (Dy^{3+}) and not Neodymium (Nd^{3+}) ions as co-dopants. $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}, \text{Nd}^{3+}$ phosphor powder can be synthesized using methods such as co-precipitation [6], solid state reaction [2] and sol-gel [7]. As compared with these conventional methods, solution-combustion synthesis technique [3–5] used in this work to prepare $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}, \text{Nd}^{3+}$ phosphor powders is facile, energy saving, safe and fast [8].

Most of the previous studies on $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ were carried out on the phosphor powder and there are few reports on thin films more so those made using the PLD technique [9]. In this paper we report the structural and luminescence properties of as-prepared $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}, \text{Nd}^{3+}$ phosphor powder and thin films. Thin film phosphors have several advantages over powders in that they exhibit better thermal stability, better adhesion to the substrate, higher lateral resolution and less out gassing in device applications [10]. Several methods have been used to grow thin films such as Chemical Bath Deposition (CBD) [11], rf magnetron sputtering [12], pulsed laser deposition (PLD) [13] and epoxide-catalyzed sol-gel methods [14]. However PLD has several advantages over other techniques such as the homogeneous stoichiometric deposition of the ejected particles on to the substrate [15] and good quality thin films can be obtained at low temperatures [16] by varying parameters such as substrate distance, atmosphere and substrate temperature among others.

These parameters affect thickness, roughness and overall quality of the obtained films which in turn influence the host structure, inducing crystal field and hence photoluminescence (PL) properties of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}, \text{Nd}^{3+}$. In this study thin films of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}, \text{Nd}^{3+}$ were prepared using PLD. The effect of varying argon gas pressure and substrate temperatures on the structure and photoluminescent (PL) properties of the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}, \text{Nd}^{3+}$ thin films were investigated.

7.2. Experimental

7.2.1. Synthesis

Stoichiometric amounts of analytical pure grade (Sigma-Aldrich, 99.9%) $\text{Sr}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Dy}(\text{NO}_3)_3$, $\text{Nd}(\text{NO}_3)_3$ and urea ($\text{CO}(\text{NH}_2)_2$) were taken to prepare polycrystalline $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$, Dy^{3+} , Nd^{3+} phosphor via a solution - combustion method where the metal nitrates and urea were used as reactants and fuel, respectively. All the precursors were pulverized in agate mortar to obtain better homogeneity before being dissolved in the smallest possible amount of 10 ml of de-ionized water and thoroughly mixed using a magnetic stirrer for 15 minutes without heating to obtain a uniform aqueous solution. The nominal concentration was maintained at 1:0.035 mol% for Eu^{2+} : Dy^{3+} and 1:0.015 mol% for Eu^{2+} : Nd^{3+} while that of Sr to Al was 1 mol% : 2 mol% in all samples respectively. The optimum concentration was calculated to give a final composition of $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$, Dy^{3+} , Nd^{3+} .

The solutions were then poured into China crucibles and placed one at a time in a muffle furnace pre-heated to 500 °C. The mixture ignited and a fast, self-sustaining combustion reaction took place. At first, the solution boiled losing all the water in the form of steam followed by decomposition letting off large amounts of gases (oxides of carbon, nitrogen and ammonia). The mixture then frothed and swelled enormously in to foam, followed by spontaneous ignition and smoldering which gradually led to an explosion rupturing the foam with a flame that glowed to incandescence. The product of combustion was a voluminous white dry $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$, Dy^{3+} , Nd^{3+} foam. The foam was taken out of the muffle furnace, cooled then milled resulting in a dry, and usually crystalline, fine white oxide powders. The whole combustion process took about 5 minutes. The powders were then stored in transparent glass sample bottles for characterization and PLD.

The $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$, Dy^{3+} , Nd^{3+} powder was then pressed into a pellet and used as a target for laser deposition after initial characterization. The pellet was heated at 200 °C for 2 hrs in an oven to expel moisture that may be present and make it hard and strong for use as a target for laser ablation. The pellet was not sintered at higher temperatures to avoid causing changes to the certain properties of the material and hence maintain the initial properties of the powder from which it was formed. However the low temperature could be the reason for the high density droplets formed on the surface of the deposited films. The target was then loaded on to a rotatable carousel inside the PLD chamber. The carousel rotates and rotates the target to prevent constant ablation by the laser beam from the same spot on the target. Silicon (100) wafers of

approximately 1 cm^2 were used as substrates. The wafers were first cleaned in ultrasonic bath of acetone, ethanol and distilled water in that sequence then blow-dried with clean dry N_2 gas and placed on a fixed substrate holder in the PLD chamber parallel to the target at a distance of 4.5 cm. The chamber was then pumped down to vacuum of about 3.0×10^{-6} mbar. The target was first ablated in vacuum and then under varying argon working atmosphere of 10mTorr, 20mTorr and 30 mTorr each for 60 minutes at a constant substrate temperature of $100\text{ }^\circ\text{C}$ and again ablated under varying substrate temperatures of 100, 200 and $300\text{ }^\circ\text{C}$ at a constant 20mtorr argon partial pressure respectively using a 266 nm Nd:YAG nanosecond (ns) pulsed laser with energy and frequency fixed at 45mJ/pulse (fluence of 0.2 Jcm^{-2}) and 10 Hz, respectively. Low laser fluence is one way for reducing particulate formation on the deposited films[17].

7.2.2. Characterization

The structural composition of the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}, \text{Nd}^{3+}$ phosphor powder and thin films were determined using a Bruker-AXS D8 Advance x-ray diffractometer (Bruker Corporation of Germany) operating at 40 kV and 40 mA using $\text{Cu K}\alpha = 0.15406\text{ nm}$ from 15° to 65° (2θ), with a scan rate of 0.39° (2θ)/min and step scans with a step time of 152s and step size of 0.02° (2θ). The morphologies of the phosphor powders and films were obtained using a JSM-7800F field emission Scanning Electron Microscope (SEM) coupled with an Energy Dispersive X-ray Spectrometer (EDS) for analysis of elemental composition and mapping while the surface topography and roughness were examined in contact mode using a Shimadzu SPM-9600 atomic force microscopy (AFM) with an in-built commercial software for calculating the root mean square (rms) values which indicates roughness of the films. The (PL) spectra were recorded at room temperature using a 325 nm He-Cd Laser. Reflectance (UV-Vis) characteristics were measured in the range 200 nm -700 nm using a Perkin Elmer Scan-Lambda 950 UV-Vis spectrophotometer using 319 nm excitation lamp and a 860 nm monochromator with a slit width of 2.0 nm and scan speed of 141 nm/min and step size of 0.5 nm to select a single frequency (wavelength) from all of those provided by the lamp source and to scan over a desired frequency range.

7.3. Results and Discussion

7.3.1. Structure and morphology analysis

XRD patterns of the $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$, Dy^{3+} , Nd^{3+} phosphor powder and thin films deposited in vacuum, 10, 20 and 30 mTorr argon and at 100, 200 and 300 °C substrate temperatures for 60 minutes, are shown in figure 7.1(a) and (b) respectively. The peaks fitted well with the powder and the JCPDS card number 74-0794 for the monoclinic SrAl_2O_4 of space group P1211 (4), cell ratios $a/b=0.9581$ $b/c=1.7075$ $c/a=0.6112$ and cell parameters; $a=8.4470\text{\AA}$, $b=8.8160\text{\AA}$, $c=5.1630\text{\AA}$ and $\beta=93.42^\circ$. A peak representing SrAl_4O_7 phase was also detected as indicated by * which could be due to a small percentage change during the synthesis stage of the powder samples.

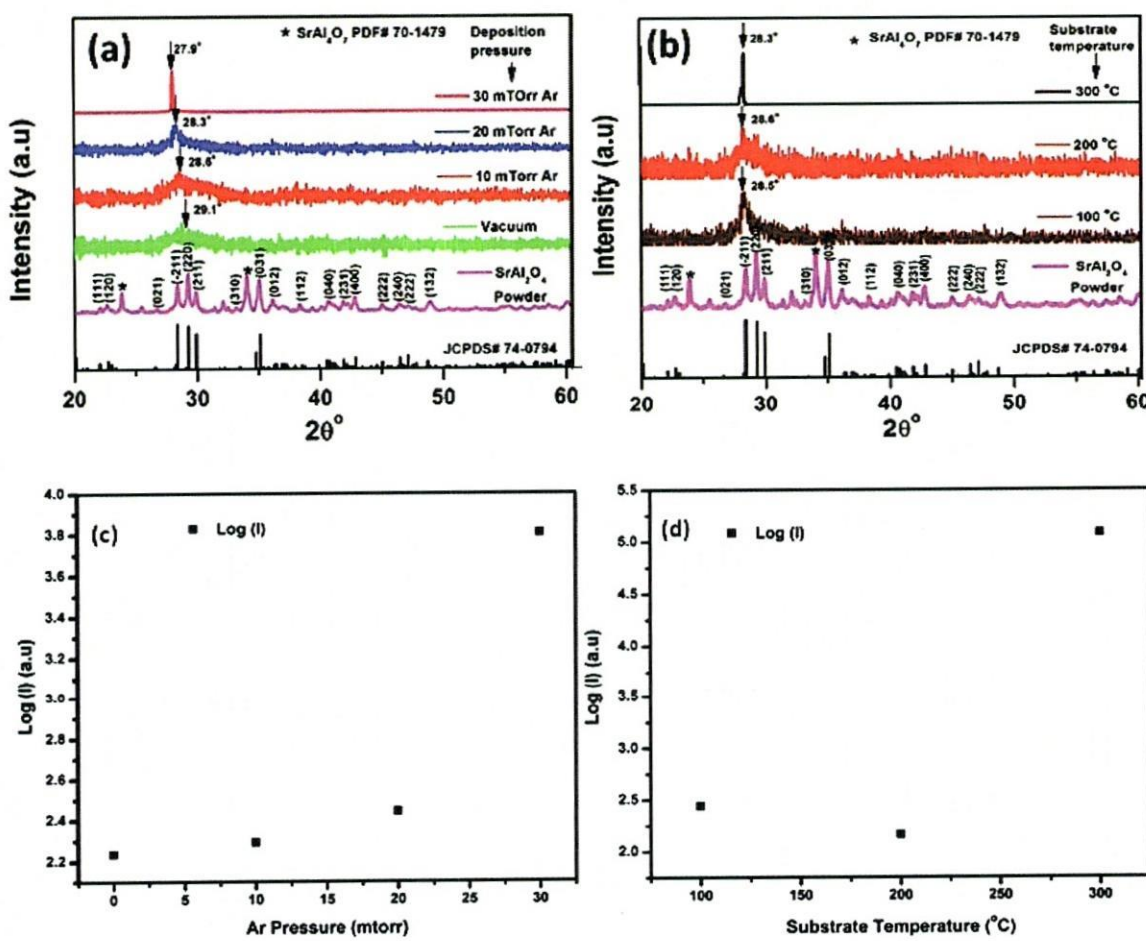


Figure 7.1: XRD patterns of the $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$, Dy^{3+} , Nd^{3+} phosphor powder (SrAl_2O_4) and thin films that were deposited in (a) vacuum, 10, 20 and 30 mTorr argon, (b) at 100, 200 and 300 °C substrate temperatures for 60 minutes and log (intensity) plots for vacuum (c) and substrate temperatures (d)

Figure 7.1(c) and (d) show log of XRD Intensity versus argon pressure and substrate temperature. It is observed that the intensities increase exponentially with argon pressure and substrate temperature respectively. It can be seen in figure 7.2(a) that with increasing argon pressure the peaks in the direction (220) shifted to the lower 2-theta angles from 29.1° in vacuum to 27.9° in 30 mTorr argon pressure accompanied by width - narrowing and increased intensity, an indication of increasing particle size as displayed in figure 7.2(b).

The average crystallite sizes calculated for the (220) direction were obtained using Scherrer's equation,

$$D = \frac{\kappa \lambda}{\omega \cos \theta} \dots\dots\dots 7.1$$

where D is the mean particle size, κ is a geometric factor, λ is the X-ray wavelength and ω is Full Width at Half Maximum (FWHM). The same trend was observed when substrate temperature was varied as seen in figures 7.1 (b), 7.2(c) and 7.2(d). With increasing substrate temperature, the peaks in the direction (220) shifted to the lower angle from 28.5° at 100 °C to 28.3° at 300 °C accompanied by width -narrowing and increased intensity, an indication of increasing particle size as displayed in figure 7.2(b).

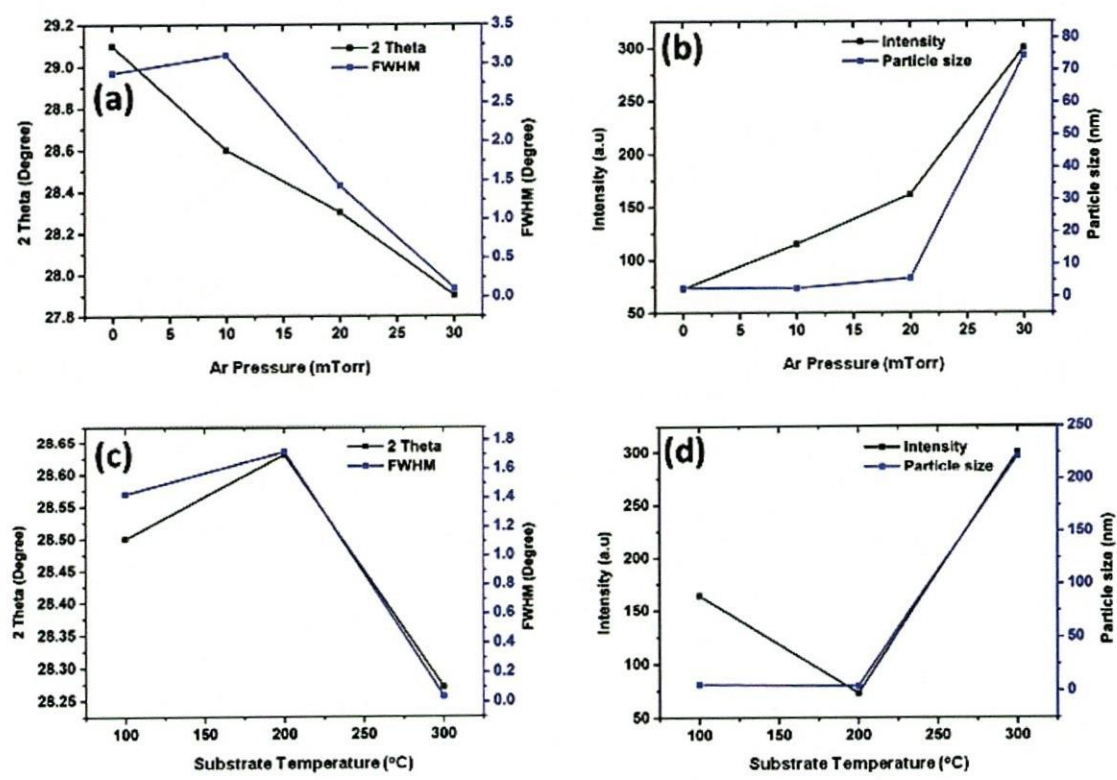


Figure 7.2: 2theta, FWHM, particle size and intensity as a function of argon pressure; (a) and (b) and substrate temperature; (c) and (d).

Broad XRD peaks is an indication of decreasing particle size, beginning of crystallization and short-range ordering [18] while the reverse case would mean that the material is amorphous which can be observed from the XRD patterns . However the drastic increase of particle size at 300 oC is not that evident from the AFM images but SEM.

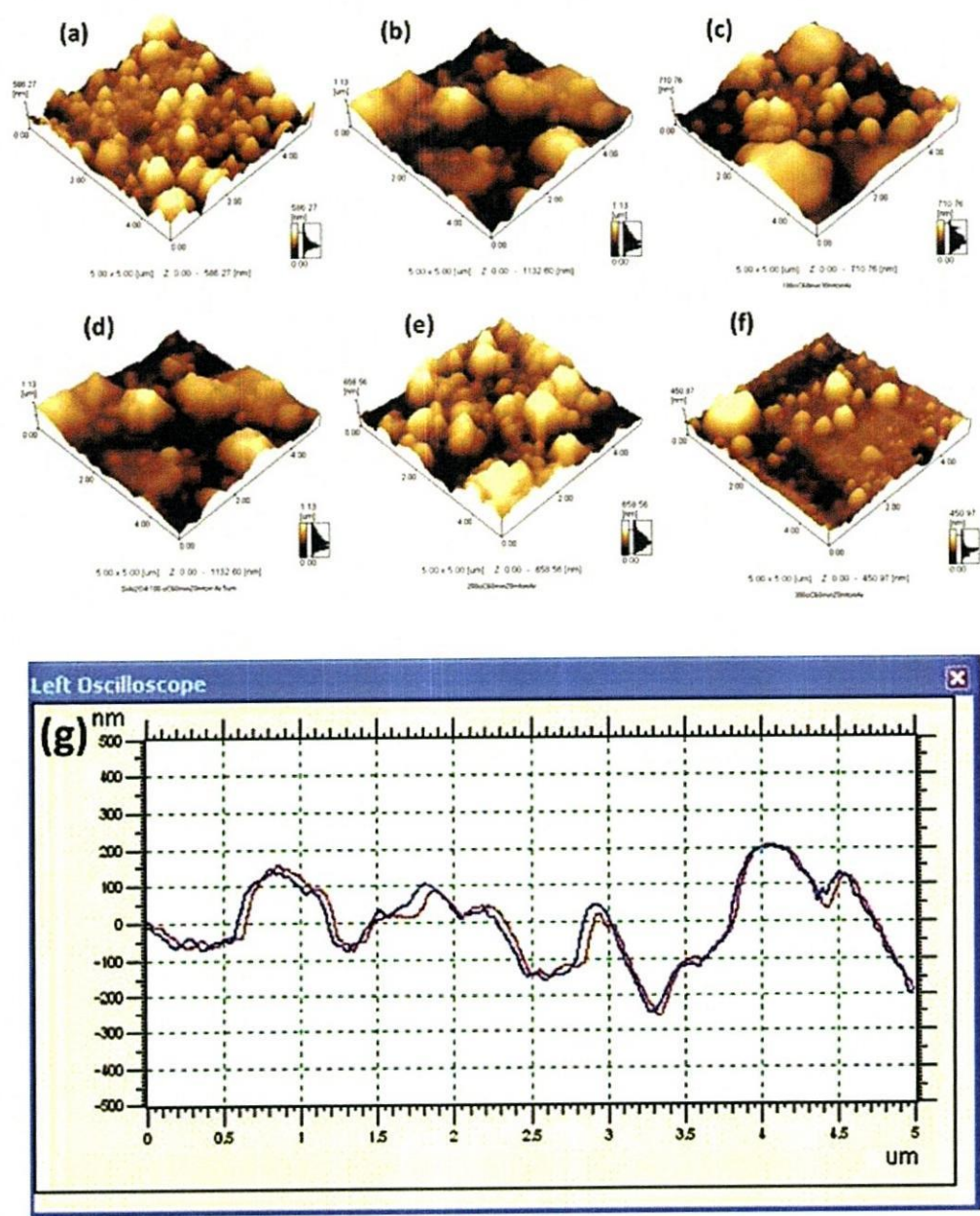


Figure 7.3: 3D AFM images of SrAl₂O₄:Eu²⁺, Dy³⁺, Nd³⁺ thin films deposited in (a) 10mTorr, (b) 20mTorr (c) 30mTorr argon pressures; (d) 100 °C (e) 200 °C, (f) 300 °C substrate temperatures; and (g) AFM oscilloscope showing surface topography profile of SrAl₂O₄:Eu²⁺, Dy³⁺, Nd³⁺ thin films.

