Chapter 1
Introduction

1.1 Introduction

This work comes under the general domain of condensed matter physics, more precisely optical properties of materials. However, within the ambit of optical properties, it is the field of luminescence to which this work exactly belongs.

To begin with, luminescence is a specific field of study of materials and phenomena dealing with the emission of light using a particular kind of mechanism. The simple concept is to get emission of light from a material by giving certain kind of stimulus, based on which the luminescence phenomena is categorized into different types as given in the table 1.1.

1.2 Photoluminescence

As evident from the table 1.1, the excitation source in this type of luminescence are the photons. Primary to this is the availability of band gap in a solid material, which happens only in case of semiconductors and insulators. The process begins with the absorption of photon by an electron in the valence band. If this photon provides energy to the electron in excess of its energy gap, the electron goes to the conduction band. Here, the electron looses energy in small steps or transitions, which are generally referred to as non-radiative transitions or relaxations and reach the bottom of the conduction band. From this point, the electron falls back to the valence band. In the process, a photon is emitted whose energy is less than the energy of excitation photon. Hence, this is the down-conversion luminescence. The entire cycle from excitation to emission constitutes the phenomena of photoluminescence. It is displayed in figure 1.1.

Sr. No.	Types of luminescence	Source of Excitation	Applications
1	Photoluminescence	Photons	Fluorescent lamps, plasma displays
2	Cathodoluminescence	Electrons	Televisions, Color monitor
3	X – ray luminescence	X – ray	X – ray amplifier
4	Electroluminescence	Electric field	LEDs, electroluminescence displays
5	Thermo luminescence	Heat	Radiation dosimetry
6	Chemiluminescence	Chemical reaction energy	Analytical chemistry
7	Triboluminescence	Mechanical energy	Mechanical failure, automobile crashes
8	Sonoluminescence	Ultrasound	Destruction of toxic chemicals
9	Bioluminescence	Bio-chemical reaction energy	Analytical chemistry and bioimaging

Table 1.1: Types of luminescence

Among these categories, the phenomena of photoluminescence one of the most common and has numerous applications. Hence, it deserves a closer look.

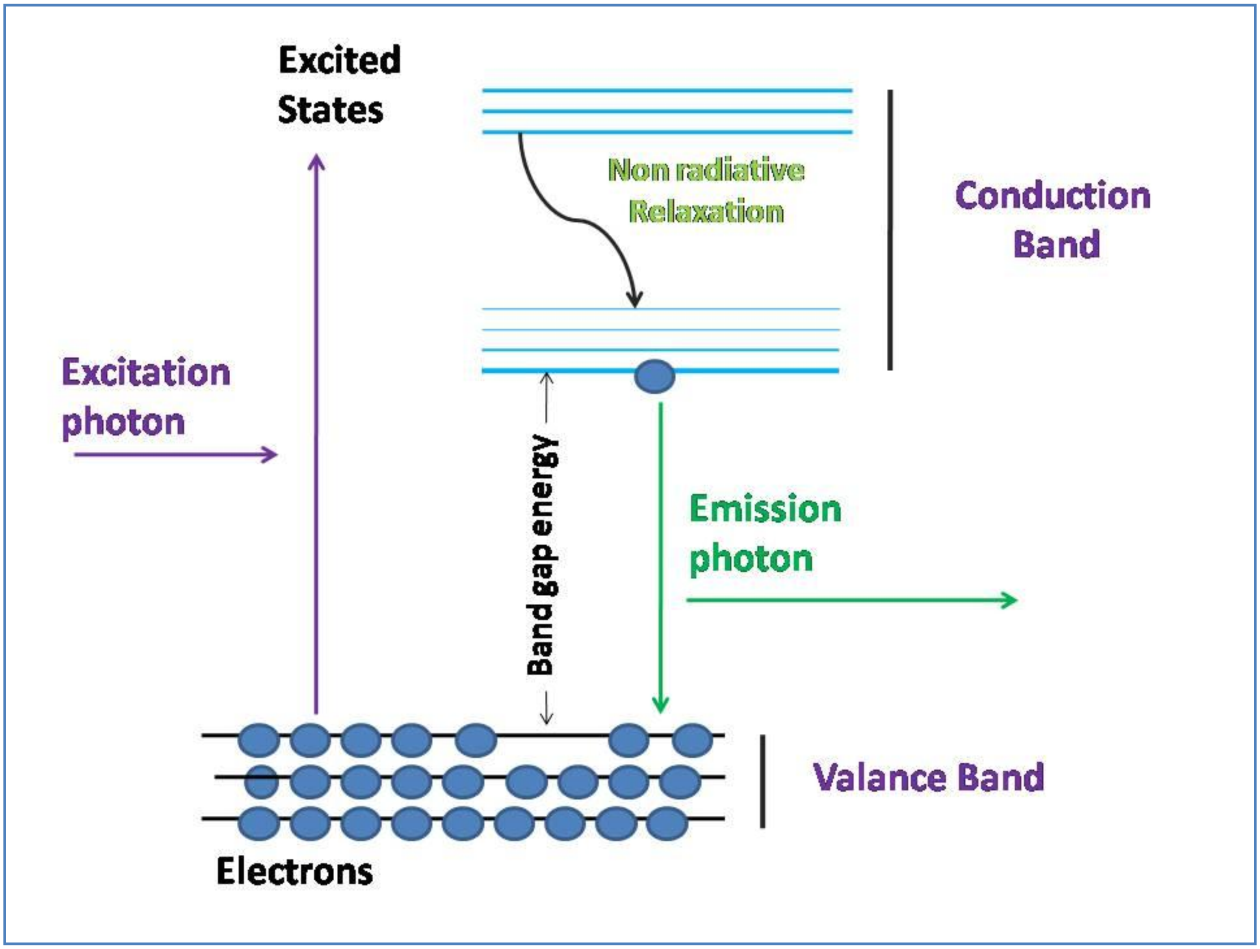

Figure 1.1: Diagram showing the process of luminescence.

The pathway of the process given in figure 1.1 may vary further, depending on which the time scale and temperature dependence of the phenomena can vary. The categorization of such processes is expressed in terms of fluorescence and phosphorescence. The process of fluorescence is that of quick decay, generally less than one nanosecond. It is independent of temperature. The process of phosphorescence is temperature dependent and lasts longer with decays longer than one millisecond. The excitation process for both the phenomena remains same. The molecules are propelled to the excitated states S_1 and S_2 or any other from the ground state S_0 as shown in figure 1.2, on absorption of a photon of energy hv_A.

The molecule in the excited states being unstable, it would eventually return to the ground state, which is stable. However, the return journey is not a direct one. Some energy is lost in the form of vibrational or thermal energy by a series of transitions which are also generally termed as Internal Conversions (IC). In such a scenario, the subsequent step might be a radiationless or a radiative transition. In case of the later, a photon with energy hv_F is emitted leading to an overall process with short decay time of less than ten nanoseconds and is called Fluorescence.

