Chapter 1

Introduction and Motivation

Chapter 1 presents an introduction to the luminescence phenomenon, its classification, the theory of phosphor materials and trivalent lanthanide elements, and the discussion of the various applications of phosphor materials. The current research in the field of white LED and optoelectronic devices is also discussed in the chapter. At the end of the chapter motivation regarding thesis work is discussed.

1.1 Low dimensional materials

The limitations of traditional materials with poor optical and electrical performance for modern optoelectronic applications leads to the exploration of a novel class of materials having high absorption coefficient, high thermal stability, band gap tenability, non-toxicity, environment friendly nature and involving low-cost synthesis routes. Over the past few decades, the research in the field of low-dimensional materials have gained momentum by offering innovative solutions in a variety of scientific domains owing to their unique physical, chemical and optoelectronic properties which are spectacularly different than their bulk counterparts. There are two factors that prevent the classical rules of physics and chemistry from easily applying at this extremely tiny scale. First one is that, the electronic properties of low-dimensional materials greatly vary from their bulk counterparts and the second reason is that at very small scale the surface area to volume ratio becomes very much high, leading to a large number of atoms on the surface. Hence the reactivity of the materials become very much high and subsequently the properties of low-dimensional materials differ from the bulk materials[1,2].

1.1.1 Classification of low-dimensional materials

The general classification of low-dimensional materials is based on the scale of dimension (at least one of its three dimensions ranging from 1 to 100 nm) and the quantum confinement effects. The quantum confinement refers to the restrictions on electron movement in three dimensions. When all the dimensions of materials are scaled down less than the Bohr's radius, the quantum confinement comes into the picture and discretizes the energy levels between the valance and conduction bands in comparison to bulk materials. On the basis of above parameters, low-dimensional materials can be divided into three categories: zero-dimensional (0-D), one-dimensional (1-D), and two-dimensional (2-D), while three-dimensional (3-D) material represents the bulk state of

materials. The three dimensions (x, y, and z) of 0-D materials are all in the nanoscale range (between 1-10 nm). In this class of materials, the motion of carriers or excitons (bound state of an electron-hole pair by the electrostatic Coulomb force) are confined in all three directions. The prominent example of 0-D materials are quantum dots (QDs). In case of 1-D material, two dimensions (x, y) are at the nanoscale and one dimension lies beyond the nanoscale. The carriers in 1-D materials are restricted to move in only one direction and are constrained in two directions. The most common example of 1-D materials are nano-rods, nano-tubes, and nano-wires. Materials in which, only one dimension is in the nanoscale and other two dimensions are outside the nanoscale are termed as two-dimensional (2-D) or layered materials. Thin films and nano-sheets are examples of 2-D materials in which the motion of carriers (excitons) is restricted in one dimension whereas they are free to move in the other two dimensions. Those materials in which all the three dimensions are beyond the nanoscale regime are called bulk materials. The ease of synthesis for 1-D, 2-D, and quantum dots can vary depending on the specific materials, methods, and conditions used in the synthesis process[3,4].

In general, the synthesis of 1-D nanostructures, such as nanowires and nanotubes, is relatively straightforward and has been extensively studied over the past few decades. The most common method for synthesizing 1-D nanostructures include chemical vapour deposition (CVD), solution-based methods (such as sol-gel or hydrothermal synthesis), and physical methods (such as template-assisted synthesis). These methods can yield highly ordered and uniform nanostructures with controllable dimensions and properties. The synthesis of 2-D materials, such as grapheme and transition metal dichalcogenides (TMDs), can be more challenging and requires specialized equipment and techniques. The most common method for synthesizing 2-D materials include chemical vapour deposition (CVD), exfoliation from bulk materials, and bottom-up synthesis methods.

These methods can yield high quality 2–D materials with tunable properties, but the process can be time-consuming and expensive. In our study, we have synthesized 2-D Bi_2O_3 nanosheets via facile and low-cost co-precipitation methods. Quantum dots are small nanoparticles that exhibit unique electronic and optical properties due to quantum confinement effects. The synthesis of quantum dots typically involves chemical methods, such as colloidal or chemical vapour deposition (CVD). These methods can be relatively easy to implement and can yield high-quality quantum dots with tunable properties. However, the synthesis of quantum dots can also require specialized equipment and conditions, such as high temperatures or use of toxic chemicals. Overall, the ease of synthesis for 1-D, 2-D, and quantum dots depend on the specific materials used, and each type of nanostructure has its unique challenges and advantages[5,6].

1.2 Metal oxides

Metal oxides are crystalline solids comprised of both, a metal cation and an oxide anion. Metal oxides (MOs) are the most prevalent materials in the Earth's crust and are widely used in a variety of optoelectronic applications such as light emitting diodes (LEDs), detectors, sensors etc. Traditional inorganic semiconductors like silicon and III-V compounds differ greatly from metal oxide semiconductors in various aspects like electronic structure, materials design principles, defect levels, charge transport methods, thin-film production and optoelectronic properties. Among several host matrices such as oxides[7,8], aluminates[9,10], silicates[11,12], phosphates[13,14], fluorides[15,16], tungstates[17,18], molybdates[19,20], vanadates[13,21], titanates[22], etc., the metal oxides have been employed as promising host materials for various optoelectronic applications. In our thesis we have chosen Bi_2O_3 and ZnO as host materials for the application in light emitting diodes and UV detectors, respectively.

1.2.1 Bismuth Oxide (Bi_2O_3)

Among several metal oxide based phosphors, bismuth Oxide (Bi_2O_3) has received massive attention of the research fraternity owing to its remarkable properties such as near-ultraviolet (UV) to visible excitation, broadband emission in the visible region, excellent thermal and chemical stability, and high solubility for rare-earth ions, making it suitable to realize efficient optoelectronic devices. Bi_2O_3 exists in several polymorphic forms such as α-Bi_2O_3 (monoclinic), β-Bi_2O_3 (tetragonal), γ-Bi_2O_3 (body-centered cubic), δ-Bi_2O_3 (face-centered cubic), and ω-Bi_2O_3 (triclinic). Among them, α-Bi_2O_3 is stable at room temperature, and δ-Bi_2O_3 is stable at high temperatures (~750 °C). It is a semiconductor with wide bandgap (2-3.8 eV) and high carrier mobility, making it a promising candidate for optoelectronic devices such as solar cells, photodetectors, and light emitting diodes (LEDs). In recent years, there has been significant progress in utilizing Bi_2O_3 in optoelectronics, and researchers are exploring various ways to improve the performance and stability of these devices [23].