Argon being a heavier gas scattered away more particles in the plume and this affected the arrival rates of all the species. Light atoms are scattered more than heavy atoms [19,20]. From figures 7.2(a-d) it was deduced that the XRD peak positions, FWHM, intensity and crystallite size were influenced by the ambient gas pressure and the variation of substrate temperature. 3D AFM images of the surface topography of the films deposited on Si (100) under different argon pressures were shown in figures 7.3(a, b and c) and those deposited under different substrate temperatures were shown in figures 7.3(d, e and f).

The films showed well defined and generally spherical grains of different sizes uniformly distributed over the surface which could be attributed to the reduced speed and hence arrival rates of the particles in the plume by the gas molecules thereby allowing a better nucleation process of the film particles on the substrate during the ablation process [21]. The AFM oscilloscope signal obtained from a section of the sample during the scanning of the surface topography of the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}, \text{Nd}^{3+}$ thin films was shown in figure 7.3(g). It depicted the spherical shapes of the grains and revealed sections where the particles agglomerated and formed larger clusters. From the figure the average particle size estimated from the vertical z-axis was found to be 100 nm which is within the same range as those shown in figures 2 calculated using the Scherrer equation.

The variation of film roughness indicated by the root mean square (rms) or Rq values with argon pressure and substrate temperature were shown in figure 7.4(a) and 7.4(b) respectively.

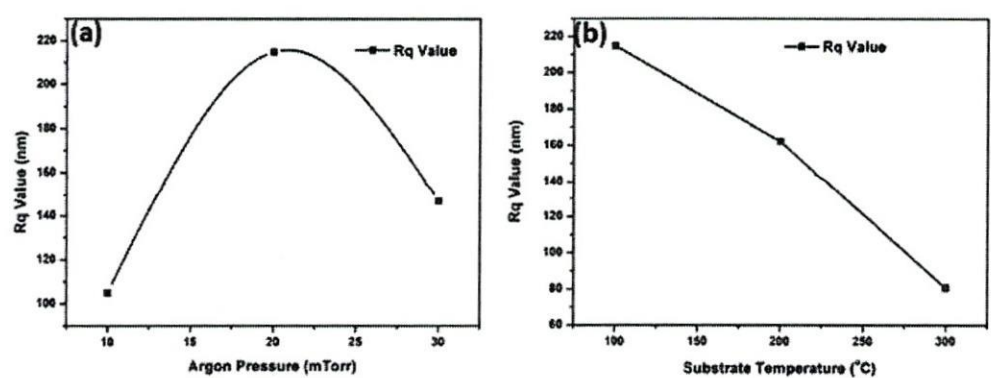


Figure 7.4: Variation of film roughness (Rq value) with (a) argon pressure and (b) substrate temperature.

It was observed that the film roughness increased with increasing argon pressure and decreased with increasing substrate temperature. A decrease in surface roughness with the increase in substrate temperature has also been reported elsewhere [9]. Also from figure 7.2 it was observed

that the grain sizes increased as the ambient argon gas pressure increased. The reason for this is that when the gas pressure in the chamber is low the mean free path (MFP) of the particles is longer hence yielding less effective collisions, whereas as the gas pressure increases the MFP also increases resulting in more effective collisions between the particles leading to nucleation and growth resulting in bigger particles [21,22]. It was also reported elsewhere that background gas of Ar has a higher mass density and therefore tends to reflect lighter atoms in the plume more and these results in a film with big particles on the substrate [23].

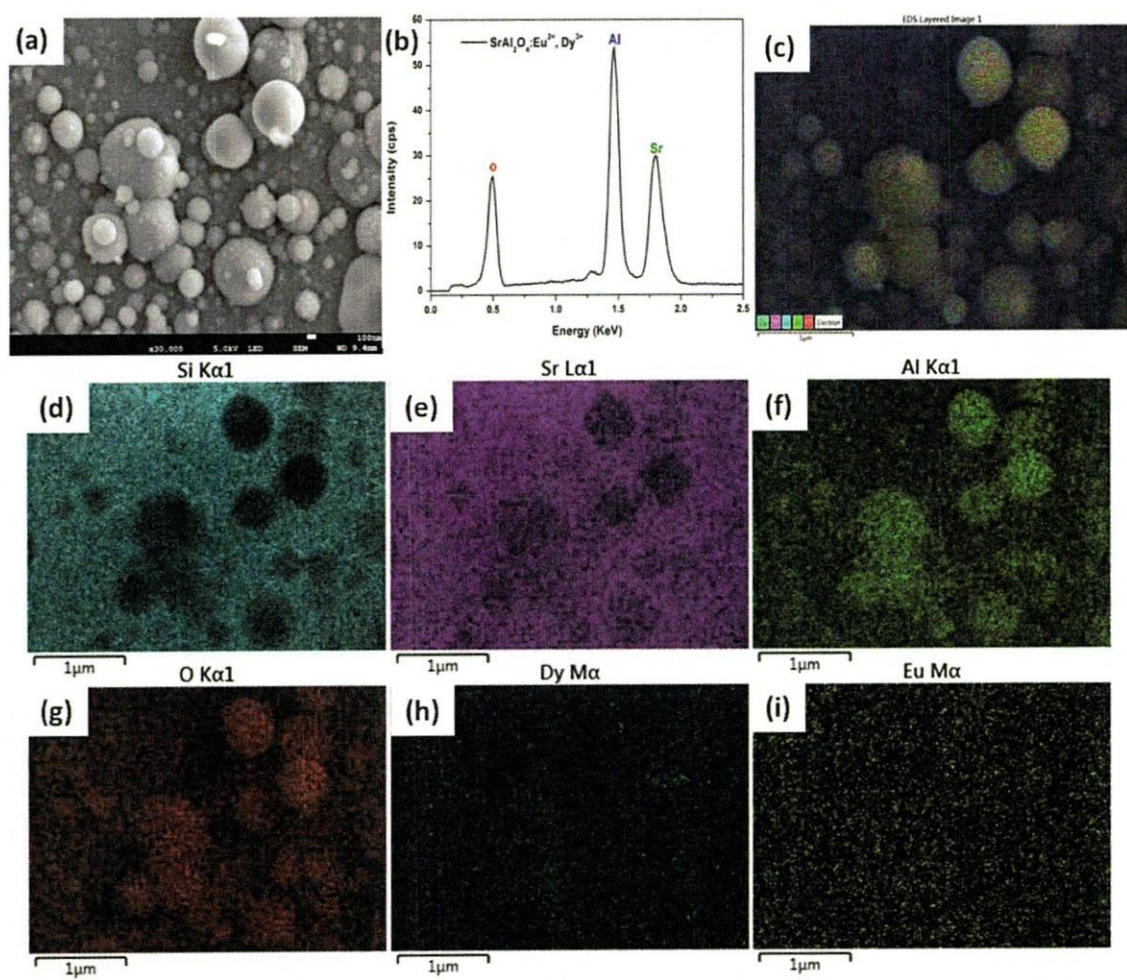


Figure 7.5 : (a) SEM micrograph, (b) EDS profile, (c) Elemental map (d) SiKα1 (e) SrLα1 (f) AlKα1 (g) OKα1, (h) DyMα and (i) EuM α energy distributions of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}, \text{Nd}^{3+}$ thin films.

The SEM micrograph, elemental map, and EDS energy distribution micrographs of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}, \text{Nd}^{3+}$ thin films and $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}, \text{Nd}^{3+}$ powder are shown in figures 7.5(a) to (h). In the SEM micrograph, figure 7.5(a) it is clear that the thin films have larger particles on the surface. In the past these particles showed more intense luminescence than the

rest of the film due to less internal reflection [23]. Figure 7.5(b) shows the relative compositional quantities of the individual elements in the sample. The EDS energy microanalysis was employed to approach elements' contribution in the sample. However the very low concentration of the rare earth dopants could be the reason for not being detected in the EDS spectra. Also Nd^{3+} was not detected even in the SEM owing to the very low concentration as compared to Eu^{2+} and Dy^{3+} .

The 2D elemental maps revealing the coordination and distribution of the different species (Sr, Al, O and Dy) in the SrAl_2O_4 host nanophosphor at the nanoscale are shown in 7.5(c). It confirmed their elemental composition, locations and distributions within the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} phosphor thin films. The EDS elemental mapping micro images of Si, Sr, Al, O, Dy and Eu in the films are also shown in figures 7.5(d) to (i). From the mapping images it seems that the bigger particles were slightly enriched with Al and O with respect to the rest of the thin film and as such 7.5(e) and 7.5(f) droplets seem to contain more Al, O and less Sr in accordance with the relative chemical composition of SrAl_2O_4 . The rest of the elements were uniformly distributed in the thin films.

7.3.2. Photoluminescence analysis

PL emission spectra recorded with the F-7000 FL Spectrophotometer from the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} as prepared powder and He-Cd laser at an excitation of 325 nm from $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} , Nd^{3+} thin films deposited on Si (100) under different argon pressures and substrate temperatures respectively was shown in figure 7.6. Figure 7.6(a) represents the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} phosphor powder which yielded a bright green luminescence emission peaking at 507 nm resulting from transitions between the $4f^65d^1-4f^7$ electron configurations of Eu^{2+} with only one emission broad band which is symmetric, an indication that only one luminescent centre, which is Eu^{2+} exists [5].

The effect of the varied chamber parameters was observed as shown in figure 7.6(b) and 7.6(c) whereby emission peaks are shifted to the longer wavelength side as also seen in figure 6(d). In RE ions the $4f^n$ electron shell is shielded from outside by the 5s and 5p electrons thereby screening them from surrounding crystal field effects hence Nd^{3+} acts as traps of holes and the trap level lie in between the excited and ground states of Eu^{2+} which enhances luminescence [24]. The slight wavelength shift could therefore be attributed to the different deposition conditions of argon pressure and substrate temperatures which induced crystal field effect within the SrAl_2O_4 host lattice.

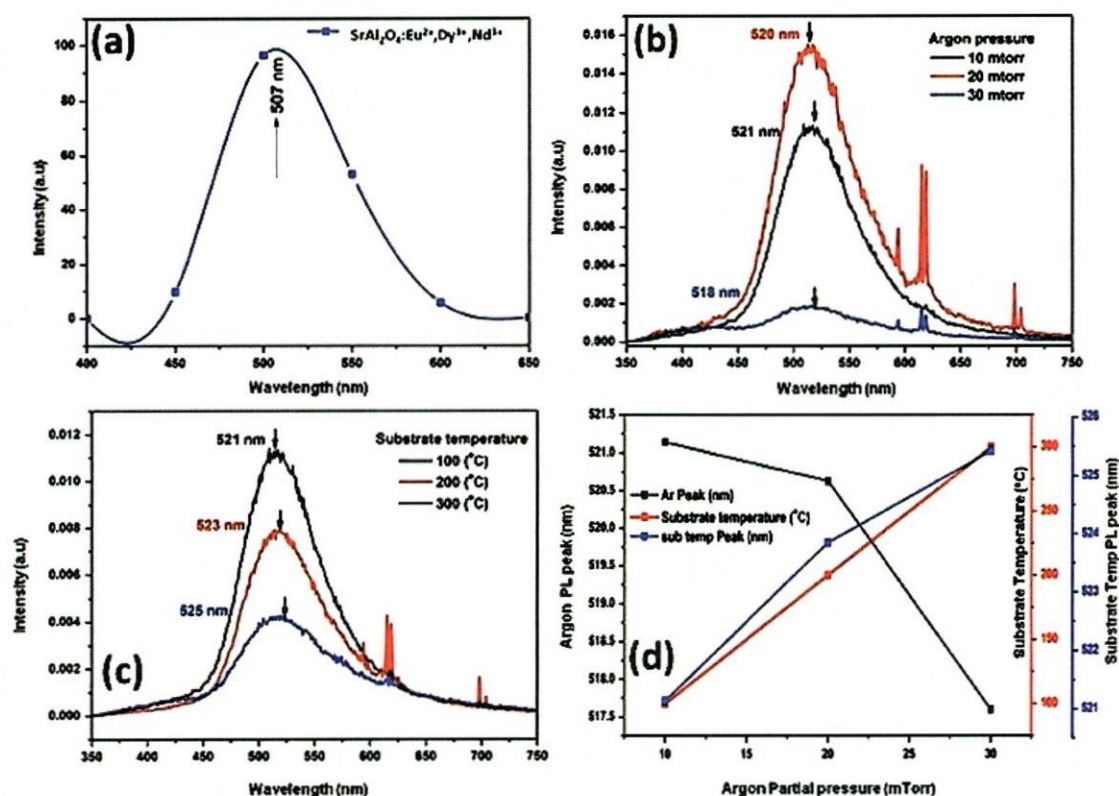


Figure 7.6: Emission spectra for (a) $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}, \text{Nd}^{3+}$ phosphor powders (b) $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}, \text{Nd}^{3+}$ thin films variation with argon pressure (c) $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}, \text{Nd}^{3+}$ thin films variation with substrate temperature and (d) Comparison of emission peak shifts due to argon partial pressure (black) and substrate temperature (blue) as a function of argon partial pressure and substrate temperature (red) for $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}, \text{Nd}^{3+}$ thin films.

The PL intensities of the films are generally low compared to those of the powder due to total internal reflection in thin films [25]. However thin films have advantages over the powders in that they possess better thermal stability, better adhesion to the substrate, higher lateral resolution and less out gassing in device applications [10,26]. The shift in the PL emission peaks of figure 7.6 is clearly seen on the CIE color chromaticity plots of figure 7.7(a) and 7.7(b) depicting color shifts with respect to changes in argon partial pressure and substrate temperature, respectively. As indicated by the arrows it is clear that as the argon gas pressure varies from 10 to 30 mTorr and substrate temperature from 100 to 300 °C, the CIE co-ordinates shift toward the longer wavelength of the CIE map. The arrows correspond to the peak shifts of the PL spectra in figure 7.6.

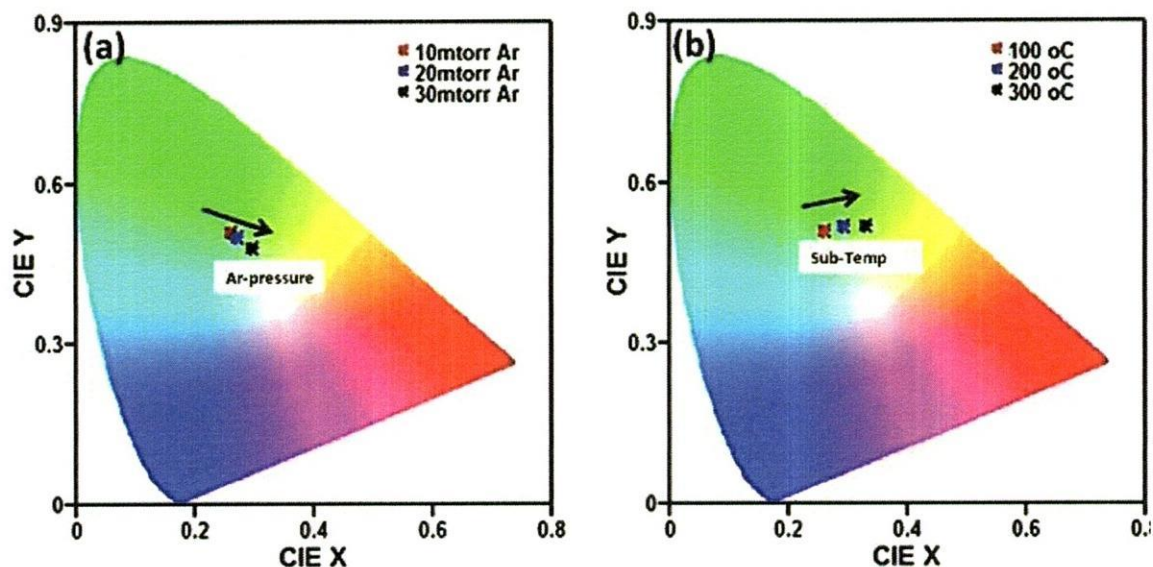


Figure 7.7: Chromaticity diagram depicting CIE color co-ordinates with respect to the changes in (a) argon pressure and (b) substrate temperature during ablation.