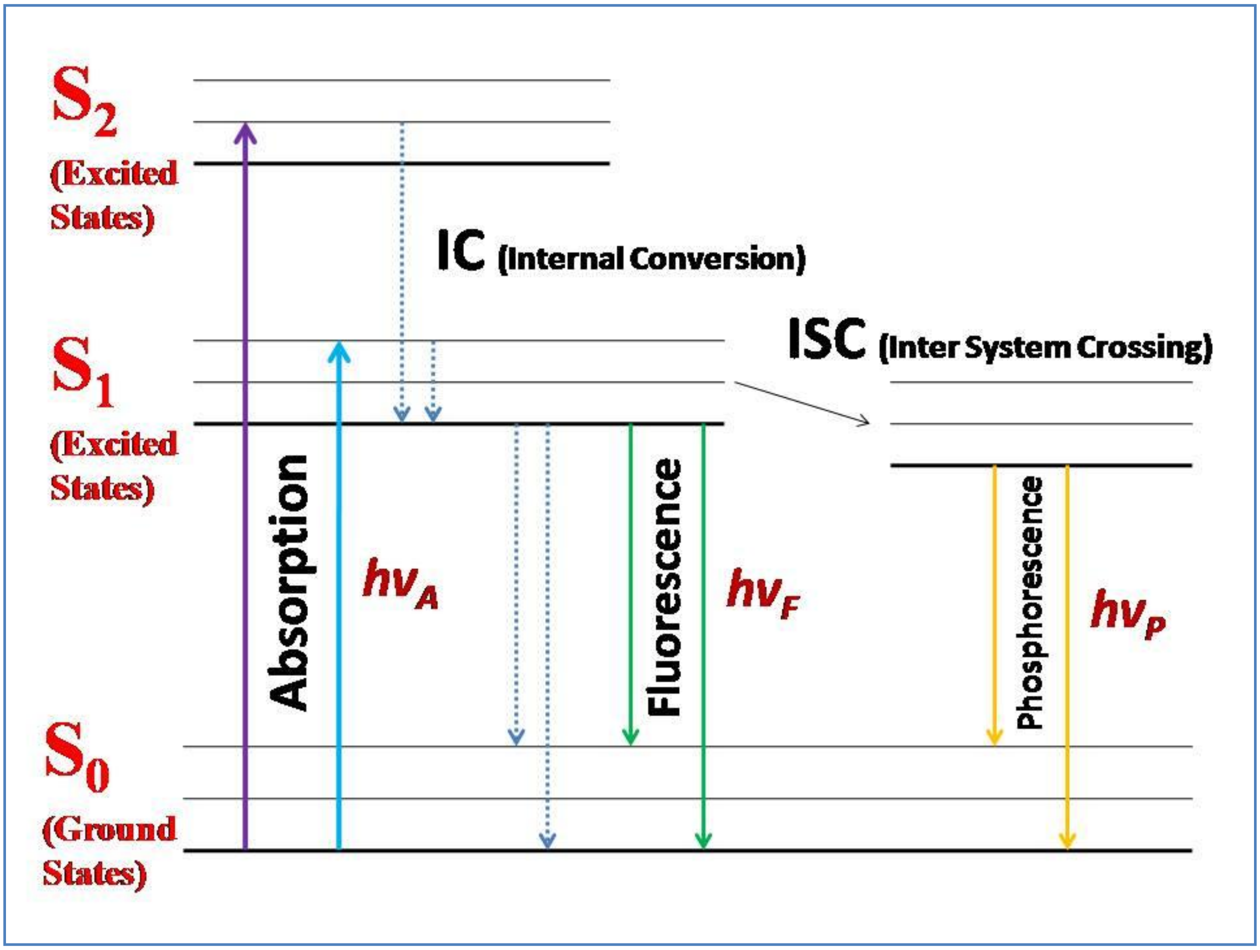

Figure 1.2: Schematic representation of Fluorescence and Phosphorescence

Alternatively, a quantum mechanically less probable process, which involves the reversal of electron spin may occur. It is referred to as Inter System Crossing (ISC) which also results into emission of photon of energy $h\nu_P$. However, the process has a longer decay time of more than millisecond and is called Phosphorescence. It is schematically presented in figure 1B.

Apart from the above description, the conventional way in which the luminescence phenomena is described is in terms of a diagram called configurational coordinate diagram. It provides important information. The measurement and study of photoluminescence is done by recording the excitation and emission spectra. These spectra may be narrow band or wide band. The shape of the optical absorption band is explained by the configurational coordinate diagram, shown in figure 1.3.

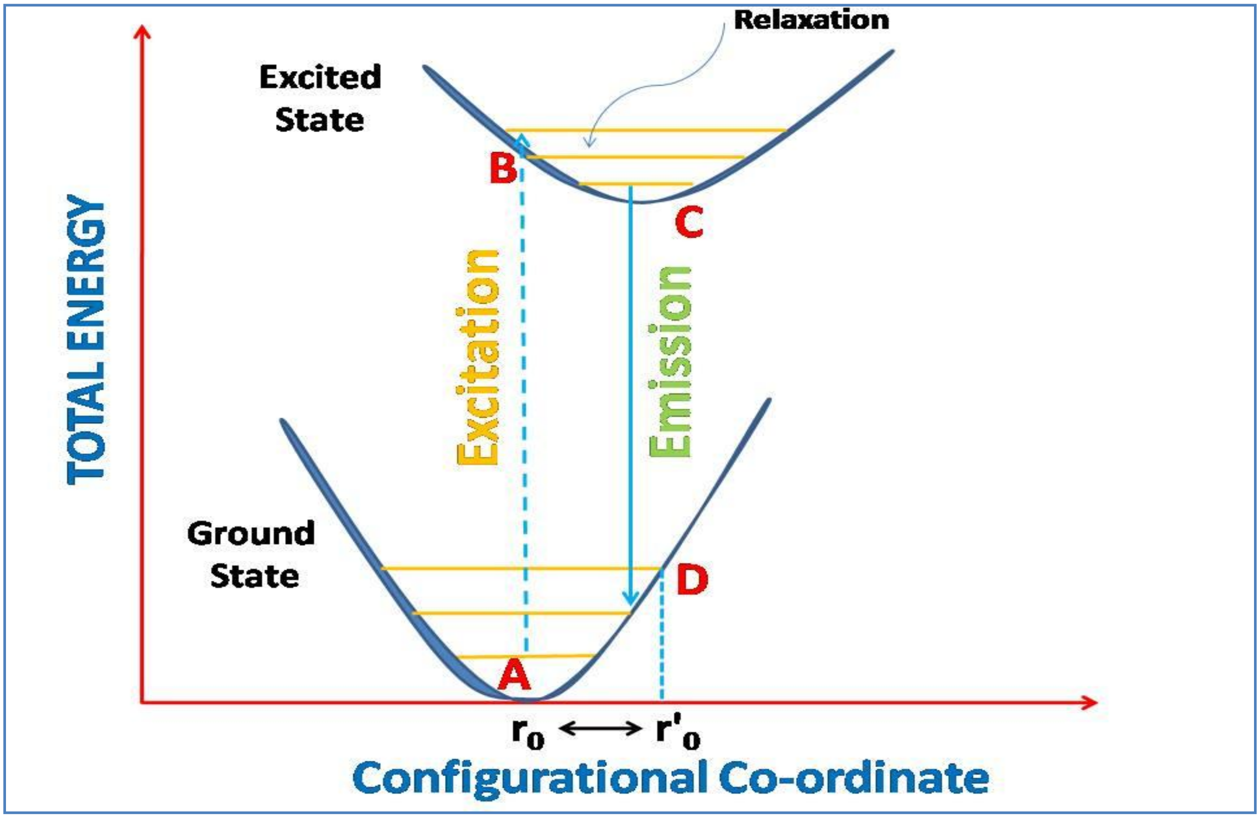

Figure 1.3: Configurational Coordinate Diagram

This diagram can explain the presence or the absence of characteristic luminescence [1]. The potential energy of the absorbing centre in the crystal lattice is plotted as a function of a configurational coordinate r. This coordinate describes one of the vibrational modes in which the central metal ion is at rest and the surrounding ligands will oscillate in relation to one another. The vibration is assumed to be in symmetrical stretching mode i.e. the central metal ion is at rest and surrounding ligands are moving in-phase away from the metal ion and coming back which is called symmetrical stretching mode as shown in figure 1.4.