Solar Cells: Bi_2O_3 has been extensively studied as a potential electron transport material in perovskite solar cells (PSCs). PSCs have emerged as a promising alternative to traditional silicon solar cells due to their high power conversion efficiency (PCE) and low cost. Bi_2O_3 is used as a hole blocking layer in PSCs to improve the device performance and stability. Bi_2O_3 has also been used as a window layer in PSCs, which can improve light harvesting and enhance the PCE. Recently, researchers have demonstrated that a Bi_2O_3 buffer layer can reduce the hysteresis effect in PSCs and improve their stability [24].

Photodetectors: Bi_2O_3 has been explored as a promising material for ultraviolet (UV) photodetectors due to its wide bandgap and high carrier mobility. Bi_2O_3-based photodetectors have demonstrated high responsivity, low dark current, and fast response

time. Researchers have also reported the use of Bi_2O_3 as a hole-blocking layer in organic photodetectors, which can improve their performance and stability [25].

Light-Emitting Diodes: Bi_2O_3 has been utilized as a promising material for light-emitting diodes (LEDs). LEDs are currently used in various lighting applications due to their high efficiency, long lifetime and low power consumption. Bi_2O_3 based LEDs have demonstrated a high color rendering index (CRI) and a high luminous efficiency. Researchers have also demonstrated that Bi_2O_3 can be used as a transparent conductive layer in LEDs, which can improve their efficiency and reduce their manufacturing cost [26].

Overall, the present state of the art in using Bi_2O_3 in optoelectronic devices is very promising. Bi_2O_3 has demonstrated excellent performance in solar cells, photodetectors, and light-emitting diodes, and researchers are exploring various ways to improve the performance and stability of these devices. Further research is required to optimize the device structures and improve the manufacturing processes for these devices.

In our study the Bi_2O_3 phosphor has tetragonal and monoclinic crystal structures with $\bar{P}42_1/c$ and $P2_1/c$ space groups corresponding to auto-combustion and co-precipitation synthesis processes, respectively. The tetragonal and monoclinic crystal structures of Bi_2O_3 are depicted in Fig. 1.1 (a, b).

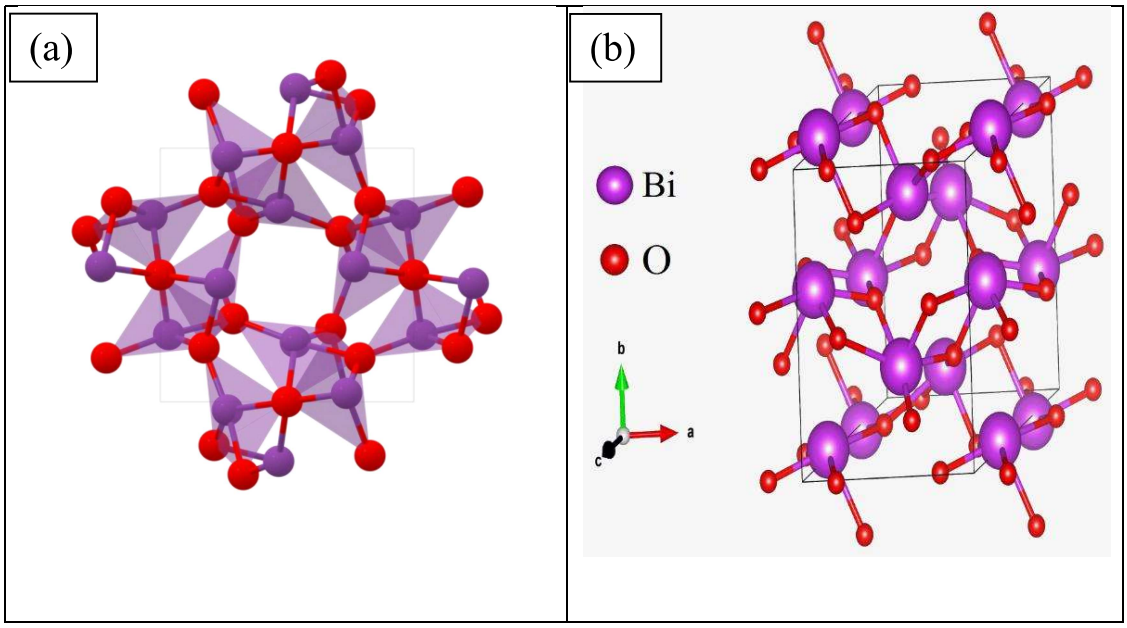

Fig. 1.1 (a) Tetragonal and **(b)** monoclinic crystal structures of Bi_2O_3.

1.2.2 Zinc oxide (ZnO)

Zinc oxide, abbreviated as ZnO, is an inorganic substance. It is a white, odourless powder that is almost insoluble in water. The research on ZnO has led to the development of new technologies such as transparent conducting films, UV light-emitting diodes, photovoltaics, sensors, and photocatalysis. In recent years, researchers have also been exploring its potential for biomedical applications, such as drug delivery and imaging. It is a material of curiosity owing to its nontoxicity and abundance. Since zinc and oxygen belong to the second and sixth groups of the periodic table, respectively, ZnO is frequently referred to as an II-VI semiconductor in material science, respectively. It is a natural n-type, direct wide band gap semiconductor, with band gap energy 3.37 eV at room temperature and large exciton binding energy (~ 60 meV), which makes it thermally stable at room temperature, and hence useful for optoelectronic device applications. The wide band gap and large excitonic energy make is technologically important and crucial for scientific and industrial applications [27]. ZnO is a versatile and promising material for optoelectronic devices due to its unique properties such as wide bandgap energy, high

electron mobility, high transparency in the visible spectrum, and low toxicity. The present state of the art in using ZnO in optoelectronic devices can be discussed in terms of its applications in various devices, such as transparent electrodes in liquid crystal displays, heat-protecting windows, light-emitting diodes (LEDs), photovoltaic cells (PVCs), and sensors.

LEDs are semiconductor devices that emit light when a current is passed through them. ZnO-based LEDs have been extensively studied due to their high luminous efficiency, low cost, and easy fabrication. One of the main challenges in ZnO based LEDs is the difficulty in achieving p-type doping, which is necessary for the formation of a p-n junction. To overcome this issue, various approaches such as Mg doping, nitrogen doping and hydrogen doping have been explored. Recently, ZnO based LEDs have been demonstrated with high external quantum efficiency and long-term stability [28].