7.3.3. UV-VIS analysis

Figures 7.8(a) and (b) also show how the UV-reflectance is affected by the deposition atmospheres of argon and substrate temperature. It was observed that % reflectance decreased with increase in the gas pressure and substrate temperature. Also the absorption edges of the different spectra varied according to the different PLD chamber environment. This could be explained in the same way as the PL wavelength shifts attributed to the crystal field effect due to changes in the host structure.

The average band gap energies were obtained from the intercept of the extrapolated linear portion from of the $(f(R(v)hv))^n$ versus hv plot known as Tauc's plot along the hv axis as shown in figures 7.8(c) and (d) for vacuum, 10, 20 and 30 mTorr Ar and substrate temperature respectively. It revealed that absorption was greatly influenced by the presence of a background gas. The band gap energy reduced as the amount of ambient gas increased (figure 7.8(c)) and increased with increasing substrate temperature (figure 7.8(d)). This energy gap shift corresponds with the shifts observed in figure 7.6(d). Since Energy is inversely proportional to the wavelength ($E_g \propto (1/\lambda)$), as the wavelength increased the E_g decreased. Also as the wavelength shifted towards the higher wavelength side the E_g is reduced. Narrow band gap materials exhibit novel properties such as small effective masses, improved surface and interface properties and the possibility of incorporating more impurity/dopant ions [27].

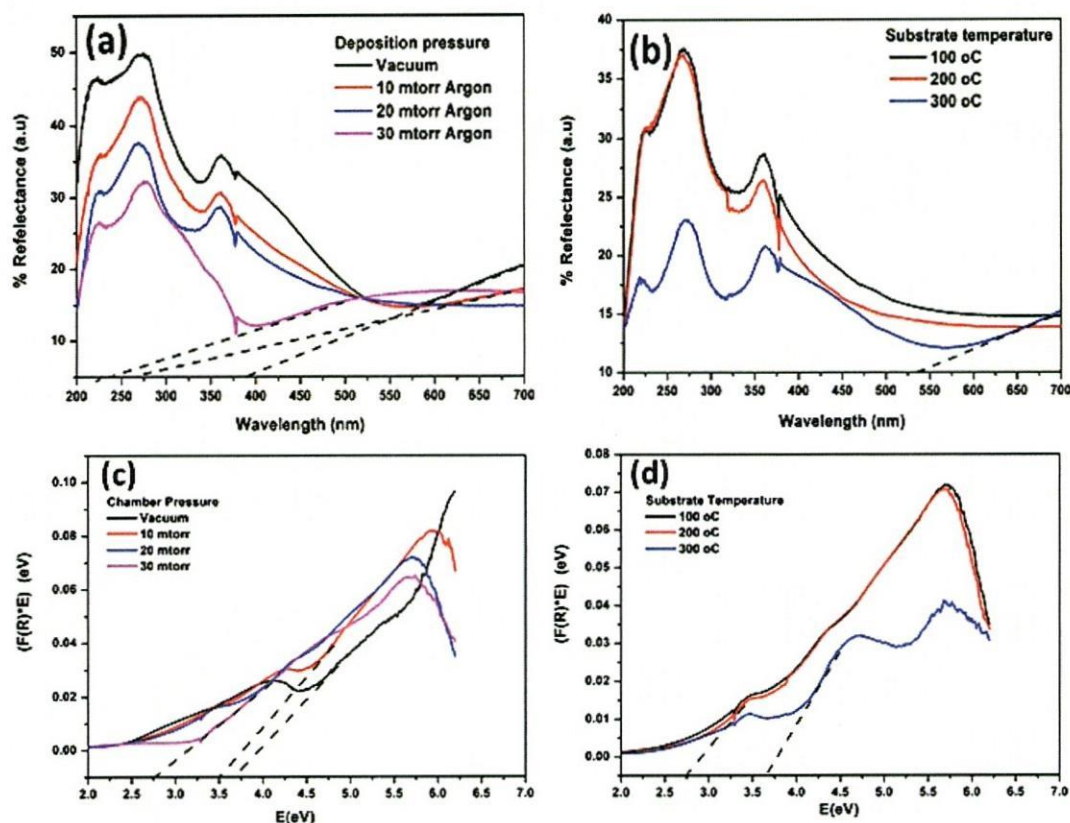


Figure 7.8: (a) – (d) UV-VIS reflectance and Tauc's plot as per the deposition atmospheres of argon and substrate temperature.

Conclusion

In this study thin films of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} , Nd were prepared using the PLD technique. The effect of varied background gas pressure and substrate temperature on the structure and PL properties of the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} , Nd^{3+} thin films were investigated. It was found that with increasing argon pressure and substrate temperature the peaks in the direction (220) shifted to the lower angle accompanied by width - narrowing and increased intensity an indication of increasing particle size. Also the film roughness increased with increasing argon pressure and decreased with increasing substrate temperature. The emission peaks were observed to shift to the longer wavelength side which could be attributed to the different deposition conditions of argon partial pressure and substrate temperatures which induced crystal field effect within the SrAl_2O_4 host lattice. The reflectance intensity decreased with increasing gas pressure and substrate temperature.

References

- [1] S. Nagamani and B. S. Panighrahi, *J. Am. Ceram. Soc.*, **93** (2010) 3832.
- [2] P. Taylor, X. Duan, S. Huang, F. You, and Z. Xu, *J. Exp. Nanosci.*, **4** (2009) 169.
- [3] V. Singh, J. Zhu, V. Natarajan, *Phys. Status Solidi.*, **203** (2006) 2058.
- [4] N. M. Son, L. T. T. Vien, L. V. K. Bao, N. N. Trac, *J. Phys.*, **187** (2009) 012017.
- [5] T. Peng, H. Yang, X. Pu, B. Hu, Z. Jiang, C. Yan, *Mater. Lett.*, **58** (2004) 352.
- [6] S. Choi, N. Kim, Y. Yun, S. Choi, *Journa Ceram. Process. Reas.*, **7** (2006) 62.
- [7] P. Huang, C. E. Cui, S. Wang, *Chinese Phys. B* **18** (2009) 4524.
- [8] A. H. Wako, B. F. Dejene, H. C. Swart, *Phys. B Condens. Matter*, **439** (2014) 153.
- [9] P. D. Nsimama, O. M. Ntwaeaborwa, E. Coetsee, H. C. Swart, *Phys. B Condens Matter*, **404** (2009) 4489.
- [10] K. T. Hillie and H. C. Swart, *Appl. Surf. Sci.*, **183** (2001) 304.
- [11] L. F. Koao, F. B. Dejene, H. C. Swart, *Mater. Sci. Semicond. Process.*, **27** (2014) 3340.
- [12] Y. Deng, *Opt. Mater. (Amst.)*, **29** (2006) 183.
- [13] A. Yousif, H. C. Swart, J. J. Terblans, R. M. Jafer, V. Kumar, R. E. Kroon, O. M. Ntwaeaborwa, M. M. Duvenhage, *Appl. Surf. Sci.*, **305** (2014) 732.
- [14] S. Murai, M. A. Verschuuren, G. Lozano, G. Pirruccio, A. F. Koenderink, J. G. Rivas, *Opt. Soc. Am.*, **2** (2012) 1707.
- [15] J. Lancok, C. Garapon, V. Vorlíček, M. Jelinek, M. Čerňanský, *Opt. Mater. (Amst.)*, **28**, (2006) 360.
- [16] X. W. Sun, H. S. Kwok, *Appl. Phys. A.*, **69** (1999) 39.

- [17] L. I. U. Chun-jia, Y. U. Rui-min, X. U. Zhi-wei, C. A. I. Jing, Y. A. N. Xing-huang, L. U. O. Xue-tao, *Trans. Nonferrous Met. Soc. China.*, **17** (2007) 1093.
- [18] Y. Nakata, W. K. A. Kumuduni, T. Okada, M. Maeda, *Appl. Phys. Lett.*, **2599** (2005) 1.
- [19] J. M. Warrender, M. J. Aziz, *Phys. Rev. B*, **75** (2007) 1.
- [20] P. D. Nsimama, *Tanzania J. Appl. Sci.* **2011**, 2, 268.
- [21] H. C. Swart, O. M. Ntwaeaborwa, P. D. Nsimama, J. J. Terblans, *Phys. B Condens. Matter.*, **407** (2012) 1660.
- [22] S. T. S. Dlamini, H. C. Swart, J. J. Terblans, O. M. Ntwaeaborwa, *Solid State Sci.*, **23** (2013) 65.
- [23] E. Coetsee, H. C. Swart, J. J. Terblans, O. M. Ntwaeaborwa, K. T. Hillie, W. A. Jordaan, U. Butner, *Opt.Mat.*, **29** (2007) 1338.
- [24] H. Ryu, K. S. Bartwal, *Res. Lett. Mater. Sci.* **2007** (2007) 1.
- [25] J. Choe, *Mater. Res Innov.*, **6** (2002) 238.
- [26] A. Yousif, H. C. Swart, O. M. Ntwaeaborwa, E. Coetsee, *Appl. Surf. Sci.* **270** (2013) 331.
- [27] T. C. McGill, D. Collins, *Semicond. Sci. Technol.*, **8** (1993) 1.

Chapter 8

Effect of Ga^{3+} and Gd^{3+} ions substitution on the structural and optical properties of Ce^{3+} -doped yttrium aluminium garnet phosphor nanopowders.

8.1. Introduction

Extensive research on inorganic luminescent materials with activators showing allowed f-d transitions has gained momentum over the past decade. Lanthanide ions are very sensitive to the chemistry of their environment because the d –states are not shielded. This is important for the manufacture of white light emitting diodes (LEDs) since the f-d absorption has to be in the UV to blue spectral region. Changes in the chemical environment can be due to a number of factors such as changes in the charge density of the bond-lengths caused by differences in electronegativity between the dopant and its surroundings leading to changes in the covalency, changes in the crystal field splitting of the 5d state due to differences in the charge of the surrounding ion or changes in the metal-ligand distances [1] etc. Increase in crystal field splitting and high covalency will shift the f-d transition to lower energies and vice versa.

Yttrium aluminium garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$) is one of the most important optical materials which finds a wide range of applications such as in cathode ray tubes (CRTs), field emission displays (FEDs) and scintillators owing to their wide band gap and excellent radiation conversion efficiency [2]. It is also suitable for use as a host material for solid state phosphors due to its good chemical stability, high quantum yield, low toxicity, low thermal expansion and a tunable emission wavelength [3]. Next generation solid- state lighting are preferred over the conventional light sources such as incandescent and fluorescent lamps due to their brightness, high radiation efficiency, long life time, compatibility with the environment, low cost, mercury free, compactness, energy saving and reliability [4,5,6].

Conversion of UV/blue radiation by a phosphor into white radiation is one of the most significant technologies of solid state lighting [7]. Cerium activated yttrium aluminum garnet; $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, upon excitation with blue radiation, emits a yellow broad band which when combined with a blue LED produces white light [6]. The yellow emission band ranging from 510 nm to over 600 nm originates from the allowed 5d-4f electronic transition of Ce^{3+} to the spin-orbit split $^2\text{F}_{7/2}$ and $^2\text{F}_{5/2}$ levels [8] which efficiently absorbs blue excitation light from 450

nm to 470 nm to produce white light [4]. For general lighting purposes ideal white light need to be generated. Hence there is a need to obtain a phosphor with a broad emission band covering the green and red regions in the blue-light excitation [5].

One way to achieve this is to modify the composition of the host lattice so as to obtain phosphors with adjustable wavelength matching blue LEDs. This can be done by doping the garnet lattice with suitable cations to slightly adjust the emission color [6] either by expanding the $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ emission band to induce a red shift [7] or reducing the $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ emission band to cause a blue shift. The emission wavelength can be tuned by partially or totally substituting trivalent ions of different sizes in the $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ lattice matrix. Larger ions will cause lattice expansion resulting in a red shift while smaller ions will blue shift the emission wavelength. This is because by increasing or decreasing the ionic radii in the garnet host lattice, the cubic symmetry around the rare earth ions gets distorted [3].

In the present work, we report the effect on the structure and emission wavelength of commercial $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ phosphor when Y^{3+} was substituted with Gd^{3+} to obtain $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ and Al^{3+} substituted with Ga^{3+} to obtain $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ respectively vis-à-vis the variation of the crystal field energy levels of Ce^{3+} .

8.2. Experimental

Commercial $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ and $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ phosphor powders were obtained from Phosphor Technology. The structural and phase compositions were determined using a Bruker-AXS D8 Advance x-ray diffractometer (Bruker Corporation of Germany) operating at 40 kV and 4 mA using $\text{Cu K}\alpha = 0.15406$ nm from 15° to 65° (2θ), with a scan rate of 0.39° (2θ)/min and step scans with a step size of 0.02° (2θ). (UV) Absorption/Reflectance characteristics were measured in the range 250 nm - 700 nm using a Perkin Elmer Scan-Lambda 950 UV-Vis spectrophotometer using 319.20 nm excitation lamp and 860.80 nm monochromator with a band pass slit width of 2.0 nm and scan speed of 141.20 nm/min and data interval of 0.5 nm. Photoluminescence (PL) excitation and emission spectra were measured at room temperature (RT) using a Cary Eclipse luminescence spectrometer (model LS-55) with a built - in 150W xenon flash lamp as the excitation source and a grating to select a suitable excitation wavelength with excitation and emission slit of 2.5 nm, scan rate of 600 nm/min, medium PMT Voltage, excitation filter of 335-620 nm and emission filter of 550-1100 nm. Thermoluminescence (TL) analysis were done above RT by use of Nucleonix 1009I TL reader to investigate traps and defects in the band gap of the phosphors. The samples were

excited with UV radiation and the heating performed from RT upto 400 °C at a constant heating rate of 1 °C/s under thermal stimulation.

8.3. Results and Discussion

8.3.1. Structure and morphology analysis

Figure 8.1 shows a cubic garnet-type structure for $\text{Y}_3\text{Al}_5\text{O}_{12}$ commonly represented in a general form as $\{\text{A}\}_3[\text{C}]_2[\text{D}]_3(\text{O})_{12}$. It has a bcc structure of space group I a-3d (230) with 160 atoms in the cubic (primitive) cell and cell parameters; $a=12.01 \text{ \AA}$, cell ratio; $a/b=1.0$, $b/c=1.0$, $c/a=1.0$ and cell volume $1732.32 \text{ \AA}^3$.

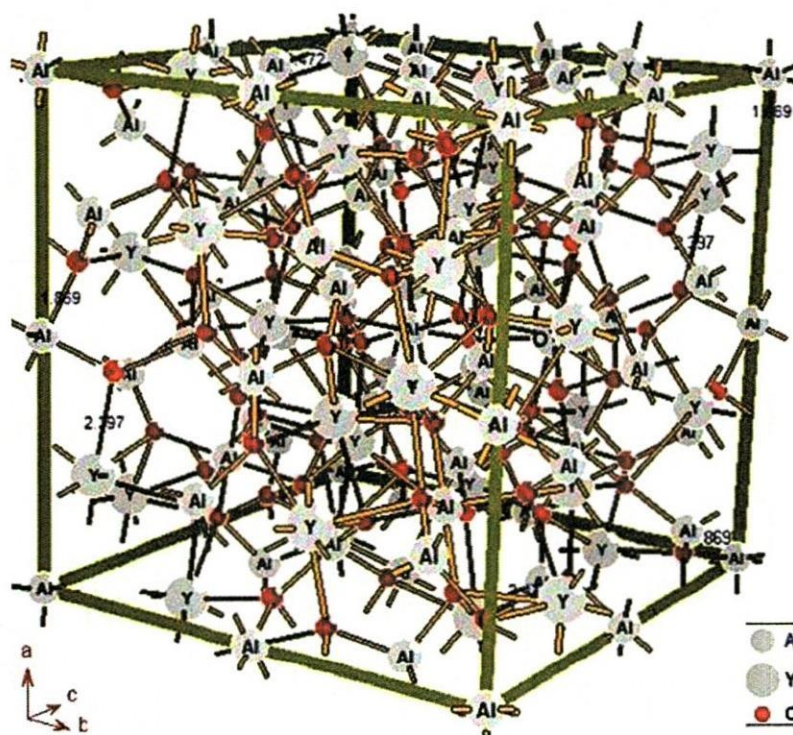


Figure 8.1: 3D-crystal structure of YAG. The large balls are yttrium (Y), the intermediate balls are aluminium (Al) and the small (red) balls are oxygen (O).

The $\text{Y}\{\text{A}\}$ -cations are eight-coordinated to eight O in a dodecahedra and occupy the $24(c)$ sites. Al occupies two different sites; the Al $[\text{C}]$ -cations occupy the $16(a)$ sites octahedrally bonded and the Al $[\text{D}]$ -cations tetrahedrally bonded occupying the $24(d)$ sites [8]. The O atoms occupy the $96(h)$ sites and their specific positions within the unit cell vary for different garnets [9].