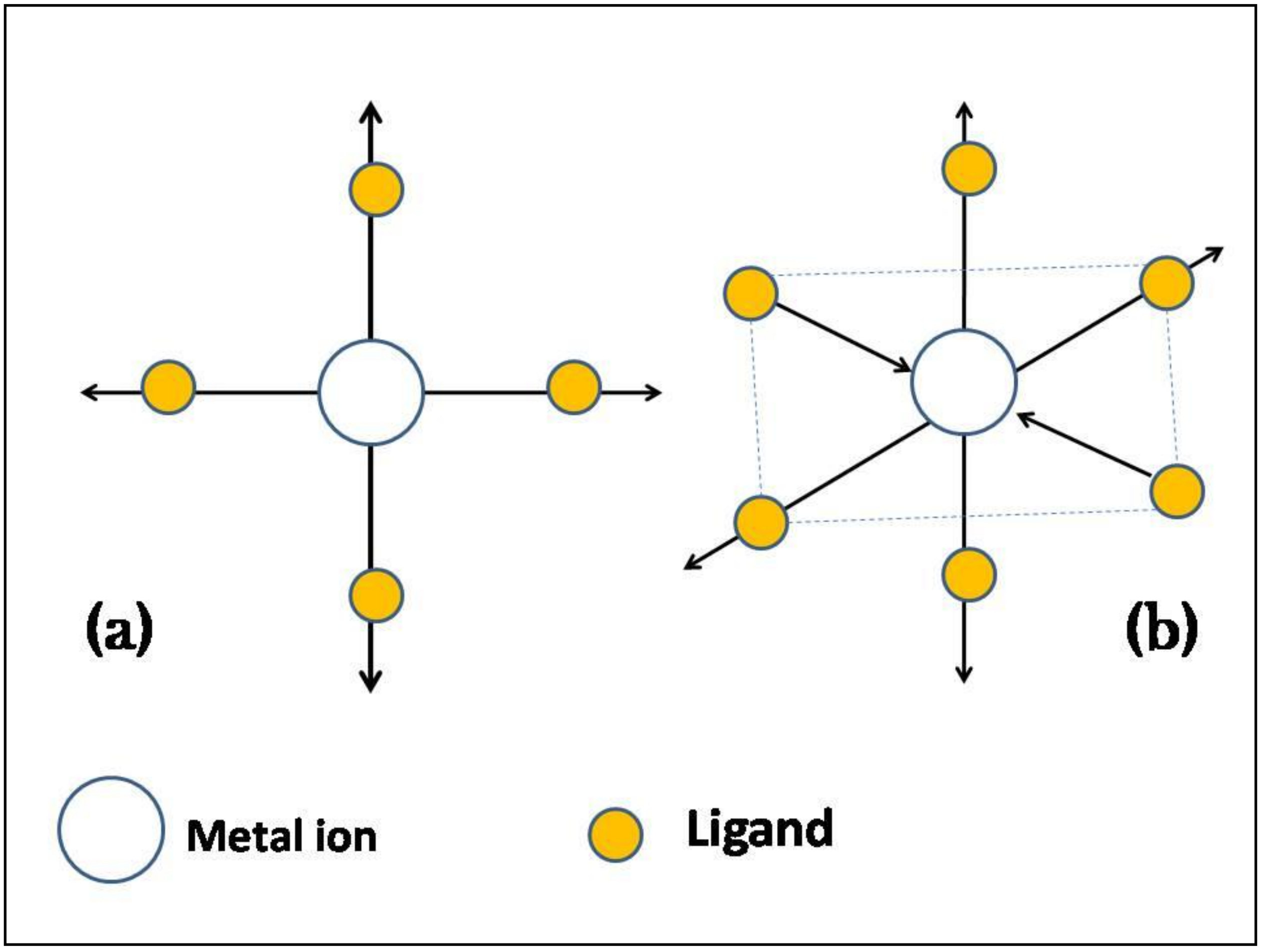

Figure 1.4: (a) Symmetrical stretching of square planar and (b) asymmetrical stretching of octahedron

To draw the configurational co-ordinate diagram (see figure 1.3) only symmetrical stretching mode is considered. The quantity ‘r’ (configurational co-ordinate) represents the metal – ligand distance. The ground state and the excited state in the figure 1.3 are parabolic as the vibrational motion is assumed to be harmonic. The horizontal lines represent vibrational states. The lowest vibrational level is r_0 which is the equilibrium distance in the ground state. The equilibrium distance r_e of the excited state is different from the ground state as the chemical bond is different for the excited state and the ground state.

At 0° K electron transition occurs to the excited state following the absorption of radiation from the equilibrium position of the ground state A → B as shown in the figure 1.3. The probability for an excited state to lose energy to the lattice vibration is 10^{12} to 10^{13} Sec^{-1} while probability for emission of light is 10^{9} Sec^{-1}. Accordingly, the electrons in the excited state B relaxes to the lower vibrational level C by dissipating heat till it reaches the equilibrium state before it emits luminescence. From this point, it emits radiation returning to the ground state D followed by relaxation to he equilibrium distance at r_0 completing the cycle.

The emission process is indicated by C → D and relaxation process by D → A. the difference Δr (= $r_0 - r'_0$) between the two parabolas of the excited state and the ground state gives the width of the absorption band. Larger the value of Δr, broader is the absorption band. The value of Δr measures the coupling between the electrons and the vibrations of the centre. At higher temperatures, the ground state may be at vibrational levels greater than at zero. This leads to the band broadening. Due to the heat dissipation to the crystal lattice the emission is always at lower energy than the absorption. This displacement of emission with respect to absorption is called Stokes shift [2].

1.3 Luminescent Materials

The luminescent material or the material, which shows the phenomena of luminescence, is also called a Phosphor. It may be a micro or nano scale material or pigment, organic or inorganic. The organic materials are usually aromatic compounds with extended π – electron system. The inorganic materials are usually a combination of host and dopant in trace amount. The dopants are referred to as activator and sensitizer, depending upon their role. The activator is generally responsible for the emission while the sensitizer generally absorbs the energy and transfers it to the activator. Both the activator and sensitizer are metallic ions that get substitutionally incorporated into the host lattice at the site of the metallic components of the host matrix. e.g. LaPO4: Ce,Tb, Here Ce (Cerium) is the sensitizer and Tb (Terbium) is the activator. It gives emission in green, as the characteristic emission of the activator i.e. Terbium is in green. Both get incorporated into the host lattice at the La (Lanthanum) ion site.

1.4 General synthesis method to prepare phosphors

There are several physical and chemical techniques like solid state method, ball milling, co-precipitation, hydro (solvo) thermal synthesis, sol-gel processing, combustion synthesis, etc., which are used to synthesize luminescent materials. Some materials, especially those with narrow size distribution and high aqueous solubility, require a special method or a combination of several methods, but others can be prepared by many complementary approaches. Optimization of the synthesis or fabrication procedure is critical to obtain crystals with tailored crystal size, morphology, chemical composition, surface functionalization and optical properties.

The simplest and most convenient method to synthesize phosphors in tunable sizes and narrow size distributions is the precipitation method. Compared to other techniques, there is no need for costly equipment, stringent reaction conditions and complex procedures, resulting in less time consumption. In some rare cases, crystalline phosphors were formed directly by co-precipitation, eliminating the need for calcinations step or post-annealing process.