PVCs are devices that convert light into electricity. ZnO-based PVCs have attracted much attention due to their high power conversion efficiency (PCE), low cost and abundance of raw materials. The use of ZnO nanowires and nanorods as electron transport layers has been reported to enhance the efficiency of PVCs. Additionally, surface modification of ZnO with organic or inorganic materials has been investigated to improve the interface properties between ZnO and other materials in PVCs [29].

Sensors are devices that can detect and respond to changes in the environment. ZnO-based sensors have been extensively studied due to their high sensitivity, selectivity, and stability. ZnO based gas sensors have been reported for the detection of various gases such as H_2, CO, NO_2, and NH_3. ZnO-based biosensors have also been developed for the detection of biomolecules such as DNA, proteins, and glucose [30]. Zinc oxide crystallizes in three forms: hexagonal wurtzite, cubic zinc blende, and the rarely observed cubic

rocksalt. Among them, hexagonal wurtzite is the most stable structure at ambient conditions. The lattice structure of ZnO belongs to the space group $P6_3mc$. The lattice parameters are a=3.25Å and c=5.206Å. Each anion in the wurtzite hexagonal structure is surrounded by four cations in the corners of the tetrahedron, demonstrating tetrahedral coordination and thereby exhibiting sp^3 covalent bonding. The crystal structure of hexagonal wurtzite ZnO is displayed in Fig. 1.2.

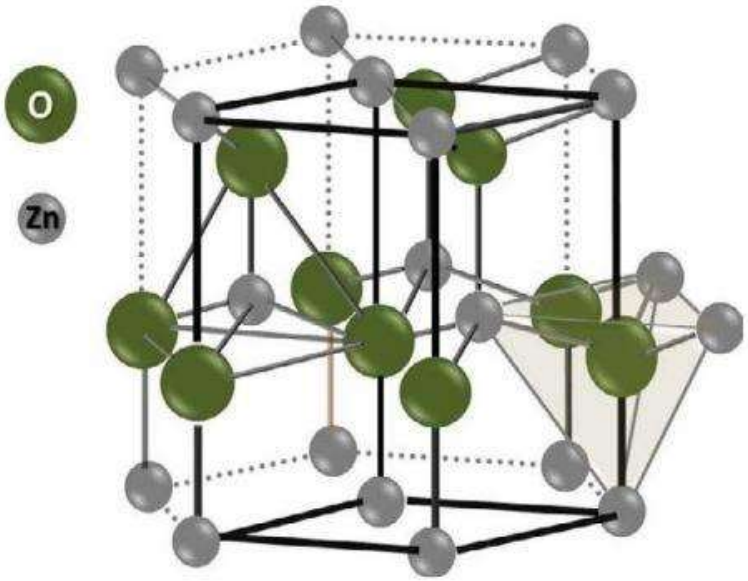

Fig. 1.2 Hexagonal crystal structure of ZnO.

1.3 Optoelectronic devices

Optoelectronics is the intersection of electronics and optics, and it includes the design, development, and manufacture of devices that convert electrical energy into light and light into energy. Optoelectronics is centred on how light interacts with electronic materials, particularly semiconductors, in a quantum mechanical way. It is the study and implementation of electronic equipments that source, detect, and regulate light. Optoelectronic devices are used in a wide variety of optoelectronics applications, including pharmaceuticals, broadcast communications, computerised access control

systems, military operations, gas sensors, lasers, solar cells, light emitting diodes, and UV detectors etc [31].

Advancements in device concepts, precise fabrication techniques, material control, and overcoming materials-related challenges like doping have enabled the development of optoelectronic devices with enhanced performance and capabilities.

1.3.1 Light emitting diodes

The solid-state semiconductor diodes which produce visible radiation when the electric current is passed through them are known as light emitting diodes (LEDs). It is a device that allows unidirectional flow of current from the anode to cathode within a certain range of voltage. The diode is made up of two distinctly doped materials that come together to form a p-n heterojunction, with the p-side having excess positive charges (holes) and the n-side having excess negative charges (electrons). When the diode is made forward biased, the current flows from p-side to n-side. Consequently, the holes move from p-side to n-side and the electrons move from n-side to p-side. As the charge carriers cross the depletion region, near the junction, their recombination takes place and this phenomena results in the release of visible energy photons. Owing to their distinctive characteristics including eco-friendly nature, low power consumption, low operating current and voltage (~ 600 mA, 3V), high efficiency, longer lifetime (~ 50,000 h), high brightness, small size, and excellent reliability, light emitting diodes (LEDs) are regarded as the most promising light sources for the future. Applications in communications, display backlighting, advertising boards, healthcare, and general illumination have all contributed to the growing interest for LEDs [32–35]. Depending upon colour mixing and package design, LEDs can emit light in a variety of spectral bands, from a narrow band emitting a single color like red, green, blue, or yellow to a broader band emitting white light with a variable distribution of luminous strength.

Fig. 1.3 Schematic representation of Fluorescent LEDs

1.3.1.1 Phosphor converted white light emitting diodes (PC-wLEDs)

In recent years, phosphor converted white light emitting diodes have gained much attention and rapidly replacing traditional compact fluorescent lamps (CFLs), halogen lamps, and incandescent lamps in lighting applications, owing to their superior energy efficiency, eco-friendly nature, longer lifetime (≥50,000 hours), extraordinary luminous efficiency (~100 lm/W), good color rendering index, and low power consumption (~8.5 W). Nowadays, LEDs are employed as essential components in a variety of applications, including display devices, medical applications, outdoor and indoor lighting for our homes, workplaces, showrooms, as well as vehicle illumination. Y. Shimizu and his co-workers at Nichia labs laid the cornerstone of first working wLED based on a blue InGaN chip and coated with yellow YAG:Ce^{3+} phosphor. Later, Shuji Nakamura, and co-workers worked on improving the luminous efficacy of wLEDs from 25 lm/W to approximately 200 lm/W by producing high-efficient blue-emitting LEDs. The yellow phosphor is excited by the blue light produced by the LED chip, and the mixing of the yellow light (photoluminescence) with the blue light (electroluminescence) results in the emission of bluish-white light (Fig. 1.4 (a, b)).