XRD patterns of the $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ and $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ phosphor powders are shown in figure 8.2. It can be seen that the diffraction peaks slightly shifted to the

lower 2-theta angles for $Y_3(Al,Ga)_5O_{12}:Ce^{3+}$ and slightly to higher 2-theta angles for $(Y,Gd)_3Al_5O_{12}:Ce^{3+}$ with respect to $Y_3(Al,Ga)_5O_{12}:Ce^{3+}$. This is also well depicted in figure 8.3(c). It is well known that the size of ionic radius of the substituting cation influences the resultant change in lattice parameters. This could be attributed to the change in the host lattice caused by the larger ionic size of Ga^{3+} (0.062 nm) as compared to that of Al^{3+} (0.053 nm), which causes an increase in the d-spacing as confirmed in figure 2(a) and hence XRD peak shift of towards lower angles[10]. On the same note since the ionic size of Gd^{3+} (0.1053 nm) [11] is larger than that of Y^{3+} (0.102 nm) [12] substituting Gd^{3+} also results in lattice expansion causing XRD peak shift to lower angles with respect to $Y_3Al_5O_{12}:Ce^{3+}$.

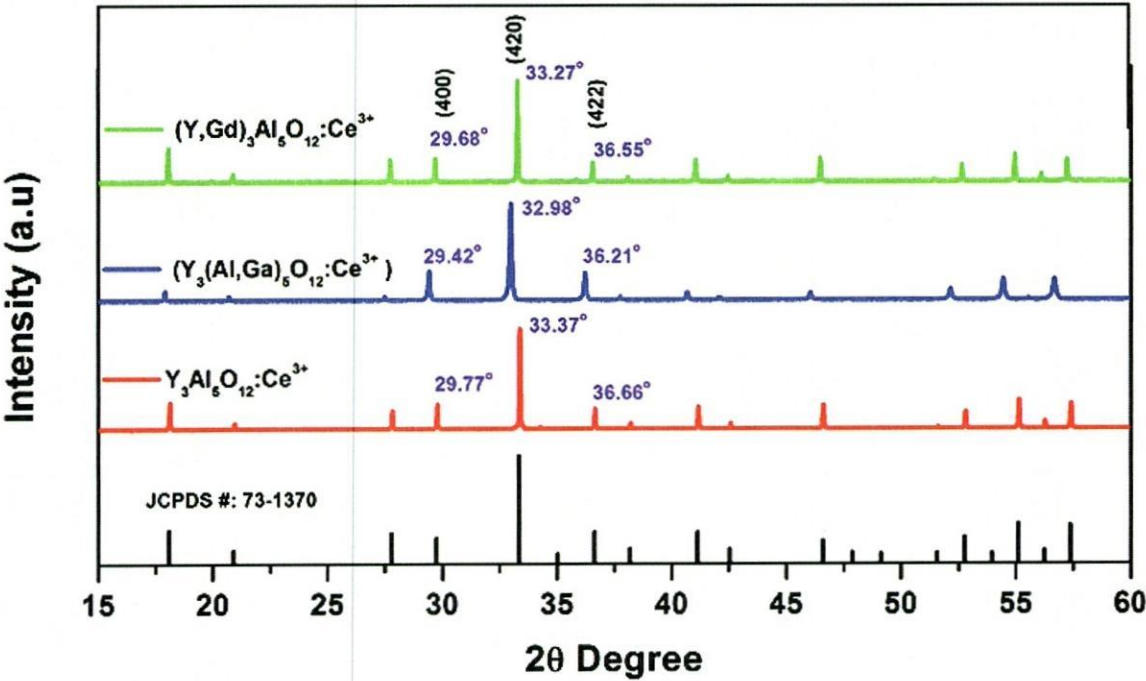


Figure 8.2: XRD patterns of the $Y_3Al_5O_{12}:Ce^{3+}$, $Y_3(Al,Ga)_5O_{12}:Ce^{3+}$ and $(Y,Gd)_3Al_5O_{12}:Ce^{3+}$.

It is worth noting that with reference to $Y_3Al_5O_{12}:Ce^{3+}$ the shift is -0.39° for Ga^{3+} and -0.1° for Gd^{3+} . So Ga^{3+} is slightly towards lower angles and Gd^{3+} to higher angles compared with the $Y_3(Al,Ga)_5O_{12}:Ce^{3+}$. This effect is due to the resultant difference in radii after substitution which is smaller between Gd^{3+} and Y^{3+} (0.003 nm) and larger between Ga^{3+} and Al^{3+} (0.009 nm).

The average crystallite sizes calculated for the (420) direction were obtained using Scherrer’s equation;

$$D = \frac{\kappa \lambda}{\omega \cos \theta} \dots\dots\dots 8.1$$

are shown in figure 8.3(b), where D is the mean particle size, K is a geometric factor, λ is the X-ray wavelength and ω is Full Width at Half Maximum (FWHM). It was observed that particle sizes reduced with Ga^{3+} substitution, which resulted in a blue shift in PL spectra (figure 8.3(a) and 8.3(b)) as the size of the particle decreased [13] and increased again with Gd^{3+} inducing a red-shift as supported by figure 8.3(d) showing variation of full width at half maximum (FWHM) with addition of Ga^{3+} and Gd^{3+} ions into the $Y_3Al_5O_{12}:Ce^{3+}$ structure which is larger for Ga^{3+} and narrow with Gd^{3+} substitution.

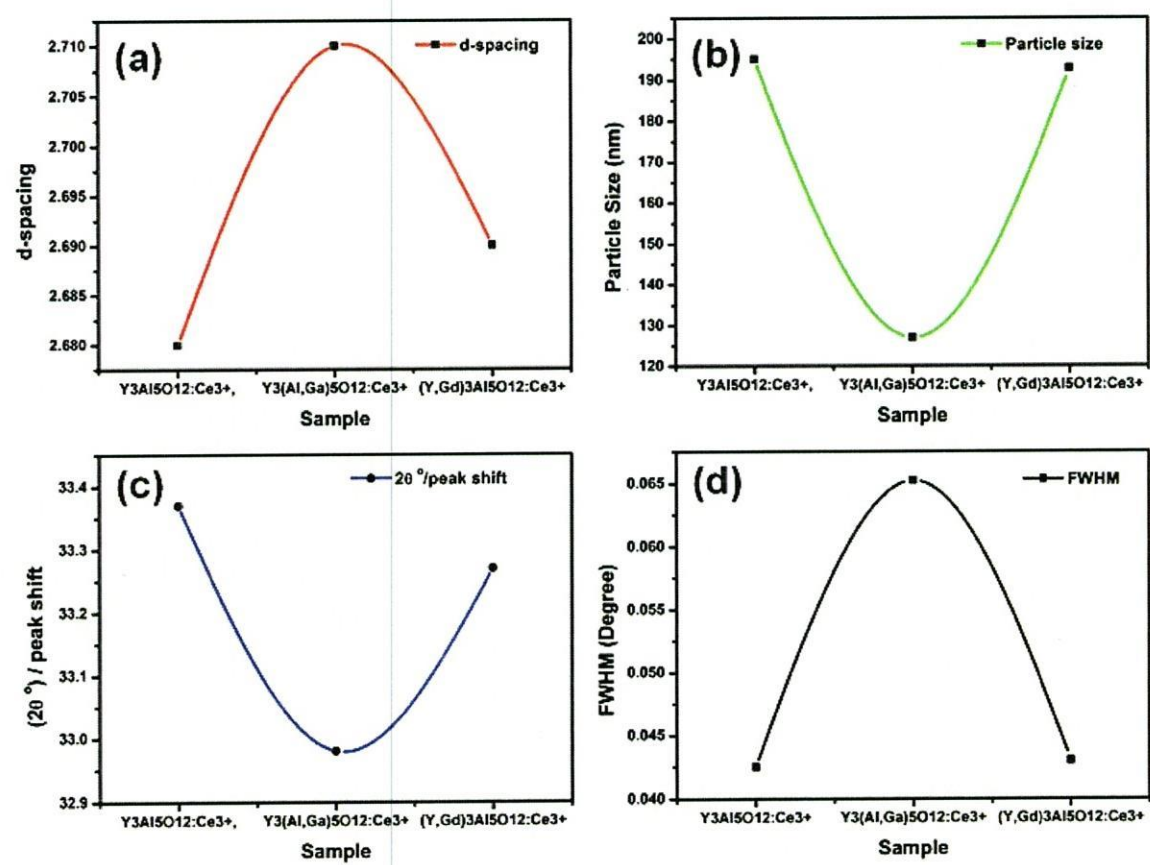


Figure 8.3: The effect of Ga^{3+}/Gd^{3+} ion substitution in to the $Y_3Al_5O_{12}:Ce^{3+}$ composition on the (a) d-spacing (b) particle size (c) 2-theta peak shift and (d) FWHM.

8.3.2. Photoluminescence

Figure 8.4(a) shows the normalized room temperature (RT) PL excitation spectra at emission wavelengths of 568, 578, and 588 nm while figure 8.4(b) shows emission spectra at excitation wavelength of 438, 462 and 467 nm for the $Y_3Al_5O_{12}:Ce^{3+}$, $Y_3(Al,Ga)_5O_{12}:Ce^{3+}$ and $(Y,Gd)_3Al_5O_{12}:Ce^{3+}$ powders respectively recorded with Cary Eclipse photoluminescence spectrometer.

The broad band excitation 400-525 nm are due to the electronic transition from the 4f ground state to the crystal field-split 5d states of Ce^{3+} ion. The blue excitation raises the electron in the Ce^{3+} ion from the 4f ground state to the 5d level, which would then be transferred to the lower 2D(5d) excited state [6]. The green-yellow emission emanates from within the cubic $\text{Y}_3\text{Al}_5\text{O}_{12}$ lattice due to electronic transitions from the 5d excited states to the split 4f($^2\text{F}_{7/2}$ and $^2\text{F}_{5/2}$) ground states [4] characteristic of Ce^{3+} ions. The electrons excited to the 5d level of Ce^{3+} ions decay non-radiatively to the 4f levels of Ce^{3+} ions [14] resulting in the broad emission bands centred at 568, 578, and 588 nm $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ and $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ powders respectively. The emission from Ce^{3+} is very sensitive to and is affected by changes in the local lattice structure due to the resultant crystal field effects. Hence, the peak position of the emission depends on the garnet host environment which may bring about a blue - or a red - shift of Ce^{3+} emission when co-activated with Ga^{3+} or Gd^{3+} . Aluminate garnets are relatively flexible in substituting Y^{3+} ions in the dodecahedral sites and Al^{3+} in tetrahedral/octahedral sites which makes it is easy to modify the host $\text{Y}_3\text{Al}_5\text{O}_{12}$ composition to alter the Ce^{3+} emission band to meet spectral requirements [5].

When Gd^{3+} (or La^{3+}) was used to substitute for the Y^{3+} site in the $\text{Y}_3\text{Al}_5\text{O}_{12}$ lattice, the emission peak of the phosphor powder shifted to a longer wavelength [15]. The substitution of Y^{3+} with Gd^{3+} shifted the emission peak towards longer wavelength (588 nm) relative to emission 578 nm from $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ as shown in figure 8.4(b). Such shift is mainly due to the changes in the lowest 5d¹ crystal-field energy level which is strongly affected by local electrostatic field determined by the crystalline structure of the YAG lattice. The lowest/first excited state of Ce^{3+} originates from the 5d configuration. Since Y^{3+} occupies a dodecahedral site in $\text{Y}_3\text{Al}_5\text{O}_{12}$ which has a tetragonal symmetry and because of the symmetry or the crystal field exerted by the host ligand ions and spin-orbit interaction, the 5d state degenerates into 5 levels resulting into five absorption bands; 460, 340, 261, 224, and 205 nm of which 460 nm and 340 nm are commonly observed at RT as shown in the absorption spectra of figure 8.6.

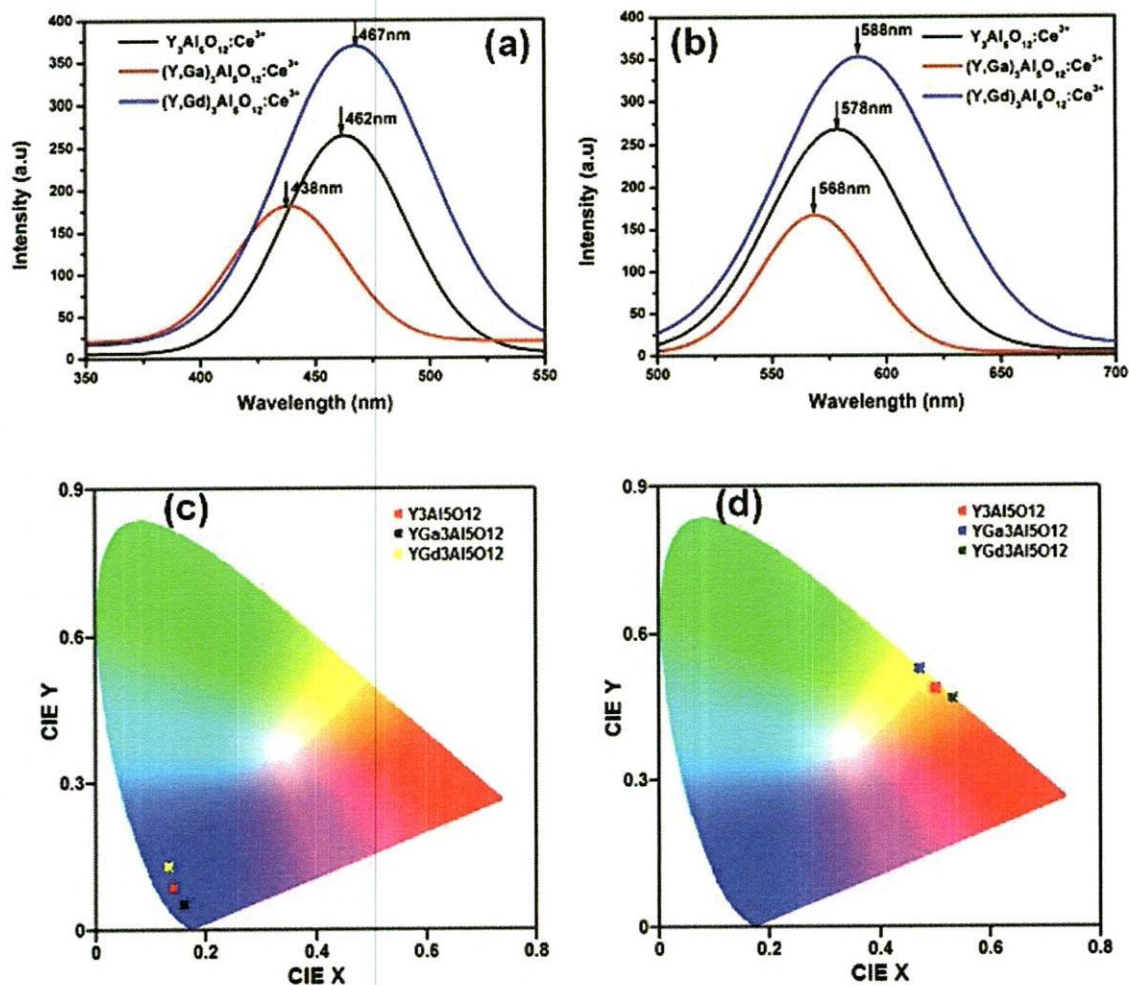


Figure 8.4: (a) excitation (b) emission spectra; (c) and (d) chromaticity diagram depicting CIE color co-ordinates for the $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ and $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ powders respectively.

Since the ionic size of Gd^{3+} is larger than that of Y^{3+} , replacing Y^{3+} with Gd^{3+} causes lattice expansion which leads to an increase in the crystal-field interaction of Ce^{3+} [7]. As the crystal field splitting of 5d energy levels of the Ce^{3+} ion increases and the energy difference between the lowest 5d sub-level and the ground state of 4f configuration of Ce^{3+} become smaller the emission band shifts to a longer wavelength (red shift). In other words, more splitting downshifts the lowest excited 5d states of Ce^{3+} to lower energies causing to emit light of longer wavelengths. It is well known that ionic radius decreases and electronegativity (χ) increases with atomic number. In the ionic relationship; Me/Re–O–Ce (Me/Re = Gd subs Y), the electronegativity (χ) of Gd^{3+} (1.20) is smaller than that of Y^{3+} (1.22) and the ionicity of Me/Re–O band decreases with the addition of Gd^{3+} content, which induces the increase in the ionicity of O–Ce in Lu–O–Ce and therefore, the red shift of the emission occurs[15]. The increase in ionicity brings the 5d energy level of the Ce^{3+} ion closer to the 4f ground state, which shifts the

emission to higher wavelengths; this is consistent with what is observed in emission properties shown in figure 8.4. The magnitude of crystal field splitting is mainly affected by the Ce–O bond length (lattice constant), the molecular orbital overlap between Ce^{3+} and O^{2-} , and the electronegativity (χ) value. The dependence of crystal field splitting D_q on the (bond length) lattice constant can be shown using the equation;

$$D_q = \frac{Ze^2r^4}{6R^5} \dots\dots\dots 8.2$$

where Z is the charge of the anion ($Z=2$ for O^{2-}), e is the charge of an electron, r is the radius of the d wave function and R is the bond length [11]. Therefore when Ce^{3+} - O^{2-} bond length (lattice constant) become shorter it increases the magnitude of the crystal field strength and since crystal field splitting D_q is proportional to $1/R^5$, it lowers the 5d band of Ce^{3+} which results in red-shift [5]. Hence compared with $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, the spectrum of the $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ is slightly shifted to the red, because of reduced local symmetry [16]. On the other hand substitution of Al^{3+} with Ga^{3+} shifts the emission towards shorter wavelength (568 nm) as seen in figure 8.4(b) relative to emission peak of 578 nm from $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$. It was reported that substituting Ga^{3+} ion in the Al^{3+} site induces a blue shift in the emission wavelength [8].