The hydro (solvo) thermal synthesis uses a solvent under pressures and temperatures above its critical point to increase the solubility of solid and to speed up the reaction between solids. Potential advantages of this method over other types of synthesis methods include the ability to create highly crystalline phases at much lower temperatures. Disadvantages of the method include the need for specialized reaction vessels known as autoclaves and the impossibility of observing the material as it grows. The autoclaves usually consist of thick-walled steel cylinders with a hermetic seal for carrying out chemical reactions under pressure and high temperatures for prolonged periods. Furthermore, protective contact-type inserts typically made of Teflon and titanium materials are generally required to prevent solvent corrosion of the internal cavity of the autoclave.

Sol–gel processing is a typical wet-chemical technique to synthesize phosphors for application as thin film coating. The sol–gel process is characterized by the hydrolysis and polycondensation of metal alkoxide (or halide) based precursors. To improve the crystallinity that is directly associated with luminescence efficiency of the material, calcination at high temperatures is often needed. The sol–gel derived crystals are not particularly suitable as luminescent probes for biological assays due to lack of particle size control and considerable aggregation of the particles when dispersed in aqueous solutions.

As opposed to sol–gel and hydro (solvo) thermal methods that often require heating for a prolonged time period up to several days at high temperatures to complete a synthesis, controlled explosions in reactions known as combustion synthesis can give reaction products in minutes. Once initiated by a heat source, highly exothermic reactions with temperatures ranging typically from 500 to 3000 °C occur in the form of a combustion wave that propagates through the reaction materials in a self-sustained manner without requiring additional heat. The energy saving method represents one of the attractive techniques to synthesize a wide variety of materials.

1.5 Up-conversion phenomena, materials and mechanism

A specific and unique category amongst luminescent materials is the up-conversion material. The mechanism of luminescence, particularly excitation is also different. In this process, two photons of lower energy i.e. in the infrared region are absorbed to reach a higher excited state. The downward transition corresponds to emission in the visible region. It is a non-linear optical process with the intermediate excitation state being a long-lived state. Unlike the down conversion where the emitted photon has lower energy than the excitation photon, in up-conversion, the emitted photon has higher energy than the excitation photons.

The concept of proposed in the mid 1960's by scientists Auzel, Ovsyankin, and Feofilov as an independent formulation [3]. The up-conversion materials have generated a lot of curiosity and interest owing to their potential applications, which has also led to a lot of research activity in the field. Over the years, new areas of research have been added to it. The research in the field oriented with the use of Lanthanide compounds and remains so till date. Having being treated as a new class of materials in luminescence, it offers alternatives to organic fluorophores.

Usually rare earth compounds have been studied as host materials. However, both rare earth as well as transition metal ions have been used as activators and sensitizers. Most of the materials studied for up-conversion are rare earth activated/sensitized fluorides, sulphides and phosphates [4]. However, these materials have practical limitations due to their low chemical stability, mechanical strength and laser induced damage threshold, the last one being important because the excitation source for these materials is generally a laser diode. Hence, alternative materials used to be explored. The use of oxides and molybdates in this study is a step towards that end. Lanthanide doped up-conversion materials have suitable properties in terms of sharp emission lines, sustenance of efficiency at high doping levels and long life times suitable for time resolved methods, which makes them appropriate for use as fluorescent labels [5].

The process of up-conversion has been observed in many kinds of materials including silica fibers and waveguides. The process generally involves energy exchange between ion pairs, which are by and large rare earth ions, either of the same kind or different kinds, depending on the role of ion as activator or sensitizer.

There are generally three processes constituting the up-conversion mechanism, all based on the sequential absorption of photons, unlike the simultaneous multiple absorption [6].

The simplest process is the Ground and Excited State Absorption (GSA and ESA) as shown in figure 1.5. It generally involves a trivalent ion as the single dopant. GSA is the basic absorption ($G \rightarrow E_1$) followed by ESA ($E_1 \rightarrow E_2$). The initial photon is absorbed at level G to reach energy level E1. If the life time of E_1 is long enough, another incident photon can be absorbed to reach E_2. The downward transition is directly from E_2 to G, which results into up-conversion luminescence.

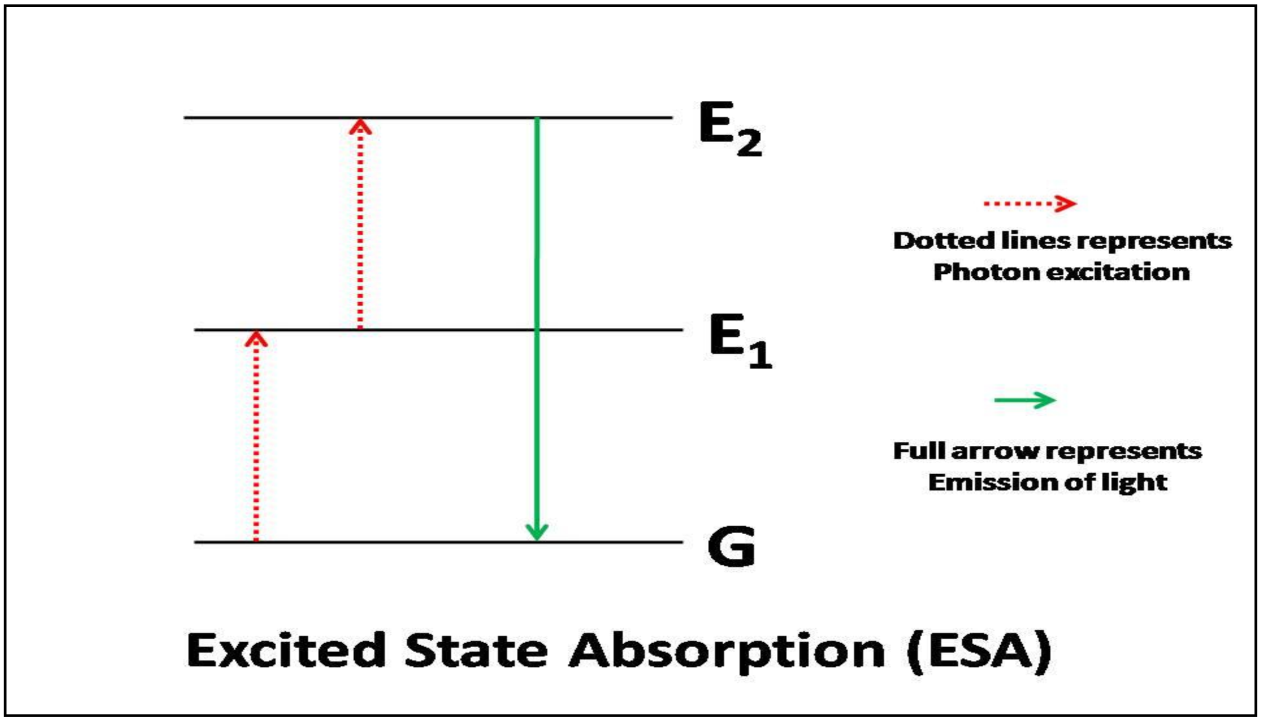

Figure 1.5: Up-conversion by Ground/Excited State Absorption.

The second type of process called Energy Transfer Up-conversion (ETU) involves a pair of ions, one sensitizer (ion 1) and other activator (ion 2) as shown in figure 1.6. The role of sensitizer is to absorb a photon and reach the excited level E_1. The sensitizer ion then relaxes to the ground state G by transferring its energy to the activator, which then reaches the excited state E_1. Subsequent excitation of the activator at E_1 enables it to reach further to the excited state E_2. The transition from E_2 to G gives up-conversion emission. As the process involves energy transfer between dopant ions, it is influenced by the dopant concentration, as it determines the average distance between the neighboring dopant ions.