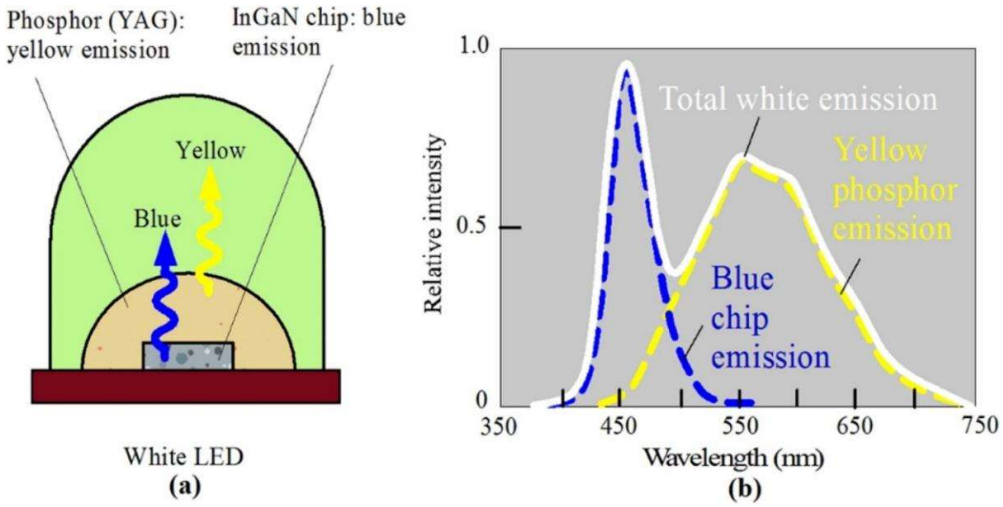

Fig. 1.4 (a) Construction of blue InGaN based and yellow YAG:Ce^{3+} phosphor coated white LED **(b)** PL emission spectra of the commercial wLED[36].

1.3.2 UV detectors

The ultraviolet (UV) radiation has been the subject of interest for the survival and development of human kind since its invention by Johann Ritter in 1801. Although, it consists of less than 10% of the solar radiation, but moderate skin exposure to natural solar radiation or artificial UV radiation helps in the synthesis of vitamin D, killing germs, treating or preventing rickets, etc. On the other hand, excessive UV radiation to human body may lead to cataracts, sunburn and skin cancer, and even may also lead to the acceleration of the aging process. Besides the living beings, the output of crops and the lifespan of buildings are also strongly affected by the UV part of solar radiation. Fortunately, such diseases in the human beings are prevented by the absorption of most of the UV radiation from the sun at the stratospheric ozone layer. However, a steady lowering of about 4% in the total amount of ozone in Earth's atmosphere (the ozone layer), and a much larger springtime decrease in stratospheric ozone around Earth's polar regions (known as ozone hole) are the alarming threats to the increase in skin cancer in recent times. It is reported that a decline of 1% in the volume of the ozone layer may lead to an increase of 2% in UV radiation at ground level, which in turn, may lead to an

increase of 3% incident rate of skin cancer. Thus the study of UV photodetection has drawn considerable attention of the researchers for monitoring the stratospheric ozone layer due to the growing effect of the UV radiation on the human life. Besides the ozone detection, UV photodetectors have also been the subject of research during last few decades for their potential applications in advanced optical communications, flame detection, air purification, blood gas monitoring, computed tomography, missile warning systems etc [37].

The UV photodetectors are the semiconductor devices used to convert the incident UV radiation on the device into an electrical signal, either in the form of current or voltage, by following the Einstein's theory of photoelectric effect by photon radiation on metals.

Based on the wavelengths, the UV spectrum can be typically classified into three kinds namely UV-A (315-400 nm), UV-B (280-315 nm), and UV-C (100-280 nm). The wavelength ranging from 220 to 280 nm, called the deep UV region, lies in the solar-blind region while the UV region below 180 nm wavelength is in the vacuum UV region. The UV-B and UV-C are the strongest and potentially most harmful UV regions in the electromagnetic spectrum.

The performance of any photodetector can be evaluated from the current-voltage (I-V) characteristics under dark and illuminated conditions. Several performance parameters such as quantum efficiency, responsivity, spectral selectivity, detectivity and time response characteristics are used to measure the performance of the detectors. In the present thesis, we have investigated the I-V characteristics and responsivity measurements of some ZnO and Ag-ZnO nanocomposite based UV photodetectors using

low cost solution processed methods. The important parameters used to express the device performance of a detector are give below [38]:

- Responsivity (R): It is defined as the generated electrical current per unit incident optical power at an incident wavelength. The unit of responsivity is generally expressed in A/W.
- Quantum Efficiency (η): The quantum efficiency of a photodetector is defined as the ratio of the number of photogenerated carriers to the number of photons of a given energy incident on the detector. It may be given either as a function of wavelength or as energy.
- Spectral Selectivity: It is defined as the ability of a photodetector to detect accurate and intended energy photons without any interference of the adjacent wavelengths. It is often expressed in terms of the full width at maxima (FWHM) of the responsivity versus wavelength characteristics of the detector.
- Time Response: The time response of the photodetectors are expressed in terms of the rise time (t_r) and fall time (t_d) of the output signal when a pulsed light is incident on the detector. The rise time is the measure of the time response of a photodetector to a stepped light output, and is defined as the time required for the output to change from 10% to 90% of the steady output level. Similarly, the fall time is measured as the decay from the 90% to 10% of the falling edge of the output rectangular pulses of the detector when a pulsed source of light is incident on the detector.

The solution processed synthesis techniques are believed to be the simplest and most cost effective techniques for nanoelectron device fabrication. Although, GaN is the most widely used semiconductor for UV applications, however, various metal oxide nanostructure based UV detector have drawn considerable attention due to their lower

processing cost. In the present thesis, an attempt has been made to fabricate and characterize some ZnO and Ag-ZnO nanocomposite based UV detector using solution processed fabrication methods.