In the bond relation; Me–O–Ce (Me = Al-doped Ga), the electronegativity (χ) of Ga (1.81) is larger than that of Al^{3+} (1.61) and the ionicity of Me–O is decreased with the addition of Ga^{3+} content, which enhances the energy gap of O–Ce in Me–O–Ce. Therefore, the blue shift of the emission occurs which means a higher energy Ce^{3+} 4f-5d absorption due to the increase in ionicity of O–Ce [15] as shown in figure 8.5(a) which compares the luminescence property of $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ and $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ with respect to variation of the crystal field energy levels of Ce^{3+} .

Cerium belongs to the lanthanides with electronic configuration of the form $[\text{Xe}]4f^n6s^m$. It can exist as an atom or as a free-ion. The 6s shell can be empty ($m=0$) especially in compounds, occupied by one electron ($m=1$) or occupied by two electrons ($m=2$). When completely filled, the 4f shell is composed of 14 electrons. The $4f^n$ energy levels are not affected by the host environment because they are completely shielded by the filled $5p^6$ and $5s^2$ shells of the $[\text{Xe}]$ configuration. However an electron in a 5d orbital is not completely shielded and its energy is very susceptible to changes in the crystalline environment.

$[\text{Xe}]4f^1 5d^0 6s^0$ ($^2F_{5/2}, ^2F_{7/2}$) and $[\text{Xe}]4f^0 5d^1 6s^0$ ($^2D_{3/2}$) states. In the ground ($4f$) state Ce^{3+} splits up in a doublet $2F_j$ ($j = 5/2$ and $7/2$) state due to spin-orbit coupling.

The energy difference between these split states is about 2000 cm^{-1} , (figure 8.5). For an isolated Ce^{3+} ion, this energy gap is significantly decreased due to the large crystal-field splitting of Ce^{3+} $5d$ states, which arises when a Ce^{3+} ion replaces a smaller Y^{3+} ion in the $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ structure. The emission wavelength of $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ is longer followed by that of $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ and then $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ due to the relative decrease in ionicity resulting from the decrease in energy due to electron transfer from O^{2-} to Ce^{3+} [15] as represented in figure 8.5(b). The symmetry of the host matrix and the chemical environment around the Ce^{3+} ions greatly affect these split energy levels and the splitting patterns [18].

The (x,y) coordinates of a CIE diagram can be used to describe the color properties of a light source. The (Commission International de l'Eclairage) CIE chromaticity of $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ and $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ powders are presented in figure 8.4(c) and 8.4(d) depicting the corresponding excitation and emission peak shifts of figure 8.4(a) and 8.4(b) respectively. The CIE co-ordinates shift toward the longer wavelength for Gd^{3+} substitution and to the shorter wavelength of the CIE map for Ga^{3+} substitution. The CIE (x,y) color coordinates of $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ and $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ are $(0.5, 0.49)$, $(0.47, 0.53)$ and $(0.53, 0.47)$ respectively. To generate white light for indoor illumination, a white LED combines the blue light emitted from the LED chip with the yellowish emission from the phosphor [15]. The wavelengths of the blue light (excitation) source are 462 nm, 438 nm and 467 nm with the chromaticity point located at $(0.14, 0.09)$, $(0.16, 0.05)$ and $(0.13, 0.13)$ for $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ and $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$.

8.3.3. UV-VIS analysis

Figure 8.6(a) shows how absorption is influenced by substitution of Y^{3+} with Gd^{3+} and Al^{3+} with Ga^{3+} in the $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ garnet structure. The absorption bands of the color centers were found to be broad and peaked approximately at 457, 432 and 460 nm for $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ and $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ powders respectively in the range between 250 nm and 500 nm. Each spectrum showed two absorption peaks corresponding with the PL excitation wavelengths of each sample as shown in figure 8.4(a). Also the main peaks shifted to lower wavelength, 432 nm for Ga^{3+} and higher absorption wavelength, 460 nm for Gd^{3+} substitutions with respect to 458 nm for $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$. Absorption intensities also vary with highest for Gd^{3+} and lowest for Ga^{3+} as compared with $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$. The optical band gap of $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ is

in the order of 6.6 eV in which the valence band comprise of filled oxygen 2p orbitals while the conduction band consist of yttrium 4d orbitals [17].

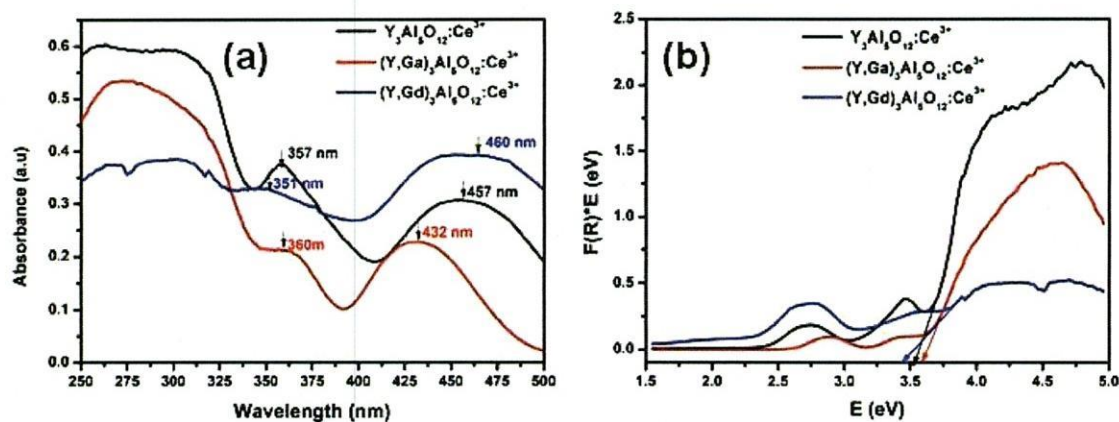


Figure 8.6: UV-VIS absorption spectra and (b) Tauc's plot for $Y_3Al_5O_{12}:Ce^{3+}$, $Y_3(Al,Ga)_5O_{12}:Ce^{3+}$ and $(Y,Gd)_3Al_5O_{12}:Ce^{3+}$.

The absorption coefficient spectra were obtained by converting from the reflectance spectra with the Kubelka-Munk function;

$$F(R) = \frac{(1-R)^2}{2R} = \frac{k}{s} = \frac{Ac}{s} \dots\dots\dots 8.3$$

Where R is the absolute reflectance, k the molar absorption coefficient, s the scattering coefficient, c concentration of the absorbing species and A the absorbance. This equation is usually applied to materials that have high light scattering and absorbing particles in their structures [19]. Equation 8.3 can be modified by multiplying the $F(R)$ function by $h\nu$ i.e.

$$(F(R) * h\nu)^n \dots\dots\dots 8.4$$

Where h is the Planck's constant and n the value of the type of transition whereby, $n = 1/2$ for a direct allowed transition, $n = 2$ for non-metallic materials, $n = 3/2$ for a direct forbidden transition, $n = 2$ for an indirect allowed transition and $n = 3$ for an indirect forbidden transition. The optical band gap energies (E_g)(eV) were estimated from the intercept of the extrapolated linear portion from the high slope region of the $(F(R) * h\nu)^n$ versus $h\nu$ plot known as Tauc's plot along the $h\nu$ axis [19] as shown in figure 8.5(b). It can be seen that (E_g) is greatly influenced by the presence of the incorporated substituent ions (Ga^{3+} and Gd^{3+}) in the matrix of the host $Y_3Al_5O_{12}:Ce^{3+}$. $E_g \approx 3.3, 3.5$ and 3.6 eV for $(Y,Gd)_3Al_5O_{12}:Ce^{3+}$, $Y_3Al_5O_{12}:Ce^{3+}$ and $Y_3(Al,Ga)_5O_{12}:Ce^{3+}$ respectively. The band gap energies are seen to correspond with the energy

difference between the lowest 5d level and the ground state of 4f configuration of Ce^{3+} as represented in the schematic energy diagram of figure 8.5(a). As the crystal field splitting of 5d energy levels of the Ce^{3+} ion increases (in case of $\text{Y,Gd}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$) or decreases (in case of $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$) the more/less splitting occurs respectively and push the lowest excited 5d state of Ce^{3+} to lower energies.

8.3.4. Thermoluminescence

In order to understand the nature of traps, trapping levels/energies and de-trapping mechanisms [20] and how these could be affected by substitution of the trivalent cations; Ga^{3+} and Gd^{3+} into the host ($\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$) lattice, thermoluminescence (TL) of the $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ and $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ samples were investigated. TL is the emission of light from an insulator or a semiconductor following the previous absorption of energy after exposure to a certain radiation [21]. The aim of the exposure to radiations is to dislodge electrons and excite them from impurity levels within the crystal lattice into the conduction band. The electrons will then be captured by the intentional or unintentional traps within the band gap of the material [22]. Upon heating, the trapped electrons relax back to their normal, stable, lower-energy positions, releasing energy in the process [23]. The traps are then analyzed during the TL measurement by heating the sample. During the TL measurements, the samples were exposed to UV radiation for the same period of time (5 minutes) and the temperature, T ($^{\circ}\text{C}$) was increased linearly at a heating rate (β) of 1°C/s as a function of time $t(\text{s})$ and the glow curves of intensity (I) as a function of temperature (T ($^{\circ}\text{C}$)) recorded shown in figure 8.7(a). The temperature of the TL peak position represents the trap depth/level while the intensity represents the number of traps within the band gap and energy corresponding to the glow peak is equal to the trap depth [13].

The glow curves for $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ and $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ feature two peaks each; one distinguished maximum peak temperature (T_m) at 74°C and a shoulder at 163°C for $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ and at 87°C and 146°C for $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, while that of $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ features only one peak at 162°C . The three peaks at 146°C for $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ and 163°C for $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ and 162°C for $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ might be equivalent to deeper traps [24] although the first two have low intensity compared to the last one. Low intensity of the phosphor can be attributed to the presence of insufficient number of shallow traps while deeper trap density is related to longer decay times. Since the concentration of Ce^{3+} remains constant in all the samples, the observed changes in the peak position and intensity could only be due to the substitution of Ga^{3+} and Gd^{3+} into the host ($\text{Y}_3\text{Al}_5\text{O}_{12}$) lattice.

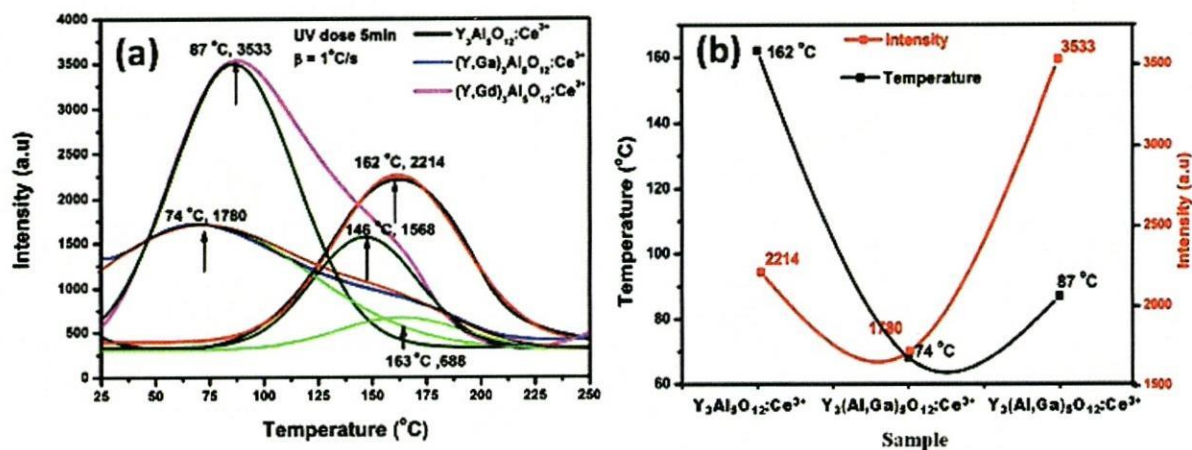


Figure 8.7: (a) Fitted TL glow curves and (b) Peak temperature and intensity curves for the $Y_3Al_5O_{12}:Ce^{3+}$, $Y_3(Al,Ga)_5O_{12}:Ce^{3+}$ and $(Y,Gd)_3Al_5O_{12}:Ce^{3+}$ samples.

As shown in figure 8.7(b), the highest TL signal was observed for $(Y,Gd)_3Al_5O_{12}:Ce^{3+}$ with peak at 87 °C followed by $Y_3Al_5O_{12}:Ce^{3+}$ at 162 °C and the lowest $Y_3(Al,Ga)_5O_{12}:Ce^{3+}$ at 74 °C suggesting presence of trap levels. It has been explained elsewhere that the trap depth is directly proportional to the glow peak maximum [25] therefore the trap depth of the samples in descending order is $Y_3Al_5O_{12}$ host > $(Y,Gd)_3Al_5O_{12}$ host > $Y_3(Al,Ga)_5O_{12}$ host. It was also observed from TL peak measurements that the energy traps of trivalent rare earth ions are in the order; $Yb^{3+} > Sm^{3+} > Dy^{3+} > Pr^{3+} > Nd^{3+} > Er^{3+} > Ce^{3+} > Gd^{3+} > La^{3+}$ [26] which is in agreement with our results. Also it has been explained by Fasoli et al (2011) [27] that Ga^{3+} doping prevents the trapping of free carriers due to shallow traps since it does not reduce the defect concentration but rather causes changes in the valence and conduction bands such that the energy level of shallow defects is no longer in the forbidden gap where electrons can be trapped. Shallow traps are detrimental to the performance application of $Y_3Al_5O_{12}:Ce^{3+}$ in Scintillators but modifications of the band gap via substitution of Ga^{3+}/Gd^{3+} can help suppress the effect [27].

Conclusion

In this study we investigated the structural and optical properties of commercial $Y_3Al_5O_{12}:Ce^{3+}$ phosphor with regards to the substitution of Al^{3+} with Ga^{3+} and Y^{3+} with Gd^{3+} in the $Y_3Al_5O_{12}:Ce^{3+}$ garnet structure. It was found that the diffraction peaks slightly shifted to the lower angles for $Y_3(Al,Ga)_5O_{12}:Ce^{3+}$ and slightly to higher angles for $(Y,Gd)_3Al_5O_{12}:Ce^{3+}$ with reference to $Y_3Al_5O_{12}:Ce^{3+}$. This shift was attributed to ionic size differences; Gd^{3+} being larger than that of Y^{3+} and that of Ga^{3+} larger than Al^{3+} . Replacing Y^{3+} with Gd^{3+} and Al^{3+} with Ga^{3+} caused lattice expansion/contraction that lead to an increase/decrease in the crystal-field

interaction of Ce^{3+} . The broad band excitation 462 nm and emission 578 nm for $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ were due to the 4f-5d electronic transition of Ce^{3+} ion. The UV absorption bands were found to be broad and peaked approximately at 457, 432 and 460 nm for $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ and $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ powders respectively. The highest TL signal was observed for $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ with peak at 87 °C followed by $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ at 162 °C and the lowest $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ at 74 °C suggesting existence of trap levels.

References

- [1] V. M. Bachmann, *PhD Thesis*, Utrecht Univeristy, 1977.
- [2] J. Li, J. G. Li, Z. Zhang, X. Wu, S. Liu, X. Li, X. Sun, Y. Sakka, *Sci. Technol. Adv. Mater.*, **13** (2012) 035007.
- [3] M. J. Kim, J. H. Park, K. Y. Lee, S. Lee, G. Han, H. J. Song, H. Shin, T. K. Ahn, H. S. Jung, *Appl. Mater. interfaces*, **6** (2014) 1145.
- [4] M. Marius, E. J. Popovici, L. Barbu-Tudoran, E. Indrea, A. Mesaros, *Ceram. Int.*, **40** (2014) 6233.
- [5] M. Upasani, B. Butey, S. V. Moharil, *J. Appl. Phys.*, **6** (2014) 28.
- [6] E. J. Popovici, M. Morar, E. Indrea, *J. Opto.Elect. and Adv.Mater.*, **13** (2011) 617.
- [7] Y. X. Pan, W. Wang, G. K. Liu, S. Skanthakumar, R. A. Rosenberg, X. Z. Guo, K. K. Li, *J. Alloys Compd.*, **488** (2009) 638.
- [8] S. J. Liu, T. J. Peng, Z. Song, L. Bian, G. B. Song, Q. L. Liu, *Chinese Phys. B*, **23** (2014) 048106.
- [9] Y. Xu, W. Y. Ching, *Phys. Rev. B*, **59** (1999) 530.
- [10] A. Yousif, H. C. Swart, J. J. Terblans, R. M. Jafer, V. Kumar, R. E. Kroon, O. M. Ntwaeaborwa, M. M. Duvenhage, *Appl. Surf. Sci.*, **305** (2014) 732.
- [11] J. Li, J. G. Li, S. Liu, X. Li, X. Sun, Y. Sakka, *Sci. Technol. Adv. Mater.*, **14** (2013) 054201.
- [12] H. Yang, L. Yuan, G. Zhu, A. Yu, H. Xu, *Mater. Lett.*, **63** (2009) 2271.
- [13] C. Burda, X. Chen, R. Narayanan, M. A. El-sayed, *Chem. Rev.* **105** (2005) 1025.
- [14] S. Murai, M. A. Verschuuren, G. Lozano, G. Pirruccio, A. F. Koenderink, J. G. Rivas, *Opt. Soc. Am.*, **2** (2012) 1707.
- [15] C. C. Chiang, M. S. Tsai, M. H. Hon, *J. Electrochem. Soc.*, **154** (2007) 326.
- [16] M. Nazaraov, *Mold. J. Phys. Sci.*, **4** (2005) 347.
- [17] S. T. S. Dlamini, H. C. Swart, J. J. Terblans, O. M. Ntwaeaborwa, *Solid State Sci.*, **23**, (2013) 65.
- [18] S. S. Uysal, A. Ege, M. Ayvacikli, A. Khatab, E. Ekdal, E. J. Popovici, M. Henini, N. Can, *Opt. Mater. (Amst.)*, **34** (2012) 1921.
- [19] L. Rosendo, G. Ricardo, *J. Sol-Gel Sci Technol*, **61**, (2012) 1.
- [20] N. L. Hom, *PhD Thesis*, Saga University (Japan), 2010.