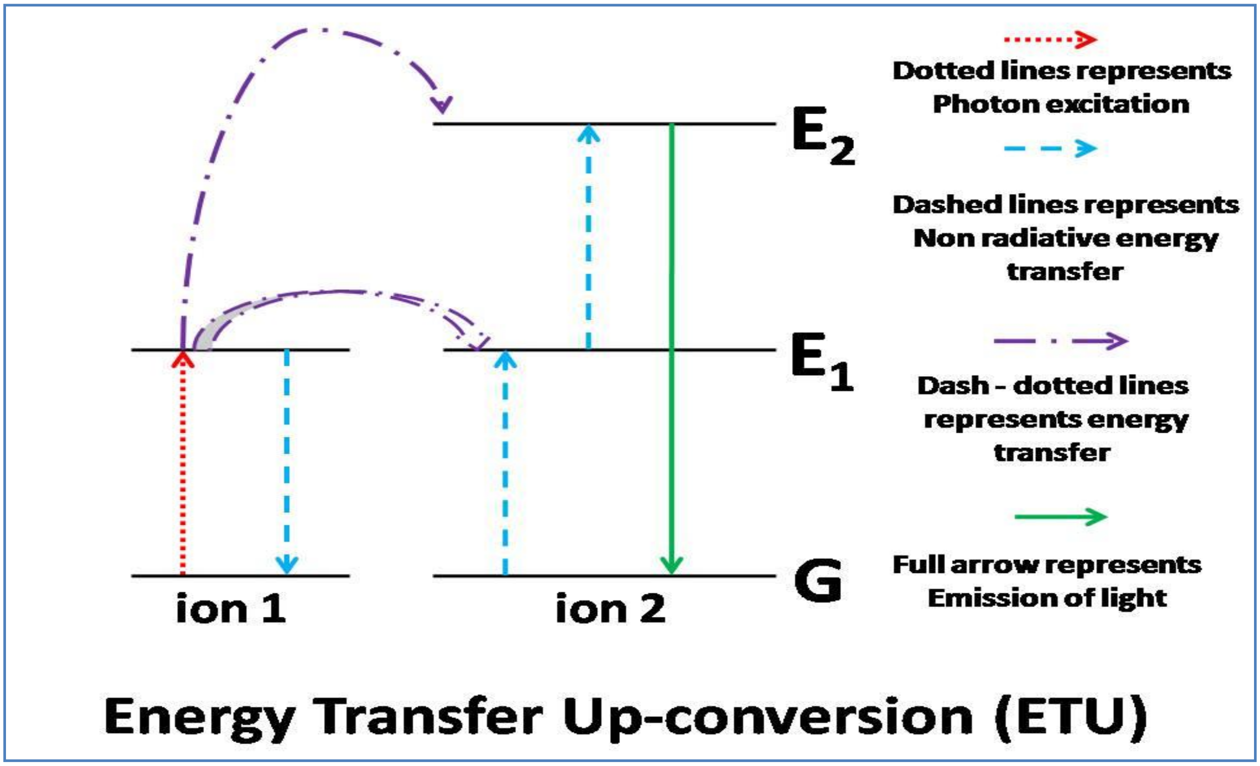

Figure 1.6: Upconversion by Energy Transfer Up-conversion process

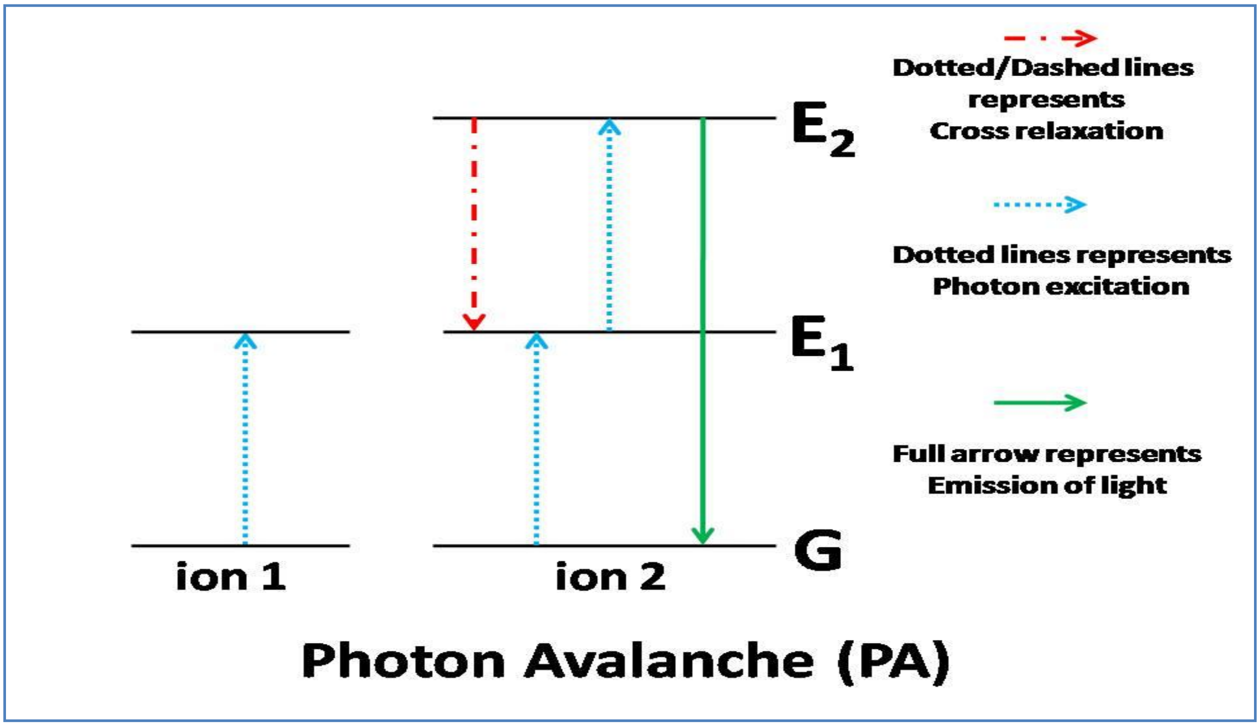

Figure 1.7: Upconversion by Photon avalanche

The third process by which up-conversion takes place is called Photon Avalanche (PA), which is characterized by an unconventional pumping mechanism and can produce strong emission even without a resonant Ground State Absorption as shown in figure 1.7.

The excited state E_1 is populated by a non-resonant weak GSA (Ground state absorption), followed by a resonant ESA (Excited state absorption) to promote the ion to the emissive level E_2. Next, a cross relaxation energy transfer occurs between the excited ion and a neighboring ion that is still in ground state. This results in both ions populating the intermediary level E_1. Subsequently, both ions can be promoted to level E_2 by resonant ESA again. This initiates further cross relaxation and exponentially increase the population of E_2 resulting in strong up conversion emission as an avalanche process.

The efficiency of up conversion in these three processes differs substantially. ESA (Excited State Absorption) generates the weakest luminescence and is only of interest in singly doped crystals. In materials with meta-stable, intermediate energy levels that can function as storage reservoir for pump energy, efficient up conversion based on PA (Photon avalanche) is feasible, though the process is disadvantageous because of its dependence on excitation power and its slow response to excitation due to the numerous looping cycles of ESA and cross relaxation processes. In contrast, ETU (Energy transfer up-conversion) happens instantaneously, is independent of excitation power, and produces emission two orders of magnitude higher than ESA. Therefore, many up conversion materials with more than one dopant ion have been developed based on the ETU process [7]. The phosphors developed in the present study also give up conversion based on the ETU (energy transfer up-conversion) process.