Fig. 1.5 Schematic representation of UV detector

1.4 General introduction of luminescence

Luminescence refers to the emission of light by a substance or material without the need for high temperatures. It is often referred to as "cold light" because it occurs at or near room temperature and does not involve the process of incandescence, which is the emission of light due to high temperatures. In luminescence, some energy source kicks an electron of an atom out of its ground state into an excited state, and then the electron gives back the energy in the form of light so it can fall back to its ground state. The diverse characteristics of luminescence and the intricate processes involved in the field of light emission render exciting challenges and open up new possibilities for researchers in this discipline. Luminescence phenomena have fascinated and perplexed humans since prehistoric times. Naturally occurring luminous phenomena include illuminating insects, vivid aurora, glowing fungus, and decomposing wood. In 1852 English physicist, Sir G. G. Stokes laid the cornerstone of luminescence phenomena by publishing a famous article entitled “On the refrangibility of light” He established the Stokes law of luminescence, which stipulates that the emitted radiation has a longer wavelength than the stimulating radiation When ultraviolet (UV) light strikes a substance, part of its energy is absorbed

and re-emitted at a longer wavelength in the electromagnetic spectrum. Later in 1888, the word luminescence was first introduced by German physicist Eilhard Wiedemann for all light-emission processes that are not caused by a temperature increase. The term luminescence originated from the Latin word lumen, meaning light. The luminescence phenomenon is thus defined as the emission of visible light from some specific organisms or materials by certain modes of excitation such as passage of electrical current, chemical reactions, physiological processes, subatomic motion, or piezoelectricity. The luminescence phenomenon is different from incandescence in such a way that the latter results from heating. Although the luminescence phenomenon is not caused by heat, it is influenced by heat [39].

1.5 Classification of luminescence phenomenon

Based on the mode of excitation, the luminescence phenomenon can be broadly classified into several categories (depicted in Fig. 1.6). Some of them are described as follows:

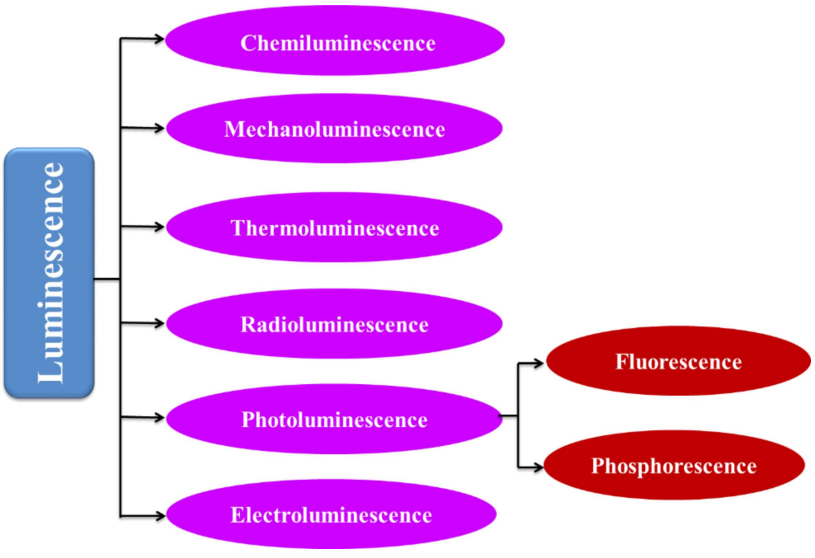

Fig. 1.6 Classification of luminescence phenomena

1.5.1 Chemiluminescene

The phenomena in which electromagnetic radiations are generated by the means of some electronic transitions induced by certain chemical reactions is called as chemiluminescence. One common example of chemiluminescence is the bioluminescence in which luminescence is generated as a result of some biochemical reactions in the living being. The bioluminescence is also called cold light because in this phenomena only less than 20% of light results in heat. The example of bioluminescent organisms are fireflies and marine organisms.

Fig. 1.7 Schematic representation of chemiluminescence

1.5.2 Mechanoluminescence

The generation of radiation caused by some mechanical actions (compressing, cutting, grinding, scratching, rubbing, cleaving, or shaking) on solids is referred as mechanoluminescence (ML). The mechanoluminescence can also be stimulated by thermal shocks caused by rapid heating or cooling of the specimen and may also be observed during phase transitions or crystal growth deformation, as well as during the separation of two different materials in contact. Piezoluminescence, triboluminescence, fractoluminescence, and sonoluminescence are some of the different names for the ML process based on the kind of mechanical stress applied to the material.

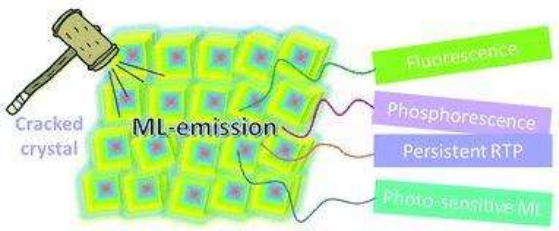

Fig. 1.8 Schematic representation of mechanoluminescence

1.5.3 Thermoluminescence

Thermoluminescence is a type of luminescence that arises when a material is gently warmed; it typically takes place below incandescence. In some crystalline solids or minerals, the electrons are previously trapped in the defects of the crystal structure. When a sufficient amount of thermal energy is imparted to these electrons, they become free and the trapped energy is emitted in the form of light, known as thermoluminescence. The information of the trap energies can be estimated by the emission curves. The applications of TL include archaeological dating and radiation dosimetry.

Fig. 1.9 Schematic representation of thermoluminescence in minearls

1.5.4 Radioluminescence

In this phenomena the optical photons are produced as a result of the interaction of ionizing radiation with matter. The materials exhibiting radioluminescence are termed as scintillators and the ionizing radiation may be α particles, β particles, or the γ rays. These ionizing particles act as the excitation source. Radioluminescence was first observed and

reported by Pierre and Marie Curie. It has traditionally been utilised in watch, clock, and other continuous phosphorescent devices.

Fig. 1.10 Schematic demonstration of radioluminescence in watch face illuminated by tritium tubes

1.5.5 Electroluminescence

Electroluminescence (EL) is a term that describes a phenomenon where a substance emits light when subjected to an electric field or current. Typically, in a semiconductor, the EL takes place as a result of radiative recombination between electron and holes. Before recombination, the holes and electrons are separated, which can be accomplished in two ways: either by doping the material to create a p-n junction or by excitation by the impact of highly energetic electrons that are driven by a strong electric field.