- [21] M. Ziyauddin, N. Brahme, D. P. Bisen, R. S. Kher, *Recent Res. Sci. Technol.*, **4** (2012) 9.
- [22] F. You, A. J. J. Bos, Q. Shi, S. Huang, *J. Phys. Condens. Matter*, **23** (2011) 215502.
- [23] D. S. Kshatri, A. Khare, P. Jha, *chalcogenide Lett.*, **10** (2013) 121.
- [24] A. H. Wako, B. F. Dejene, H. C. Swart, *Phys. B Condens. Matter*, **439** (2014) 153.
- [25] K. W. Boon, *PhD Thesis*, University of Texas, **2010**.
- [26] E. Nakazawa, Y. Murazaki, S. Saito, *J. Appl. Phys.*, **100** (2006) 113113
- [27] M. Fasoli, A. Vedda, M. Nikl, C. Jiang, B. P. Uberuaga, D. A. Andersson, K. J. McClellan, C. R. Stanek, *Phys. Rev. B*, **84**, (2011) 081102.

Chapter 9

Trap characteristics of UV-activated $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ phosphors

9.1. Introduction

In recent years, oxide materials based on the garnet structure have attracted a lot of scientific and industrial interest around the world, as they offer excellent properties such as wide band gap, good chemical, thermal and radiation resistance and excellent radiation conversion efficiency [1]. Being one of the most common host materials, yttrium aluminum garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$, or YAG) has been studied for a variety of applications, for example general lighting, cathode ray tubes (CRT's), solid-state lasers and scintillators [2] among many others.

Thermoluminescence (TL) is the emission of light from insulators or semiconductors when they are thermally stimulated following the previous absorption of energy from radiation [3]. TL measurement is a very important and convenient method of investigating materials and provides important information on the nature of the traps, trapping energies and de-trapping mechanisms in crystals [4]. During TL measurements the TL spectrum is obtained by initially filling the traps at low (room) temperatures using UV or other radiation and then raising the temperature at a constant heating rate (β) [5]. The monochromatic radiation does the work of exciting electrons from within the band gap into the conduction band (CB) generating free charge carriers (electrons and holes) which may be captured in available trapping centers and occupy levels at a trap depth (E_t) below the CB [6]. The radiation dislodge electrons within the lattice structure of the material and the trapped electrons return to their normal, stable lower-energy positions, releasing energy during the TL heating process [7].

When activated with the right amount and type of radiation, it was confirmed that the rare-earth (RE^{3+}) ions such as co-dopants work as traps of photo-carriers within the band gap of the material [8]. Formation of an electron or a hole- trap by a defect depends on the energy level position of the RE^{3+} ions within the host band gap [9]. The charge carriers trapped at different depths causes various decay components, because the recombination between the excited electron and trapped hole is influenced greatly by the trap depth (E_t) [10]. If the depth of trap level is too shallow, the phosphor would exhibit fast decay or fluorescence and if it is too deep, the phosphor would hardly show any luminescence at room temperature. Hence, it is important for a material to have trapping level at a suitable depth in relation to the thermal release rate at

room temperature [5]. The life time of the phosphor is dictated by the activation energy or trap depth of the hole/electron captured by the RE^{3+} ions and the intensity of the phosphorescence is determined by the density or amount of the trapped holes/electrons and the rate of decay.

TL spectrum shows glow intensity as a function of temperature resulting in what is known as a glow curve. Analysis of the glow curve is one of the most significant ways to measure the number of traps and also the activation energy of the trap levels in luminescent materials. The TL glow curve is associated with the trap levels situated at different depths in the band gap between the conduction (CB) and the valence bands (VB) of a solid [11]. The depth of the traps (E_t) and their concentration (n_0) in the phosphors can be obtained by analyzing the TL spectrum [12]. The depth of each trap can be estimated from the peak temperature. Usually glow curves above room temperature feature one or several distinguished peaks and the energy corresponding to the glow peak is equal to the trap depth.

Several reports are available on the different TL techniques used to monitor the trapping states in materials such as initial rise method [2,4,7], glow curve deconvolution (GCD) [13] and peak shape method [12,14]. In this paper we use the variable heating rate method, peak shape method and TL Anal Glow Curve Deconvolution (GCD) program to determine the activation energies, trap depths, pre-exponential or frequency factor (s) of the traps associated with corresponding TL peaks in a commercially obtained $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ phosphor.

9.2. Experimental

Samples of commercially available $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ phosphor powders were obtained from Phosphor Technology (UK). The structural and phase compositions were determined using a Bruker-AXS D8 Advance x-ray diffractometer (Bruker Corporation of Germany) operating at 40 kV and 4 mA using $\text{Cu K}\alpha = 0.15406 \text{ nm}$ from 15° to 65° (2θ), with a scan rate of 0.39° (2θ)/min and step scans with a step size of 0.02° (2θ). The TL studies were carried out above room temperature using a TL 10091 Thermoluminescence Reader system with PMT type 9924 B supplied by M/s Nucleonix Systems Pvt. Ltd., India interfaced to a PC where the TL signals were analyzed to investigate traps and defects in the phosphor powders. The PMT tube has sufficient response over a wide spectral range. In order to fill the available traps, the samples were at first excited for 3, 5, 10 and 15 minutes using a 254 nm UV radiation standard lamp with a power of 15 W. Then the radiation source was removed and the samples were heated at various linear rates of 0.5, 0.8, 1.0, 1.2, 1.6, 2 and 2.5°Cs^{-1} to induce thermal release or de-trapping of the charge carriers. By varying the temperature as a function of the intensity, the TL spectrum was obtained displaying the integrated TL yield. During all the TL experiments, 20 mg of the sample was used and the glow peaks were recorded from RT to 300°C .

9.3. Results and Discussion

9.3.1. XRD Analysis

XRD pattern and standard of the $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ phosphor powder is shown in figure 9.1. The peaks indexed well with the JCPDS card number 89-6660. It has a bcc structure of space group I a-3d (230) with 160 atoms in the cubic (primitive) cell and cell parameters; $a=12.1552(6)$ Å; $\beta=90^\circ$, cell ratio; $a/b=1.0$, $b/c=1.0$, $c/a=1.0$ and cell volume 1795.92 Å³.

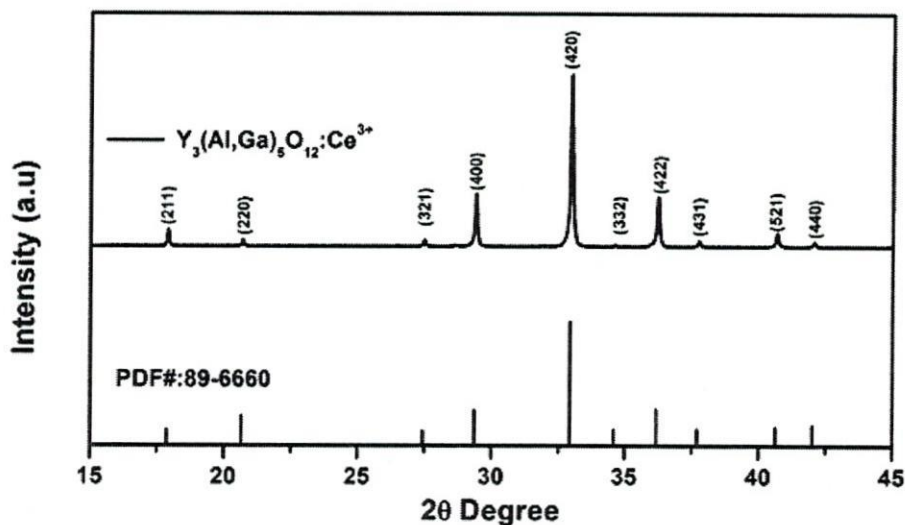


Figure 9.1: XRD pattern of the $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ phosphor powder indexed with JCPDS card # 89-6660.

9.3.2 PL Analysis

Figures 9.2(a) and (b) show the PL excitation and emission spectra recorded from the as-prepared commercially obtained $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ powders. The PL emission spectra from the powder sample with a maximum in the yellow region at 560 nm is a broad band ranging from 550 nm to 650 nm corresponding to the 440 nm blue excitation due to the 4f-5d electronic transition of Ce^{3+} attributed to the de-localization of electrons from the lowest 5d level to the crystal field split $4f(^2F_{5/2} / ^2F_{7/2})$ levels of Ce^{3+} .

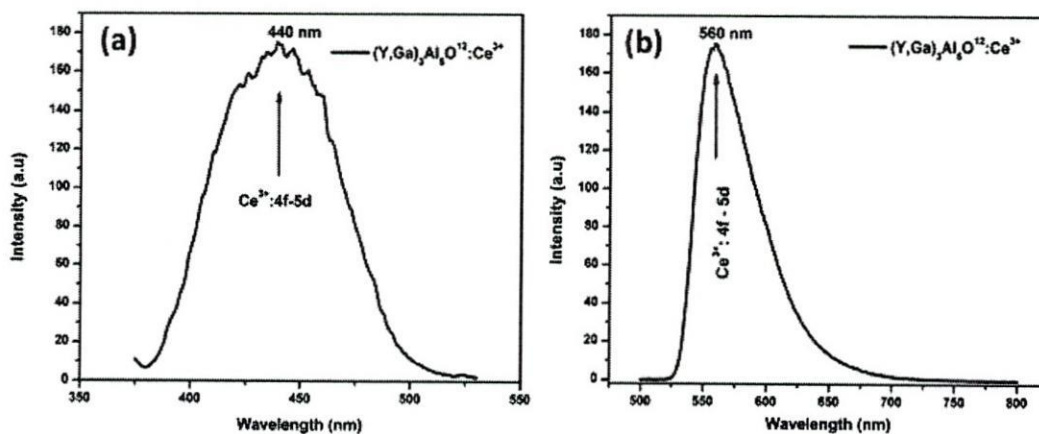


Figure 9.2: (a) Room temperature PL excitation and (b) emission spectra of $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ phosphor powder.

9.3.3. TL Glow Curves

Room temperature TL glow curves of the $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ recorded after irradiation with different UV exposure times as the temperature was increased linearly as a function of time at the rate of $1\text{ }^\circ\text{C s}^{-1}$ are shown in figure 9.3. The intensity of the glow curves is already high at room temperature due to contributions from the photoluminescence effect of the UV excited $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ phosphor material whereby as soon as the UV irradiation stops the filled electron traps begin to empty starting with room and as the temperature is increased during the TL process. The glow curves consists of two thermal peaks each indicating that more than one type of trap is involved.

From the fitted glow curve of figure 3(b), the main peak is centred at $74\text{ }^\circ\text{C}$ and the other on the higher temperature side at $163\text{ }^\circ\text{C}$ suggesting availability of two un-equivalent trap types; shallow and deep respectively. The peak at around $74\text{ }^\circ\text{C}$ is intense which is an indication of the presence of a sufficient number of shallow traps (trap 1) which means that the charge carriers do not migrate far away from the conduction band (CB) thus bringing about fast decay and the shoulder at around $163\text{ }^\circ\text{C}$ suggests the existence of a fewer deep traps (trap 2) which could be responsible for longer decay times or no emission owing to its depth. It has also been shown that Ce^{3+} favours fast decay times as short as 25-30 ns [15] and can therefore be ascribed to the shallow traps at $74\text{ }^\circ\text{C}$ since the trap depth is directly proportional to the maximum glow peak.

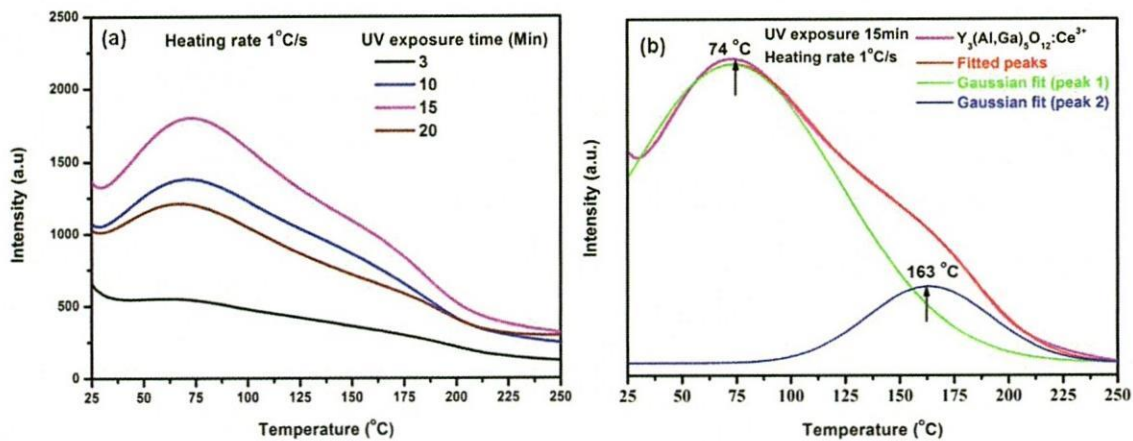


Figure 9.3: (a) Glow curves showing TL variation with UV radiation time (b) Deconvolution of peaks 1 and 2.

As can be seen from figure 3, the form of the glow curves remains the same without any observable change, except for a slight shift in peak positions, as we increased the UV dose. It has been reported that the large unit cell of YAG is prone to many defect sites and impurities especially at high temperatures due to a resultant lattice strain which arise from the presence of other RE^{3+} ion impurities or heterovalent impurity species [16].

Luminescence involves two kinds of active centers: emitters and traps. In $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ crystals Ce^{3+} is an emitter, while Al^{3+} and Ga^{3+} form substitutional defects that serve as trapping centers. The faster decay speed or fluorescence emission of Ce^{3+} is due to the existence of shallow traps nearby Ce^{3+} ions. When Ce^{3+} is excited with UV radiation generating free charge carriers (electrons and holes), electrons in the valence band (VB) of the host lattice or the ground state of activator ions are raised to the conduction band (CB) of $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ where they propagate. Some of the excited electrons relax and maybe captured by a trapping defect, Al/Ga substitutional defects or oxygen defects and are stored there. The holes resulting from this capture can also migrate in the VB and are trapped by Ce^{3+} ($\text{Ce}^{3+} + \text{h}^+ \rightarrow \text{Ce}^{4+}$). Upon thermal activation those electrons are released from the Al/Ga or oxygen defects back to the CB diffuse and relax to the excited state of the activators while the trapped hole is released back to the VB; this initiates a reverse process in which the hole recombines with the electron in the shallow Ce^{3+} (Ce^{4+}) site yielding the characteristic Ce^{3+} fluorescence emission [6,17]. If electron-hole pairs recombine immediately and emit a photon it is known as fluorescence [18] which explains the fluorescence nature of Ce^{3+} . Trapping from the conduction band to shallow traps or from shallow traps to deep traps can be the cause of the fast decay.

The peak at around 163 °C which might be equivalent to a deeper trap could therefore be attributed to traps arising from Al/Ga substitution defects induced by lattice disorder due to the

difference between the ionic radii of Al^{3+} and Ga^{3+} . Ga^{3+} acts to provide hole-trap by occupying the Al^{3+} vacancy sites and this would mean distorted Ce^{3+} sites, which would act as a trap for excited Ce^{3+} electrons. The electron-hole recombination mediated by deep trap states within the band gap may be responsible for a slower decay component. It was reported elsewhere that the presence of shallow traps was detrimental to scintillation performance of $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ [19] a problem which was overcome by tailoring the composition by introducing Ga^{3+} into the band gap of the $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ a strategy that favoured positioning of the $5d^1$ level of Ce^{3+} [20]. Since the density or amount of the traps and the rate of decay corresponds to the peak intensity of the glow curve, the electronic relaxation in $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ has a dominant fast luminescence decay due to a higher concentration of charge carrier captured in the shallow trap sites around 74 °C and a slower less dominant decay component due to deep trapping around 163 °C. Thus substitution of Ga^{3+} into the YAG: Ce^{3+} reduces the number of traps and lowers the TL signal. Previous studies have shown that substitution of Gd^{3+} for the rare-earth ion (Lu^{3+} or Y^{3+}) lowers the TL signal while samples with Y^{3+} have lower TL compared to those with Lu^{3+} [2]. Mutual change in the shape and intensity of the peaks corresponding to shallow traps in a glow curve compared with that of deeper traps may indicate the existence of inter-trap charge transfer. Electrons de-trapped from the shallower trap may be captured by the deeper trap or luminescence centre as the temperature is raised [21].