Up-conversion processes are primarily relying on the ladder like arrangements of energy levels of lanthanide ions as shown in the figure 1.8.

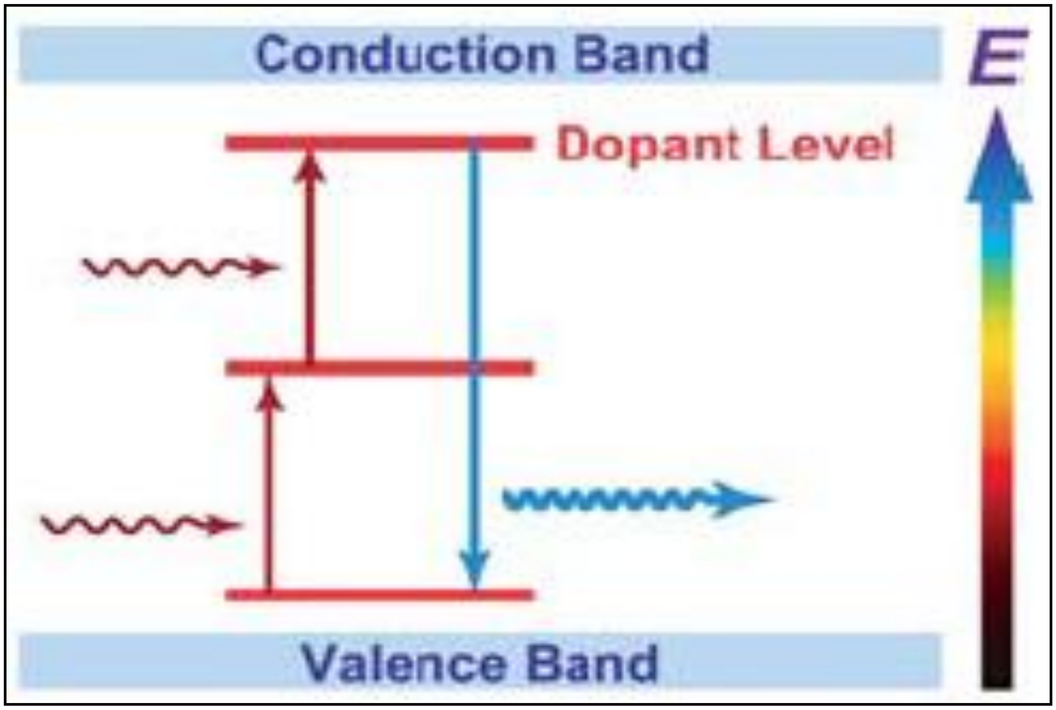

Figure 1.8: Ladder like arrangements of energy levels of lanthanide ions

In efficient up conversion processes, the crystal structure and the optical properties of host materials play important roles. Desirable host materials should have adequate transparency within the wavelength range of interest, low phonon energy and high optical damage threshold. In addition, the host materials should have close lattice matches to dopant ions for achieving high doping levels [8].

For the Energy Transfer Up conversion mechanism, two different rare earth ions are needed as dopants [9]. The dopants must exhibit multiple metastable states in order to enable efficient up conversion. Thus, lanthanides (Ln) are suited for this purpose. They basically exist in their most stable oxidation state as trivalent ions (Ln^{3+}). The 4f electrons of lanthanides are well shielded by the completely filled $5s^2$ and $5p^6$ shells resulting in weak electron-phonon coupling. This effect is responsible for the sharp and narrow f-f transition bands. Moreover, f-f transitions are Laporte forbidden, resulting in low transition probabilities and long-lived excited states.

Generally, lanthanide ions possess more than one excited 4f energy state, except for La^{3+}, Ce^{3+}, Yb^{3+} and Lu^{3+}. Most of the lanthanide ions are able to exhibit up conversion luminescence. However, excited and intermediate states have to be in proximity energetically to enable photon absorption and energy transfer to produce efficient emission. Such a ladder-like configuration of the energy levels is particularly featured by Er^{3+}, Tm^{3+}, and Ho^{3+}. Thus, these ions are frequently used as activators. Moreover, Er^{3+} and Tm^{3+} possess relatively large energy gaps, resulting in low probabilities for non-radiative multiphoton relaxations. Therefore, Erbium and Thulium doped crystals have shown the most efficient up conversion luminescence to date [7]. In singly doped host systems, the UC emission is mainly produced by ESA (Excited state absorption). There are two major parameters that affect UC processes. They are the distance between two neighboring activators ions and absorption cross-section of the ions. High doping levels can lead to deleterious cross-relaxation, resulting in quenching of excitation energy. The concentration of activator ions should be kept low and precisely adjusted to avoid the quenching effect. In addition, most lanthanide activator ions exhibit low absorption cross-sections, leading to low pump efficiency. Therefore, the overall up conversion efficiency for singly doped materials is relatively low.

An effective method to considerably increase UC efficiency is the so-called co-doping with a second lanthanide ion, called the sensitizer. By choosing a sensitizer with an adequate absorption cross-section in the NIR (near infrared) region, the ETU (energy transfer upconversion) process between sensitizer and activator can be used. Ytterbium (Yb^{3+}) is commonly used as a favorable sensitizer. The energy level scheme of Yb^{3+} is very simple with only one excited 4f state of $^2F_{5/2}$. The transition between the ground state $^2F_{7/2}$ and the excited state $^2F_{5/2}$ of Yb^{3+} occurs around 980 nm because it has a higher absorption cross-section at 980 nm wavelength in infrared region than that of any other lanthanide ions.

Furthermore, this transition is well resonant with f-f transitions of common up conversion activators such as Er^{3+}, Tm^{3+}, and Ho^{3+}, enabling energy transfer to other ions. Trivalent Ytterbium is an ideal up conversion sensitizer due to these characteristics. As a rule of thumb, in doubly doped materials, the sensitizer concentration is to be chosen high (15 – 25 mol %) while the activator dopant should be present in concentrations lower than 3 mol % to diminish emission quenching due to cross-relaxation processes [10]. Efficient up-conversion can only be achieved from a few up-conversion materials with combination of certain host and dopants.

Selection of suitable host materials is necessary in the synthesis of up-conversion phosphors with favorable optical properties such as upconversion efficiency and controllable emission properties. In general, the host materials require close lattice matches to dopant ions. They must have low phonon energies to minimize non-radiative relaxation processes and maximize radiative emission. Inorganic compound based on rare earth elements form ideal host materials for lanthanide dopants as all trivalent rare earth ions show almost similar ionic size and chemical properties.

Additionally, the ionic size of alkaline earth ions such as Ca^{2+}, Sr^{2+}, and Ba^{2+} and some transition metal ions like Zr^{4+} and Ti^{4+} is similar to that of Ln^{3+} ions. Accordingly, these ions have been used to prepare materials capable of up conversion [11]. However, doping with Ln^{3+} ions results in the formation of crystal defects such as interstitial anion and cation vacancies to maintain charge neutrality [12].

Generally, phosphates [13], oxides [14], oxysulfides [15] and fluorides [16] are used as anions in the crystal host. Phosphates and oxides are chemically stable but their phonon energies are relatively high and generally larger than 500 cm^{-1} due to the stretching vibration of the host lattice. Oxysulfides are not stable against acids. In comparison, fluorides usually exhibit low phonon energies (350 cm^{-1}) and high chemical stability, and therefore are often used as the host materials for efficient upconversion [7].