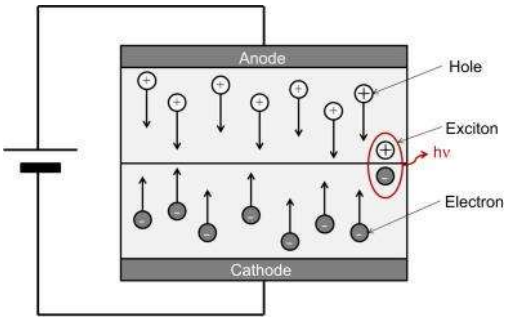

Fig. 1.11 Schematic representation of electroluminescence

1.5.6 Photoluminescence

Photoluminescence is the phenomenon of light emission from certain materials under the action of absorption of electromagnetic radiation (photons). The word "photo" is adopted

since the process begins by photo-excitation. After excitation, the emission process takes place, which is followed by several types of non-radiative relaxations. The photoluminescence phenomenon can be further sub-divided into two categories namely-

1.5.6.1 Fluorescence

The emission of light via a radiative transition from an excited singlet state to singlet ground state is termed as fluorescence. In this phenomenon, the photons of shorter wavelength are absorbed by the molecules in ground state. By absorbing these photons the molecules jump to the excited states and then revert back to ground state by emitting some visible photons of longer wavelength. Since these transitions are spin allowed they occur rapidly and the overall fluorescence phenomena typically takes around 10^{-4} to 10^{-8} sec. The spin multiplicity is preserved during the fluorescence process, implying that fluorescence does not interfere with electron spin. Fluorescent lights, neon signs, and biological markers are some common examples of fluorescence phenomena.

1.5.6.2 Phosphorescence

The emission of light via a radiative transition from an excited triplet state to singlet ground state is termed as phosphorescence. In this process, a molecule in singlet ground state jumps to a singlet excited state by absorbing lower energy photons. The excited singlet molecules then jump to triplet excited states by intersystem crossing non-radiatively and eventually revert back to the singlet ground state by emitting visible photons. Both the transitions i.e. the singlet excited to triplet excited (intersystem crossing) and also the triplet excited to singlet ground state transitions involve the spin reversal of the electrons and therefore makes the phosphorescence phenomena less favourable as compared to the fluorescence process. Since these transitions are spin forbidden they occur at a slower rate and the overall phosphorescence phenomena typically take around 10^{-6} to several seconds.

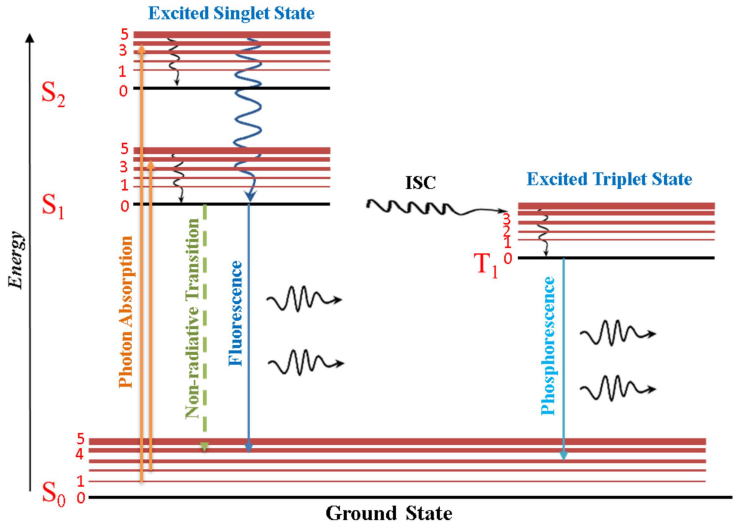

Fig. 1.12 Jablonski diagram showing the schematic representation of Photoluminescence (fluorescence and phosphorescence)

1.6 Photoluminescence mechanism

The term "phosphor" generally refers to all substances that exhibit the phenomena of luminescence. A suitable host crystal and doped impurities known as luminescent centres or activator ions are the basic building blocks of most synthetic phosphor materials. The molecule is excited when photon energy is absorbed by it, and this excitation is followed by relaxation and lead to the emission of radiation. Both the dopant ions and the host lattice have the ability to generate light. The dopant ions in which an electron transition results in the emission of photons are called *activators*. In some cases, if the absorption of the activator ion is weak, an additional kind of dopant ion is co-doped in the lattice. This co-doped ion is called the *sensitizer* and it subsequently transfers the absorbed energy to the activator ion. The various processes involved in the phosphor material, starting from the absorption of photons to the emission of radiation are demonstrated by the Jablonski diagram. The Jablonski diagram is named after Professor Alexander Jablonski, who is widely recognized as the pioneer of fluorescence spectroscopy. Fig. 1.12 depicts a typical Jablonski diagram, with the singlet ground and excited states labeled as S_0, S_1, and S_2,

respectively. The vibrational energy levels are labeled as 0, 1, 2, etc. Typically, the energy of emission is smaller than that of absorption (Stokes law). The details of various processes are discussed as follows:

1.6.1 Excitation process

Electronic excitation refers to the electronic transition that occurs as a result of a photon being absorbed by a molecule. The excitation spectrum is recorded by examining emission at the wavelength of maximum intensity while the sample is scanned through a wavelength range. The excitation energy propels the molecule from the ground electronic state to a higher vibronic sublevel of an excited singlet state. The phosphors exhibit photoluminescence after the absorption from a suitable incident of electromagnetic radiation. The radiation is absorbed by the host lattice of the activator ion. If the radiation is absorbed by the host lattice, the emission occurs either from the host itself or via energy transfer from the host to the activator ion. In most cases, high energy radiations like far ultraviolet (UV) excite the host lattice and low energy radiations like near UV and visible light excite the activator ions. In some host phosphors, the activator ions exhibit weaker absorption. These host materials are doped with sensitizers which absorb energy and transfer it to the activator ions. The initial absorption process of the radiation takes place within a few femtoseconds.

1.6.2 Relaxation process

The relaxation of the electron from the excited state to the ground state is a spontaneous process. The relaxation involves both radiative and non-radiative transitions. The excited species dissipate energy via vibrational relaxation, internal conversion, intersystem crossing, fluorescence, and phosphorescence.

1.6.2.1 Radiative and non-radiative transitions

The luminescence phenomenon generally involves two processes namely: excitation and emission. When the photons of relatively higher energy strike with the molecules in ground state, they impart their energy to the molecules. As a result, the molecules get excited and jump to the higher energy states. The molecules excited to the higher excited stated come to the bottom of the first excited state. In this process, the energy of the molecules is imparted to the crystal lattice via phonons. Such type of emission is called non-radiative emission. Now, the molecules from the bottom of the first excited state revert back to the ground state by emitting visible photons of lower energy. Such type of transition is called radiative transition.