9.3.4. UV Exposure

From figure 9.4(a) we observe that with increasing UV irradiation/exposure time from 3 - 20 min, the position of the thermal peak maximum (T_{max}) of the glow curves shifted to higher temperatures and then to the lower temperatures. The shift in the TL peaks can be attributed to be due to the different rates at which the traps get filled [22]. This shift is also an indication that second order recombination kinetics could be taking place in which case a re-trapping process of the excitation occurs. First order kinetics occurs when the glow curve peak maximum (T_{max}) is independent of the dose absorbed by the material [6, 23, 24] such that the first order kinetic equations for the calculation of relevant trapping parameters may be applicable. A part from the variation of T_{max} , the shape of the glow curve can also give an indication of the order of kinetics whereby it is asymmetrical for first order and symmetrical for second order respectively. However the symmetrical shape or broadness of a glow curve may also be because of the presence of other several overlapping first order peaks and not due to the existence of second order kinetics [23].

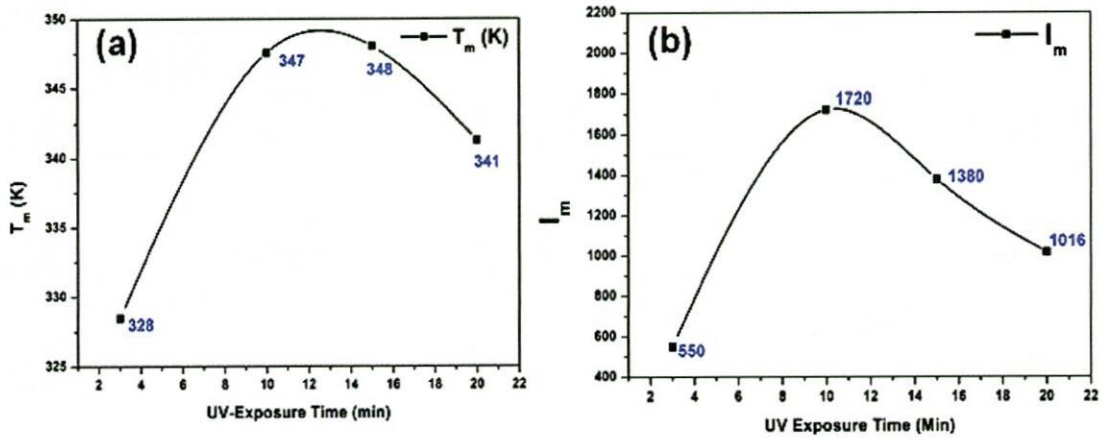


Figure 9.4: Variation of (a) $T_{\max}$ (K) and (b) $I_{\max}$ with UV exposure time.

A sharp rise in the TL maximum intensity ($I_{\max}$) was observed for the dominant peak as shown in figure 9.4(b). The TL intensity initially increased with increase in irradiation time and tends to saturate at 10 minutes and then drops with further exposure.

9.3.5. Heating rate method

The TL glow curves of $Y_3(Al,Ga)_5O_{12}:Ce^{3+}$ under different heating rates (β) are shown in figure 9.5.

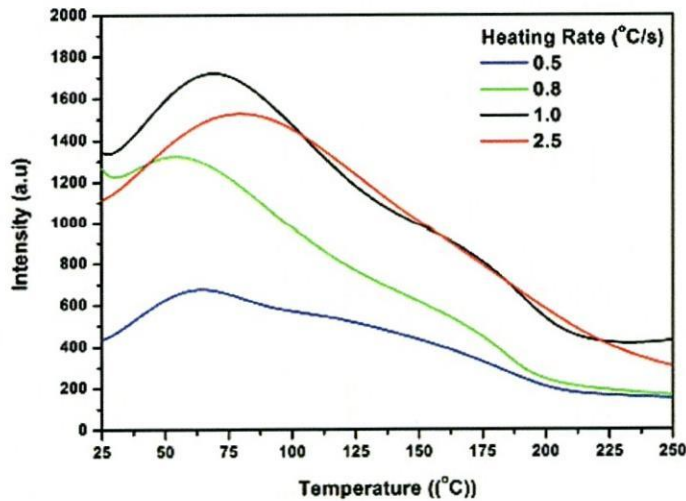


Figure 9.5: TL glow curves showing the effect of heating rate variation as a function of temperature.

The maximum temperature peak position ($T_{\max}$) shifted to a higher temperature when the heating rate was increased as seen in figure 9.6(a). Similarly the Peak intensity ($I_{\max}$) increased linearly with the heating rate as seen in figure 9.6(b).

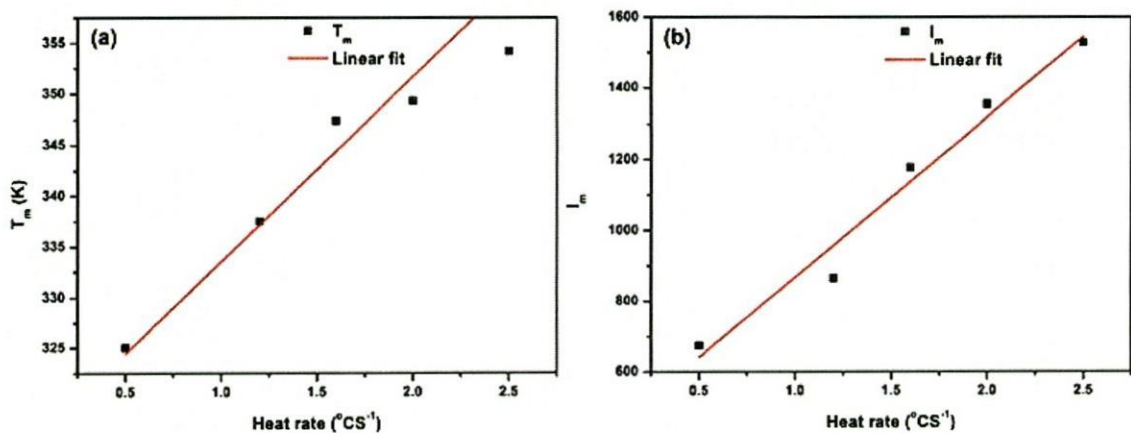


Figure 9.6: Variation of (a) $T_{\max}$ and (b) $I_{\max}$ with heating rate.

Due to the shift of $T_{\max}$ to a higher temperature when the heating rate β (in $^{\circ}\text{C s}^{-1}$) increased, we employed the Hoogenstraaten method which relates the TL peak temperature (T_m) and heating rate (β) [9,25,26] using the following equation:

$$\ln\left(\frac{T_{\max}^2}{\beta}\right) = \frac{E}{kT_{\max}} + \ln\left(\frac{E}{sk}\right) \dots\dots\dots 9.1$$

to determine the activation energy or trap depth, where E is the activation energy or trap depth, k is the Boltzmann constant, β is the heating rate, s the frequency factor in s^{-1} and T_m represents the glow peak temperature. The resultant plot of $\ln\left(\frac{T_{\max}^2}{\beta}\right)$ versus $\frac{1}{kT_{\max}}$ also known as Hoogenstraaten plot, yields a straight line with slope E and intercept $\ln\left(\frac{E}{sk}\right)$.

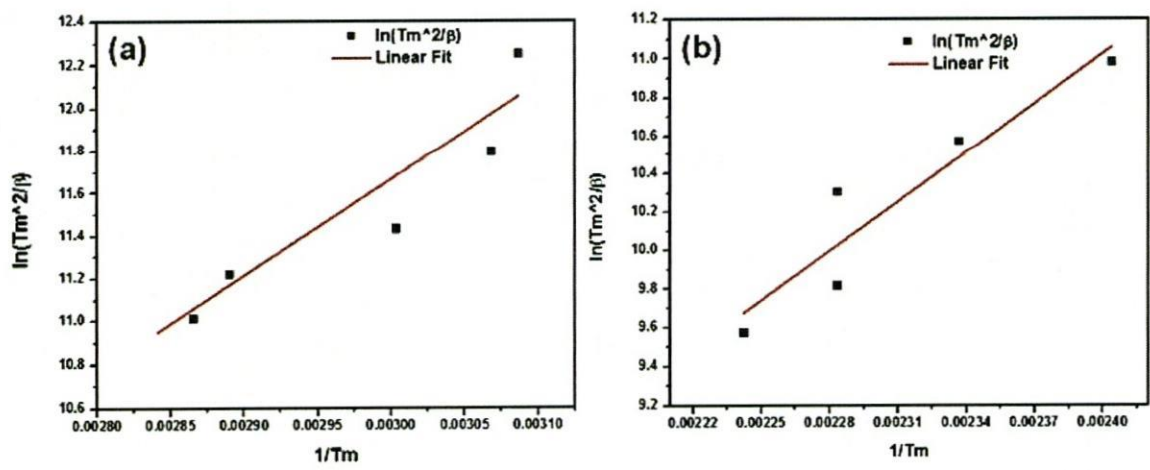


Figure 9.7: Hoogenstraaten plots showing the dependence of the peak temperatures ($T_{\max}$) of the $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ glow curves on the heating rate (β).

Figure 9.7 (a) and (b) shows the Hoogenstraaten plots calculated from the TL glow curve of the $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ phosphor at different heating rates. Both the lower and higher temperature

side peaks showed a linear relationship. The plots of the dominant lower temperature side peak gave a slope of 0.39 ± 0.08 eV as the trap depth as compared to 0.74 ± 0.15 eV calculated from slope of the less dominant peak on the higher temperature side.

In this result, the depth of trap 1, attributed to be originating from Ce^{3+} ion incorporation, was 0.39 ± 0.08 eV and the depth of Trap 2, due to Ga^{3+} ion substitution, was 0.74 ± 0.15 eV. This clearly supports the idea that Ce^{3+} form shallow traps and hence decays faster as compared with the emission due to Ga^{3+} ion substitution which forms too deep trap from which emission may not be realised at all. The corresponding frequency factors s (s^{-1}) calculated from the intercept, $\ln\left(\frac{E}{sK}\right)$ of Eq. (1) were $2.93 \times 10^4 \text{ s}^{-1}$ and $1.2 \times 10^8 \text{ s}^{-1}$ for trap 1 and trap 2 respectively.

9.3.6. Peak shape method

Due to the symmetrical nature of the glow curves, and for comparison we also used Chen's second order kinetic equation [27],

$$E = 3.54 \left(\frac{KT_{max}^2}{\omega} \right) - 2KT_{max} \dots \dots \dots 9.2$$

based on the peak shape method to estimate the activation energy needed to de-trap charge carriers from the trap centers, where E is the activation energy/trap depth in eV, $k = 8.617 \times 10^{-5} \text{ eV K}^{-1}$ is the Boltzmann's constant, T_{max} is the temperature corresponding to the maxima of a thermal peak and ω is the FWHM of the glow curve. The symmetry factor ($\mu = \delta/\omega = (T_2 - T_m)/(T_2 - T_1)$) (where T_m is the peak temperature at maximum intensity, T_1 and T_2 the lower- and upper-temperatures at half intensity) has been found to be approximately 0.52 for all glow curves, which indicates second order kinetics [28]. From the equation and the shape of the glow curve it can be inferred that the rate of thermal activation is proportional to the rate of thermal release of the trapped charge carriers [14]. The corresponding frequency factor s (s^{-1}) which is the frequency of an electron escaping the trap can be calculated using the Garlick and Gibson second order kinetics formula [29] as given by equation 9.3;

$$s = \frac{\beta E}{\kappa T_{max}^2} \frac{1}{1 + \frac{2\kappa T_{max}}{E}} \exp\left(\frac{E}{\kappa T_{max}}\right) \dots \dots \dots 9.3$$

The values of the activation energies and frequency factors for trap 1 and 2 calculated from some of the glow curves at different heating rates using equation 9.2 and 9.3 are presented in table 9.1.

Table 9.1: Characteristic parameters of traps associated with TL peaks in $Y_3(Al,Ga)_5O_{12}:Ce^{3+}$.

PEAK 1	Freq. factor(s)								
	T _m (K)	E _t (eV)	0.5°C/s	0.8°C/s	1°C/s	1.2°C/s	1.6°C/s	2°C/s	2.5°C/s
	324	0.24	6.42E ⁰⁶	1.03E ⁰⁷	1.28E ⁰⁷	1.54E ⁰⁷	2.05E ⁰⁷	2.57E ⁰⁷	3.21E ⁰⁷
	326	0.20	1.36E ⁰⁵	2.17E ⁰⁵	2.72E ⁰⁵	3.26E ⁰⁵	4.35E ⁰⁵	5.44E ⁰⁵	6.80E ⁰⁵
	342	0.25	3.86E ⁰⁶	6.18E ⁰⁶	7.72E ⁰⁶	9.27E ⁰⁶	1.24E ⁰⁷	1.54E ⁰⁷	1.93E ⁰⁷
	333	0.21	2.41E ⁰⁵	3.86E ⁰⁵	4.83E ⁰⁵	5.79E ⁰⁵	7.73E ⁰⁵	9.66E ⁰⁵	1.21E ⁰⁶
	346	0.23	5.50E ⁰⁵	8.80E ⁰⁵	1.10E ⁰⁶	1.32E ⁰⁶	1.76E ⁰⁶	2.20E ⁰⁶	2.75E ⁰⁶
	349	0.21	1.04E ⁰⁵	1.66E ⁰⁵	2.07E ⁰⁵	2.49E ⁰⁵	3.31E ⁰⁵	4.14E ⁰⁵	5.18E ⁰⁵
	352	0.22	2.04E ⁰⁵	3.23E ⁰⁵	4.07E ⁰⁵	4.89E ⁰⁵	6.52E ⁰⁵	8.14E ⁰⁵	1.02E ⁰⁶
Average:		0.23	1.64E ⁰⁶	2.63E ⁰⁶	3.29E ⁰⁶	3.95E ⁰⁶	5.26E ⁰⁶	6.58E ⁰⁶	8.22E ⁰⁶

PEAK 2	Freq. factor(s)								
	T _m (K)	E _t (eV)	0.5°C/s	0.8°C/s	1°C/s	1.2°C/s	1.6°C/s	2°C/s	2.5°C/s
	416	0.69673	5.69E ¹⁷	9.11E ¹⁷	1.14E ¹⁸	1.37E ¹⁸	1.82E ¹⁸	2.28E ¹⁸	2.85E ¹⁸
	428	0.77264	1.96E ¹⁹	3.13E ¹⁹	3.91E ¹⁹	4.69E ¹⁹	6.26E ¹⁹	7.82E ¹⁹	9.78E ¹⁹
	438	0.86445	1.89E ²¹	3.03E ²¹	3.78E ²¹	4.54E ²¹	6.05E ²¹	7.57E ²¹	9.46E ²¹
	424	0.59787	3.92E ¹⁴	6.27E ¹⁴	7.84E ¹⁴	9.41E ¹⁴	1.25E ¹⁵	1.57E ¹⁵	1.96E ¹⁵
	438	0.91235	3.72E ²²	5.96E ²²	7.45E ²²	8.93E ²²	1.19E ²³	1.49E ²³	1.86E ²³
	446	0.90656	9.28E ²¹	1.48E ²²	1.86E ²²	2.23E ²²	2.97E ²²	3.71E ²²	4.64E ²²
	448	0.76985	1.74E ¹⁸	2.79E ¹⁸	3.48E ¹⁸	4.18E ¹⁸	5.57E ¹⁸	6.97E ¹⁸	8.71E ¹⁸
Average:		0.79	6.92E ²¹	1.11E ²²	1.38E ²²	1.66E ²²	2.21E ²²	2.77E ²²	3.46E ²²

The calculated values of trap depth (E_t) which is similar to the activation energy, gave an average of 0.23 ± 0.1 eV and 0.79 ± 0.1 eV for trap 1 and 2 respectively. The value for peak 2 is quite comparable with 0.74 eV calculated from the Hoogenstraaten method using equation 9.1.

9.3.7. TL Anal GCD method

To further estimate the actual trap depths, a deconvolution of the glow curves with second order kinetics was carried out by using TL Anal GCD program. Figure 9.8 shows the deconvoluted glow curves for the different heating rates. The values of the activation energies and frequency factors for trap 1 and 2 estimated using TL Anal software for the different heating rates are given in table 9.2. This method gave values of trap depth (E_t) as 1.59 ± 0.1 eV and 2.14 ± 0.1 eV for trap 1 and 2 respectively. The corresponding frequency factors s (s⁻¹) were 7.61×10^{18} s⁻¹ and 6.9×10^{20} s⁻¹ for trap 1 and trap 2 almost in the same range as reported by Pitale et al (2008) using CGCD procedure [23]. The trap depths obtained in our results using the TL Anal GCD method are larger than those we obtained by Hoogenstraaten and peak shape methods. The discrepancy may be attributed to be as a result of a continuous trap depth distribution which

deforms the glow peaks and makes the simple glow peak models ill-suited. However it is still that assumed the figures due to Hoogenstraaten's method to be most reliable [30].