In this study, oxide materials namely Lanthanum molybdenum oxide ($La_2MoO_4)_3$), Cadmium oxide (CdO) and Bismuth oxide (Bi_2O_3) have been used as host materials to make upconversion phosphors. Because of its high content of oxygen in Earth’s atmosphere, oxides are most stable materials. Metal oxides play very important role in many fields like in Physics, Chemistry and Materials Science [17]. Metals form large diversity of oxides, which can exhibit metallic, semiconducting or insulating characteristics. Bulk oxides are usually stable with well-defined crystallographic structure.

The oxide phosphors with rare-earth photoluminescence in metal oxide matrices have appealed a great deal of attention because of their potential in a host of various applications including flat panel display devices, optoelectronics etc.[18].

The oxide phosphors have higher chemical and thermal stability than commonly used sulfide phosphors. This advantage draws these materials chemically stable in high vacuum and under electronic excitation. Hence, there is a continuous search for new oxide phosphors with high performance for new phosphor applications. Rare-earth molybdate compounds have attracted significant attention due to their potential technological application as catalysts, high-performance phosphors, up-conversion phosphors etc [19]. Based on their unique catalytic, optical and magnetic properties, these types of compounds have attracted intensive interest. The composition and structure of rare-earth compounds, especially the crystal field and the complexation state of the matrix in which rare-earth ions are coordinates. The inorganic lanthanide ions express narrow emission bands, long lifetime and prominent stokes shifts.

Lanthanum Molybdate occurs in several chemical forms like $La_2(MoO_4)_3$, La_2MoO_8, $La(Mo_8O_{14})$, $La_2O_2(MoO_4)$, $La_2Mo_2O_9$, La_6MoO_{12}, $La_6Mo_2O_{14}$, La_2MoO_6 and $La_6Mo_2O_{15}$. These may have different structures like monoclinic, orthorhombic, tetragonal, cubic, rhombohedral and hexagonal. There are several forms of lanthanum molybdate such as $La_2(MoO_4)_3$ (monoclinic), La_2MoO_8 (monoclinic), $La(Mo_8O_{14})$ (orthorhombic), $La_2O_2(MoO_4)$ (tetragonal), $La_2Mo_2O_9$ (cubic), La_6MoO_{12} (rhombohedral), $La_6Mo_2O_{14}$ (hexagonal), La_2MoO_6(tetragonal), $La_6Mo_2O_{15}$ (orthorhombic), etc.

Bismuth Oxide (Bi_2O_3) has been inquired extensively due to its optical and electrical properties such as refractive index, large energy band gap, dielectric permittivity as well as remarkable photoluminescence and photoconductivity [20]. Compounds based on Bismuth Oxide are much better solid electrolytes than well-known stabilized Zirconia, because the FCC (face-centered cubic) Bi_2O_3 exhibits the highest ion conductivity of all oxide ion conductors [21].

It is well known that there exist six polymorphs of Bismuth Oxide denoted by α-Bi_2O_3 (monoclinic), β-Bi_2O_3 (tetragonal), γ-Bi_2O_3 (BCC), δ-Bi_2O_3 (FCC), ω-Bi_2O_3 (orthorhombic) and ε-Bi_2O_3 (triclinic). The low temperature α-phase and high temperature δ-phase are stable, and the others are high temperature metastable phases such as β-Bi_2O_3 and γ-Bi_2O_3, these can be stabilized to exist at room temperature by doping with impurities [22, 23].

Cadmium Oxide (CdO) is the most important n – type semiconductor with a cubic structure. It belongs to II – VI group with a direct band gap of 2.5 eV and an indirect band gap of 1.98 eV. This difference in the band gap is attributed to intrinsic Cadmium and Oxygen vacancies. Because of its ionic nature coupled with its wide band gap, low electrical resistivity and high transmission in the visible region. Due to such characteristics CdO has been found to be a suitable candidate for applications in different fields like optical, gas sensors, solar cells, front panel displays and photovoltaic cells, etc. [24]. Cadmium oxide is available in single phase i. e. cubic phase.

1.6 Applications

There are various applications of upconversion materials in light emitting diodes, solar cells, biolabeling and biological imaging etc.

1.6.1 Light Emitting Diodes (LEDs)

A light-emitting diode (LED) is a semiconductor light source. LEDs are used as indicator lamps in many devices and are being increasingly used for lighting. In early days LEDs emitted low-intensity red light, but modern versions are available across the visible, ultraviolet and infrared wavelengths, with very high brightness. Light-emitting diodes are used in applications as diverse as aviation lighting, automotive lighting (particularly brake lamps, turn signals and indicators) as well as in traffic signals.

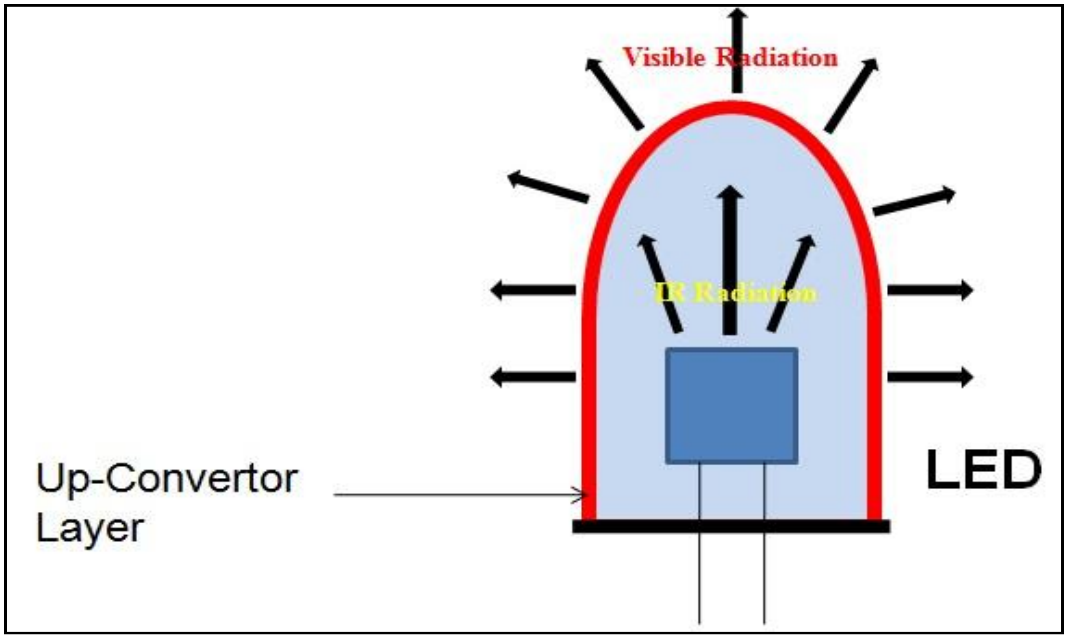

Figure 1.9: Schematic view of LED coated with upconversion phosphor layer

The compact size, the possibility of narrow bandwidth, switching speed, and extreme reliability of LEDs has allowed new text and video displays as well as sensors to be developed, while their high switching rates are also useful in advanced communications technology. Infrared LEDs are also used in the remote control units of many commercial products including televisions, DVD players, and other domestic appliances.

As shown in the figure 1.9, the emission of IR radiation by passing current through the LED, can be converted to visible radiation by coating of up-conversion phosphor inside the LED cover. Such modified LEDs can be used instead of conventional LED arrays in LED displays.