1.7 Photoluminescence decay mechanism

The average amount of time a fluorophore remains excited is referred to as its fluorescence lifetime. To further understand the meaning of fluorescence lifetime, let us suppose a sample containing several fluorophores. The excitation with an infinitely sharp pulse of light could result in the number of fluorophores reaching an excited state. Let n_0 be the initial population of fluorophores in the excited state. The population in the excited state decays with a rate of R+k_{nr} according to equation 1.1.

$$\frac{dn(t)}{dt} = (\mathrm{R} + k_{nr})\mathrm{n(t)} \qquad (1.1)$$

Where R represents the emissive rate, the nonradiative decay rate is represented by k_{nr}, and the population of excited molecules following excitation at time t is denoted by $n(t)$[40]. An emission is a random event, and each stimulated fluorophore has the same probability of emitting in a given time. This causes the excited state population to decay exponentially,

$$n(t) = n_0 \exp(-t/\tau) \quad (1.2)$$

In a fluorescence experiment, the spectrophotometer records the fluorescence intensity, which is proportional to *n(t)*. Therefore, equation 1.2 takes the form as

$$I(t) = I_0 \exp(-t/\tau) \quad (1.3)$$

Where *I(t)* is the time-dependent intensity, I_0 is the intensity at t=0, τ is the inverse of the total decay rate ($R + k_{nr}$) [40]. The slope of the log *I(t)* vs. *t* plot may be used to calculate the fluorescence lifetime.

In some samples, the fluorophores can decay by more than one process. Suppose there exist two Ln^{3+} ions in the sample such that there exists the process of energy transfer from one Ln^{3+} ion to another Ln^{3+} ion. Then the electrons in the excited state of one Ln^{3+} ion could have two decay times and the decay intensity after time *t* will follow the bi-exponential function,

$$I(t) = I_0 + B_1 \, exp\left(-\frac{t}{\tau_1}\right) + B_2 \, exp\left(-\frac{t}{\tau_2}\right) \quad (1.4)$$

Where τ_1 signifies fast decay time and τ_2 signifies slow decay time;

1.8 Rare earth elements

A set of 17 chemical elements (scandium (Sc) and yttrium (Y) along with Lanthanides (Ln)) in the periodic table are known as rare earth elements. The word "rare" signifies that the occurrence of these elements in nature is very small and it is found only around 8.4×10^{-3}% of the total earth crust. The discovery of rare earth elements was started way back in the 18th century and the first discovered element was Yttrium by a Finnish chemist and mineralogist Johan Gadolin. The rare earth elements exhibit several peculiar properties. One of the most intriguing properties of these ions is their photoluminescence

and therefore they are essential components of fluorescent materials. Owing to their unique optical properties, rare earth ions have found a variety of technological applications including lighting and display devices (LEDs and fluorescent lamps), lasers, optical fibres, rechargeable batteries, aerospace, and defence [41].

Generally, rare earth ions exhibit three types of optical transitions namely: 4f-4f intra-configurational, 4f-5d inter-configurational, and ligand to metal or metal to ligand charge transfer transition. Due to its extraordinary emission properties, rare earth ions are widely employed as activators and sensitizers in various host matrices. Ln^{3+} ions have the electronic configuration [Xe] $4f^n$ (n=0-14). The 4f-4f transitions involve the electron transfer among various energy levels of 4f orbitals. Odd-parity electric dipole (ED) or even-parity magnetic dipole (MD) transitions are the causes of the transitions found in the luminescence spectrum of Ln^{3+} elements. The Ln ion interacts with the electric field vector of the EM wave through an electric dipole to produce an ED transition, whereas the magnetic dipole interaction of the Ln ion with the magnetic field vector of the EM wave produces an MD transition. The Laporte selection rule states that 4f-4f transitions of RE ions are parity forbidden with weak oscillator strength, but when these RE elements are doped in a suitable host matrix, they are allowed due to the strong crystal field of the host. Since, the 4f orbital electrons are screened by 5s and 5p orbitals, the 4f-4f transitions are less influenced by the crystal field environment of the host lattice and exhibit narrow emission lines. Moreover, the 5d orbital in 4f-5d transitions are strongly affected by the crystal field and exhibit broad emission bands. The narrow emission band, longer excited state lifetime, and large Stokes shift (≥ 250) (difference between excitation and emission wavelength) of the trivalent rare earth ions make them an excellent choice over other conventional fluorescence organic dyes. Total spin quantum number (S) and total orbital angular momentum quantum number (L) are the two quantum numbers that characterise a

spectroscopic term, while a third quantum number (J) further distinguishes a spectroscopic level (total angular momentum quantum number). Each spin-orbit level has a 2J+1 degeneracy. The LS coupling scheme characterizes each free-ion level by $^{2S+1}L_j$.

Table 1.1 Rare earth elements, their electronic configuration and ground state spectroscopic terms

Atomic number	Element	Electronic configuration	Ground state spectroscopic term
57	Lanthanum (La)	$4f^0\ 5s^2\ 5p^6$	1_{S_0}
58	Cerium (Ce)	$4f^1\ 5s^2\ 5p^6$	$2_{F_{5/2}}$
59	Praseodymium (Pr)	$4f^2\ 5s^2\ 5p^6$	3_{H_4}
60	Neodymium (Nd)	$4f^3\ 5s^2\ 5p^6$	$4_{I_{9/2}}$
61	Promethium (Pm)	$4f^4\ 5s^2\ 5p^6$	5_{I_4}
62	Samarium (Sm)	$4f^5\ 5s^2\ 5p^6$	$6_{H_{5/2}}$
63	Europium (Eu)	$4f^6\ 5s^2\ 5p^6$	7_{F_0}
64	Gadolinium (Gd)	$4f^7\ 5s^2\ 5p^6$	$8_{S_{7/2}}$
65	Terbium (Tb)	$4f^8\ 5s^2\ 5p^6$	7_{F_6}
66	Dysprosium (Dy)	$4f^9\ 5s^2\ 5p^6$	$6_{H_{15/2}}$
67	Holmium (Ho)	$4f^{10}\ 5s^2\ 5p^6$	5_{I_8}
68	Erbium (Er)	$4f^{11}\ 5s^2\ 5p^6$	$4_{I_{15/2}}$
69	Thulium (Tm)	$4f^{12}\ 5s^2\ 5p^6$	3_{H_6}
70	Ytterbium (Yb)	$4f^{13}\ 5s^2\ 5p^6$	$2_{F_{7/2}}$
71	Lutetium (Lu)	$4f^{14}\ 5s^2\ 5p^6$	1_{S_0}

1.9. Rare earth ions studied

1.9.1 Trivalent samarium (Sm^{3+}) ion

The trivalent samarium (Sm^{3+}) ion has five electrons in the outermost 4f shell and its electronic configuration is written as [Xe] $4f^5$. The emission spectrum of Sm^{3+} ions exhibits some intense peaks corresponding to the $^4G_{5/2} \rightarrow {}^6H_J$ (J=5/2, 7/2, 9/2, 11/2, and 13/2) electronic transitions. These electronic transitions give orange-red emission. Among these transitions, the $^4G_{5/2} \rightarrow {}^6H_{5/2}$ is purely magnetic dipole transition, the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition is partly due to magnetic dipole transition and partly electric dipole transition, and $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition is purely electric dipole transition.