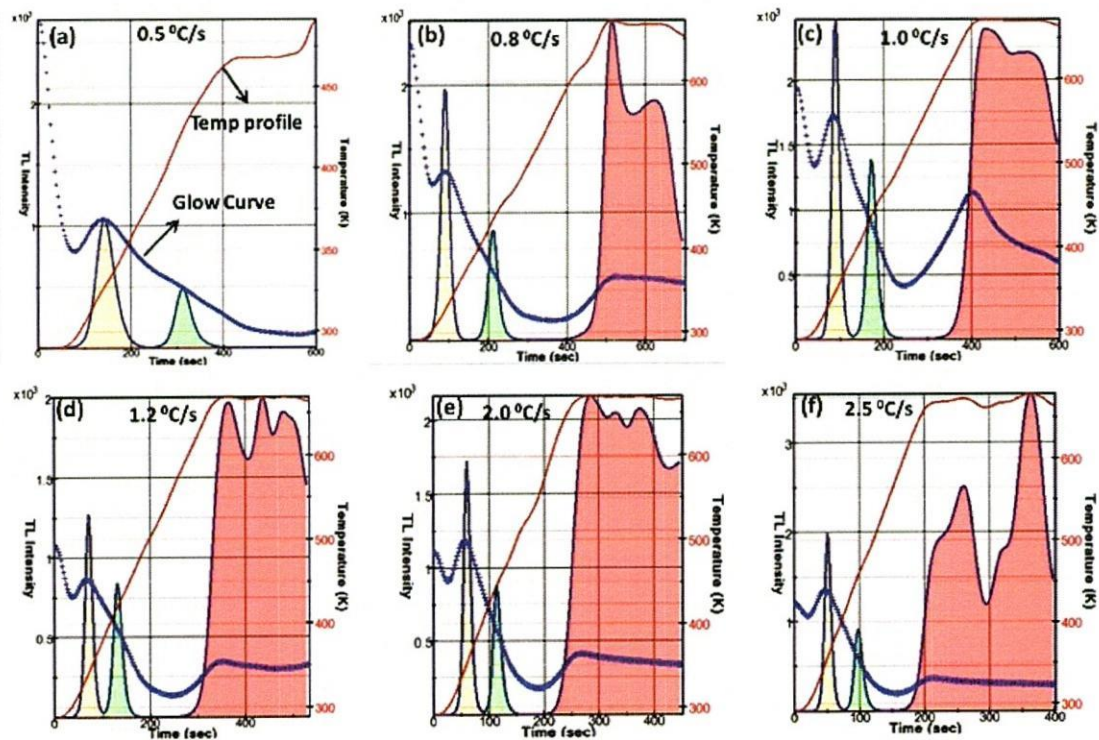


Figure 9.8: Deconvolution of the TL glow curve of the $Y_3(Al,Ga)_5O_{12}:Ce^{3+}$ powder with second order kinetics using TL Anal GCD program.

Table 9.2: Parameters of traps associated with TL peaks in $Y_3(Al,Ga)_5O_{12}:Ce^{3+}$.

Heating Rates (°C/s)	Trap Depth1 E_t (eV)	Freq. factor S (s ⁻¹)	Trap Depth2 E_t (eV)	Freq. factor S (s ⁻¹)
0.5	1.43	1.20E ¹⁶	2.03	4.59E ¹⁸
0.8	1.59	7.0E ¹⁸	2.09	6.68E ¹⁸
1.0	1.73	3.48E ¹⁹	1.92	3.71E ¹⁶
1.2	1.58	1.56E ¹⁸	2.04	2.05E ¹⁹
1.6	1.51	2.37E ¹⁶	2.31	1.39E ²¹
2.0	1.57	1.35E ¹⁷	2.13	3.80E ¹⁸
2.5	1.72	9.75E ¹⁸	2.49	3.43E ²¹
Average	1.59	7.61E ¹⁸	2.14	6.94E ²⁰

In another study, Piters et al (1999) also reported that although in some cases the deviation between the heating rate method and glow curve fitting method can be quite significant, the Hoogenstraaten's heating rate method remains a generally reliable method for determining TL trapping parameters of first order glow peaks [31]. In their study they attributed the deviation to be due to a systematic increase of a temperature lag between the measured and real temperature of the sample (i.e non-ideal heat transfer between heating element and sample) as the heating rate increased which affects the linear part of the heating rates plots more than has been previously realised. They concluded that the effect of the temperature lag on Hoogenstraaten's heating rate method is a decrease in activation energy and frequency factor and is more important for glow peaks with high activation energy and high frequency factor.

Also Sunta et al (1999) reported that the peak shape, general order peak fitting and initial rise methods of determining E values of TL glow peaks produce low values [32]. In the peak shape and general order fitting methods this happens when the retrapping probability is much higher than the recombination probability and the sample dose is higher thereby filling the traps up to near the saturation level. In the case of initial rise method it was because the exponential growth region of the TL intensity may be too weak to be measured above the instrumental back ground. The proposed the use of low sample doses for analysis of the glow peaks as a remedy for these discrepancies.

Conclusion

In this study we performed TL measurements on commercial $Y_3(Al,Ga)_5O_{12}:Ce^{3+}$ phosphor. Each of the glow curves consisted of two thermal peaks indicating existence of more than one type of trap; one of them is centred at 74 °C and the other on the higher temperature side at 163 °C corresponding to shallow and deep traps respectively. With increasing UV exposure time the position of the thermal peak maximum (T_m) of the glow curves shifted to higher temperatures and then to the lower temperatures. The TL intensity initially increased with an increase in UV exposure time and tends to saturate at after 10 min and then dropped with further exposure. The maximum temperature peak position (T_m) shifted to higher temperature when the heating rate was increased. The depth of trap 1, originating from Ce^{3+} ion was 0.39 ± 0.08 eV and the depth of Trap 2, originating from Ga^{3+} ion substitution, was 0.74 ± 0.15 eV as calculated from the Hoogenstraaten method. Values of trap depth (E_t) calculated using Chen's peak shape method gave an average of 0.23 ± 0.1 eV and 0.79 ± 0.1 eV for trap 1 and 2 respectively which was

quite comparable to 0.74 eV for trap 2 calculated from the Hoogenstraaten method. We observed that trap depths obtained with the TL Anal GCD method were much larger than those obtained by Hoogenstraaten and peak shape methods. The difference may be attributed to be a result of a continuous trap depth distribution which deforms the glow peaks and makes the simple glow peak models ill-suited. However it is still assumed that the figures due to Hoogenstraaten's method to be the most reliable.

References

- [1] J. Li, J.-G. Li, Z. Zhang, X. Wu, S. Liu, X. Li, X. Sun, Y. Sakka, *Sci. Technol. Adv. Mater.* **13** (2012) 035007.
- [2] E. Mihóková, K. Vávř, K. Kamada, V. Babin, A. Yoshikawa, M. Nikl, *Radiat. Meas.* **56** (2013) 1.
- [3] I. Bailiff, *J. Archaeol. Sci.* **18** (1991) 619.
- [4] M. Ziyauddin, N. Brahme, D.P. Bisen, R.S. Kher, *Recent Res. Sci. Technol.* **4** (2012) 95.
- [5] N.L. Hom, *PhD Thesis*, Saga University (Japan), 2010.
- [6] F. You, A.J.J. Bos, Q. Shi, S. Huang, *J. Phys. Condens. Matter* **23** (2011) 215502 .
- [7] D.S. Kshatri, A. Khare, P. Jha, *Chalcogenide Lett.* **10** (2013) 121.
- [8] H. Yamamoto, T. Matsuzawa, *J. Lumin.* **2313** (1997) 72.
- [9] P. Dorenbos, *J. Electrochem. Soc.* **152** (2005) H107.
- [10] R. Chen, Y. Wang, Y. Hu, Z. Hu, C. Liu, *J. Lumin.* **128** (2008) 1180.
- [11] V. Dubeya, S. Agrwal, J. Kaur, *Optik* **126** (2015) 1.
- [12] A.H. Wako, B.F. Dejene, H.C. Swart, *Phys. B Condens. Matter* **439** (2014) 153.
- [13] G. Kitis, J.M. Gomez-Ros, J.W.N. Tuyn, *J. Phys. D. Appl. Phys.* **31** (1999) 2636.
- [14] L.L. Noto, S.S. Pitale, M.A. Gusowki, J.J. Terblans, O.M. Ntwaeaborwa, H.C. Swart, *Powder Technol.* **237** (2013) 141.
- [15] A. Bril, G. Blasse, J.. de Poorter, *J. Electrochem. Soc.* **117** (1970) 346.
- [16] P. a Tanner, L. Fu, L. Ning, B.-M. Cheng, M.G. Brik, *J. Phys. Condens. Matter* **19** (2007) 216213.
- [17] A. Potdevin, G. Chadeyron, V. Briois, R. Mahiou, *Mater. Chem. Phys.* **130** (2011) 500.
- [18] C. Burda, X. Chen, R. Narayanan, M.A. El-sayed, *Chem. Rev.* **105** (2005) 1025.
- [19] M. Nikl, E. Mihokova, J.A. Mares, A. Vedda, K. Nejezchleb, K. Blazek, *Phys. Status Solidi* **181** (2000) 10.
- [20] M. Fasoli, A. Vedda, M. Nikl, C. Jiang, B.P. Uberuaga, D.A. Andersson, K.J. McClellan, C.R. Stanek, *Phys. Rev. B - Condens. Matter Mater. Phys.* **84** (2011).
- [21] S. Basun, G.F. Imbusch, D.D. Jia, W.M. Yen, *J. Lumin.* **104** (2003) 283.
- [22] T. Aitasalo, J. Holsa, M. Lastusaari, J. Niittykoski, *J. Phys. Chem. B* **110** (2006) 4589.

- [23] S.S. Pitale, S.K. Sharma, R.N. Dubey, M.S. Qureshi, M.M. Malik, *Nucl. Instruments Methods Phys. Res. B* **266** (2008) 2027.
- [24] a. Choubey, S.K. Sharma, S.P. Lochab, D. Kanjilal, *Radiat. Eff. Defects Solids* **166** (2011) 487.
- [25] P. Avouris, *J. Chem. Phys.* **74** (1981) 4347.
- [26] Y. Kojima, K. Aoyagi, T. Yasue, *J. Lumin.* **126** (2007) 319.
- [27] R. Chen, *J. Appl. Phys.* **40** (1969) 570.
- [28] G. Kitis, V. Pagonis, *Nucl. Instruments Methods Phys. Res. B* **262** (2007) 313.
- [29] P. Kham Suan, Thermoluminescence Studies of Naturally Occuring Salts Relevant to Dosimetry Obtained from Mizoram, Mizoram University, 2013.
- [30] L. Puust, V. Kiisk, K. Utt, H. Mändar, I. Sildos, *Cent. Eur. J. Phys.* **12** (2014) 415.
- [31] T.M. Pitors, R. Melendrez, W. Drozdowski, *Radiat. Prot. Dosimetry* **84** (1999) 127.
- [32] C.M. Sunta, A.W.E. Feria, T.M. Pitors, S. Watanabe, *Radiat. Meas.* **30** (1999) 197.

Chapter 10

Conclusions and Recommendations for Future work

This thesis mainly reports on different methods through which luminescence characteristics of Aluminate and Garnet phosphors can be tuned by tailoring their chemical and structural properties with the aim to optimize their output to meet the requirements for industrial and commercial applications. In this chapter the overall conclusions drawn from the results obtained from the studies presented in this thesis as well as recommendations for future work regarding this research are, outlined.

10.1. Conclusion

- Thermoluminescence studies of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} phosphor revealed a linear response behavior of TL signal and glow curve peaks showed and the degree of linearity increased with the energy of the incident *beta* - radiation and the temperature (T_{max}). At higher doses the intensity was observed to saturate due to higher concentration of defects that generate non-radiative states within the band gap. The calculated values of activation energy were between 0.49 and 0.55 eV.
- XRD analysis of the Blue-green emitting $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Nd}^{3+}$ phosphor revealed that several crystalline phases formed depending on the Ba/Al. XPS results showed that the 3d spectrum for Ba had two peaks of O–Ba–O bonds for $3d_{3/2}$ and $3d_{5/2}$ existing within the $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Nd}^{3+}$. Compared to the other phosphors in this thesis it is the best due to long decay time and strong luminescence intensity of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Nd}^{3+}$ which makes it suitable for PDP applications.
- The effect of varied annealing temperature on the structure and PL properties of the $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ thin films showed that as the annealing temperature increased broadening of the XRD peaks occurred. This was due to Gd^{3+} - rich impurity phases formed at higher temperatures which substitutes Y^{3+} and since the ionic size of Gd^{3+} is larger than that of Y^{3+} , lattice expansion and hence PL red-shift occurs.
- The effect of varied background gas pressure and substrate temperature on the structure and PL properties of the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} , Nd^{3+} thin films showed that with increasing argon pressure and substrate temperature the peaks in the direction (220)

shifted to the lower angle accompanied by width - narrowing and increased intensity an indication of increasing particle size. The emission peaks were observed to shift to the longer wavelength side which could be attributed to the different deposition conditions of argon partial pressure and substrate temperatures which induced crystal field effect within the SrAl_2O_4 host lattice.

- It was observed that that the diffraction peaks slightly shifted to the lower angles for $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ and slightly to higher angles for $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ with reference to $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$. This shift was attributed to ionic size differences; Gd^{3+} being larger than that of Y^{3+} and that of Ga^{3+} larger than Al^{3+} . Substituting Y^{3+} with Gd^{3+} and Al^{3+} with Ga^{3+} caused lattice expansion/contraction that lead to an increase/decrease in the crystal-field interaction of Ce^{3+} .
- TL measurements on commercial $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ phosphor revealed that each of the glow curves consisted of two thermal peaks indicating existence of more than one type of trap; one centred at 74 °C and the other on the higher temperature side at 163 °C corresponding to shallow and deep traps respectively. The maximum temperature peak position (T_m) shifted to higher temperature when the heating rate was increased. The depth of trap 1, originating from Ce^{3+} ion was 0.39 ± 0.08 eV and the depth of Trap 2, originating from Ga^{3+} ion substitution, was 0.74 ± 0.15 eV as calculated from the Hoogenstraaten method.

10.2. Recommendations for future work

- More investigations using Pulsed Laser Deposition technique should be explored.
- Elaborate and accurate phase change monitoring techniques needs to be incorporated in future research activities.
- More enhanced surface and optical characterization such as Time of Flight (ToF SIMs) should be emphasized for the powder and thin film samples.
- Device Fabrication methods for different applications.

Publications

The following papers have been submitted for publication by the authors;
Wako A.H., Dejene B.F. and Swart H.C,

1. Thermoluminescence of beta (β)-irradiated $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} phosphor, *Proc., SAIP* 2013.
2. Combustion synthesis, characterization and luminescence properties of barium aluminate phosphors; *J. Rare Earths* 2014.
3. Roles of Doping Ions in Afterglow Properties of Blue $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ Phosphors, *Physica B, Condensed Matter Physics*, 2014.
4. Properties of blue emitting $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}$, Nd^{3+} phosphor by optimizing the amount of flux and fuel, *Physica B, Condensed Matter Physics*, 2014.
5. Characterization of cerium doped yttrium gadolinium aluminate garnet $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ phosphor thin films fabricated by pulsed laser deposition, *Proc., SAIP* 2014.
6. Influence of alkaline earth metal cations; Ca^{2+} , Sr^{2+} and Ba^{2+} on the structural and optical properties of $\text{MAl}_2\text{O}_4:\text{Eu}^{2+}$, Nd^{3+} phosphors. *Proc., SAIP* 2015.
7. Structural and luminescence properties of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} , Nd^{3+} phosphor thin films grown by pulsed laser deposition, Submitted to *Physica B, Condensed Matter Physics*, 2015.
8. Effect of Ga^{3+} and Gd^{3+} ions substitution on the structural and optical properties of Ce^{3+} -doped yttrium aluminium garnet phosphor nanopowders, submitted to the *J. Solid State Sciences*, 2015.
9. Trap characteristics of UV-activated $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ phosphors, submitted to *OPTIK-International Journal for Light and Electron Optics*, 2015.
10. Structure, morphology and optical properties of undoped and Mn-doped $\text{ZnO}(1-x)\text{Sx}$ nano-powders prepared by precipitation method F.B. Dejene, M.O. Onani, L.F. Koao, A.H. Wako, S.V. Motloun, M.T. Yihunie, Published in *Physica B, Condensed Matter Physics*, 2015.

Conferences

- **5th South African Conference on Photonic Materials (SACPM)**, 29th April-3rd May 2013, Kariega Game Reserve, Eastern Cape, South Africa.
 - ✓ Roles of Doping Ions in Afterglow Properties of Blue $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ Phosphor, Wako A.H., Dejene B.F. and Swart H.C.
- **5th South African Conference on Photonic Materials (SACPM)**, 29th April-3rd May 2013, Kariega Game Reserve, Eastern Cape, South Africa.
 - ✓ Properties of blue emitting $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ phosphors by optimizing the amount of flux and fuel, Wako A.H., Dejene B.F. and Swart H.C.
- **58th Annual Conference of the South African Institute of Physics (SAIP)**, 8th - 12th July 2013, University of Zululand, Kwazulu Natal, South Africa.
 - ✓ Thermoluminescence of beta (β)-irradiated $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor, Wako A.H., Dejene B.F. and Swart H.C.
- **7th International Conference on Rare Earth Development and Application and the 2nd China Rare Earth Summit (ICRE)**, 10th -13th August, 2013 Ganzhou, China.
 - ✓ Combustion synthesis, characterization and luminescence properties of barium aluminate phosphors, Wako A.H., Dejene B.F. and Swart H.C.
- **59th Annual Conference of the South African Institute of Physics (SAIP)**, 7th - 11th July 2014, University of Johannesburg, Gauteng, South Africa.
 - ✓ Characterization of cerium doped yttrium gadolinium aluminate garnet $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ phosphor thin films fabricated by pulsed laser deposition, Wako A.H., Dejene B.F. and Swart H.C.

- **6th South African Conference on Photonic Materials (SACPM),**

4th April-8th May 2015, Mabula Game Lodge , Limpopo, South Africa.

- ✓ Structural and luminescence properties of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} , Nd^{3+} phosphor thin films grown by pulsed laser deposition,

Wako A.H., Dejene B.F. and Swart H.C.

- **60th Annual Conference of the South African Institute of Physics (SAIP),**

28th June – 3rd July 2015, Boardwalk Hotel and Convention Centre, Port Elizabeth, South Africa.

- ✓ Influence of alkaline earth metal cations; Ca^{2+} , Sr^{2+} and Ba^{2+} on the structural and optical properties of MAl_2O_4 : Eu^{2+} , Nd^{3+} phosphors.

Wako A.H., Dejene B.F. and Swart H.C.