1.9.2 Trivalent europium (Eu^{3+}) ion

The trivalent europium ion (Eu^{3+}) has six electrons in the outermost 4f shell and its electronic configuration is written as [Xe] $4f^6$. The Eu^{3+} ion in several compounds exhibits intense luminescence owing to the $^5D_0 \rightarrow {}^7F_J$ (J=0 - 6) electronic transitions. The $^5D_0 \rightarrow {}^7F_0$ transition is strictly forbidden by the selection rules of the Judd-Ofelt theory. The occurrence of the $^5D_0 \rightarrow {}^7F_0$ transition indicates that the Eu^{3+} ion occupies C_{nv}, $C_{n,}$ or C_s site symmetry in the lattice. The $^5D_0 \rightarrow {}^7F_1$ transition is a magnetic dipole (MD) transition and its intensity is largely independent of the environment around the Eu^{3+} ion. The $^5D_0 \rightarrow {}^7F_1$ transition is the direct consequence of the crystal field splitting of $^7F_1$. In compounds with centrosymmetric crystal structures, the intensity of the peak corresponding to the $^5D_0 \rightarrow {}^7F_1$ transition is most intense. The $^5D_0 \rightarrow {}^7F_2$ transition is the electric dipole transition whose intensity is significantly influenced by the local environment of the Eu^{3+} ion and therefore they are termed hypersensitive transitions. The intensity of the $^5D_0 \rightarrow {}^7F_2$ hypersensitive transition is often used as a measure for the asymmetry around the Eu^{3+} ion. Therefore, if the intensity of $^5D_0 \rightarrow {}^7F_2$ transition is maximum then the Eu^{3+} ion must have occupied the lower symmetry in the host lattice.

The typical red luminescence of the Eu^{3+} ion is the consequence of the $^5D_0 \rightarrow {}^7F_2$ transition. The $^5D_0 \rightarrow {}^7F_3$ transition is generally very weak as it is forbidden according to the Judd-Ofelt theory. $^5D_0 \rightarrow {}^7F_4$ transition is again an electric dipole transition. The dominance of the $^5D_0 \rightarrow {}^7F_4$ transition is an indication of D_{4d} symmetry in compounds. The other $^5D_0 \rightarrow {}^7F_5$ and $^5D_0 \rightarrow {}^7F_6$ transitions are rarely observed as they lie beyond 800 nm where the detectors of most spectrophotometers have low sensitivity. In some inorganic hosts, the luminescence from the Eu^{3+} ion can also originate from $^5D_1$, $^5D_2$, and $^5D_3$ levels. The characteristic peaks in the absorption spectra result from the $^7F_0 \rightarrow {}^5D_J$ (J=0, 1, 2) transitions. The Eu^{3+} doped compounds are explored for wide applications such as red phosphors in lighting and display applications, luminescent markers in biological applications, etc. Moreover, the spectra of the Eu^{3+} ion can also be used to probe the local symmetry around the rare-earth ion.

1.10 Motivation of the thesis

The thesis work is directed along the luminescence study of alkali metal ion and rare earth (RE) ions doped Bi_2O_3 phosphors and also structural and electrical studies of Ag-ZnO nanocomposites. The shortcomings of commercially available wLEDs, such as their low color rendering index (CRI <75) and high correlated color temperature (CCT > 4,500 K), have encouraged research fraternity to create red phosphors for the emission of warm white light. Although numerous researchers have investigated different red phosphors for lighting applications, their drawbacks, including the need for high temperatures and reduced atmospheres for synthesis, low thermal and chemical stability, and emission lying beyond the range of human eye sensitivity limit (700 nm), have inspired us to develop red phosphors that could be developed by facile, low-cost and an environmentally friendly preparation method with good chemical and thermal stability. Furthermore, it is well established that co-doping certain alkali metal ions (Li^+, K^+, and

Na^{+}) can enhance the emission intensity of RE ions. These dopants can be easily incorporated in the host matrix and occupy substitutional or interstitial sites owing to their comparatively small ionic radius, and by increasing the asymmetry, they modify the crystal field around the RE ion and also lead to an improvement in the crystallinity of the materials and reduce defect states. All of these factors contribute to an increase in the luminescence intensity of RE ions. Therefore, we have examined the effect of Li^{+} and Na^{+} ions on the optical and structural properties of Sm^{3+} doped Bi_2O_3 red phosphor. Additionally, we have investigated the thermal stability of the best-prepared red phosphor and compared our observations with some of the earlier published scientific literature.

To examine metal oxide phosphors as an alternative to the commercially available yellow phosphor, we have investigated bismuth oxide phosphor. The Bi_2O_3 phosphor as a host is a noteworthy host for Ln^{3+} ions as it enables efficient energy transfer between the energy levels of the doped rare-earth ions. Therefore, it is possible to get a good emission corresponding to the two rare-earth ions by varying the excitation wavelengths. We have studied the thermal stability, and energy transfer phenomena in Sm^{3+}/Eu^{3+} co-doped Bi_2O_3 phosphor. Moreover, metal oxide phosphors can be synthesized by low-cost synthesis processes and at ambient conditions. The use of a red phosphors in a variety of applications such as display devices, encrypted information storage, white light-emitting diode (wLED), biological applications, and fluorescent sensors have motivated us to work in this field.

Apart from that, In order to fulfill the demand for highly sensitive and fast response ZnO based UV detector, we have also thoroughly studied the structural, optical and electrical properties of various compositions of Ag-ZnO nanocomposites and compared the results with the other reported literatures. The improvement in optical absorption, emission and electrical properties of transition metal-doped ZnO is required for optoelectronics device

applications. The extraordinary optical and electrical properties exhibited by these materials motivated us to further enhance their electrical parameters such as I-V characteristics and photo response values.