1.6.2 Solar Cell

The transmission of sub-band gap light is one of the major loss mechanisms in conventional solar cells. Wolf proposed a possibility to reduce these transmission losses in the so-called impurity photovoltaic effect (IPV), i.e. the insertion of impurities with energies located in the band gap of a solar cell material [25]. Gibart et al. presented a method to reduce the transmission losses by up converting the transmitted low energy photons from the solar spectrum to high energy photons, which can then be utilized by the solar cell [26]. A newly improved photovoltaic system involving an up-converter is schematically illustrated in the figure 1.10 and energy levels in the up-converter in figure 1.11.

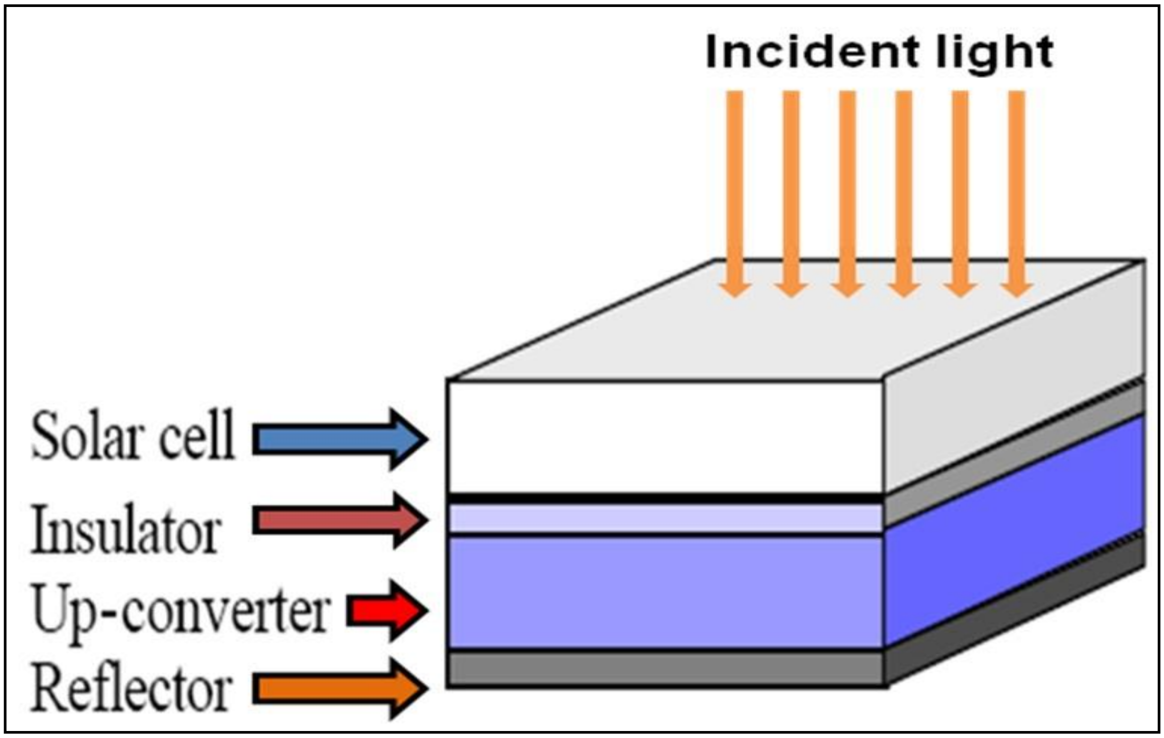

Figure 1.10: Schematic view of a new system consists of a solar cell and up-converter

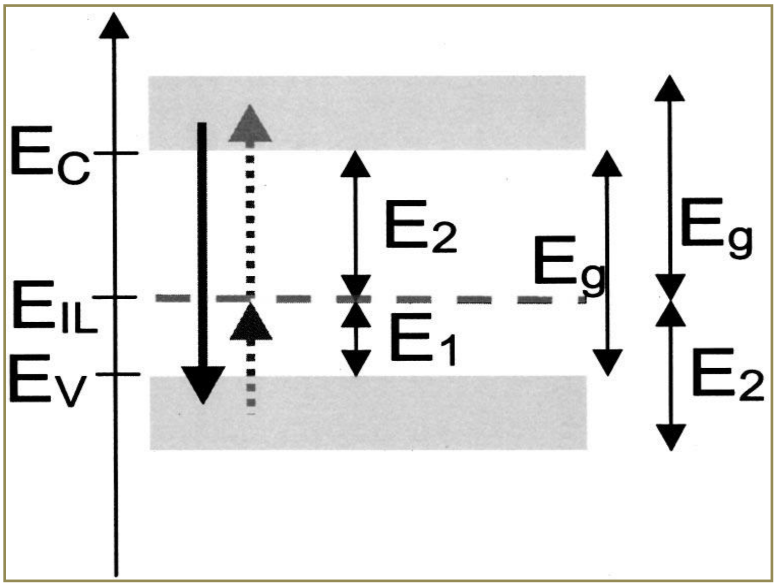

Figure 1.11: A schematic energy-level diagram of up-converter

It is based on a conventional bifacial single-junction solar cell made of a material with band gap E_g. The second main element of the system is the up-converter, which partially transforms the sub-band-gap photons transmitted by the solar cell into high-energy photons. In our theoretical treatment, we assume that the up-converter is electronically isolated from the solar cell and located behind it. A perfect reflector is located at the rear surface of the up-converter. In a real system, the up-converter could also be present in the form of rare earth atoms implanted directly into the solar cell material itself.

A schematic energy-level diagram of up-converter is shown in figure 1.11. The up-converter consists of a material with a band gap that ideally equals the band-gap energy of the solar cell E_g and contains intermediate levels (IL) with energy E_1 above the valence band edge and energy E_2 below the conduction band edge. The absorption of sub-band-gap photons in the up-converter leads to the generation of electron-hole pairs (electrons in the conduction band and of holes in the valence band) via two sequential transitions from the valence band into the IL and from the IL into the conduction band. Dotted arrows in figure 1.11 present these transitions.

A fraction of the excess electron-hole pairs generated inside the up-converter recombines via radiative band-to-band transitions (solid arrow in the figure 1.11) which is followed by the emission of photons with energies above the band gap. As the solar cell and the up-converter is assumed to have equal band gaps these up-converted photons can be absorbed by the solar cell, which leads to an additional generation of electron-hole pairs.

As the up-converter is electronically isolated from the solar cell, no additional recombination channel is introduced into the active solar cell material. Recombination of electrons and holes via the intermediate level is therefore possible only inside the up-converter.

An optimized up-converter might be stacked behind any existing bifacial solar cell, potentially increasing its efficiency [27].

1.6.3 Biological Imaging

In medical diagnosis, biological imaging techniques like X-ray, CAT scan, and MRI are widely used to examine the structure and defects in biological tissues and living cells at the organ level. However, these methods have some limitations. There are harmful effects of ionizing radiation, they cannot distinguish between benign and malignant tumors and they do not have real time response. Thus, there is a need to have improved bioimaging technique, which has the capability to analyze what is happening at the cellular and molecular levels with high resolution in an efficient way.

A modern bioimaging approach using up-conversion fluorescence can resolve these drawbacks of conventional bioimaging techniques. Up-conversion fluorescence technique with excitation in the near infrared region can be used for imaging of biological cells and tissues because it has several advantages including absence of photo-damage to living organisms, very low auto-fluorescence, non-harmful, real time response, high detection sensitivity and high penetration depth in biological tissues. This technique utilizes tailor-made nano dimensional up conversion phosphor materials. These phosphors can easily be coupled to protein or other biological macromolecular systems and tissues by injecting into living cells intradermally, intramuscularly or intravenously which is ascribed to their small physical dimensions and surface functionalized biocompatibility. A schematic view of optical instrumental setup for bioimaging is illustrated in the figure 1.12.

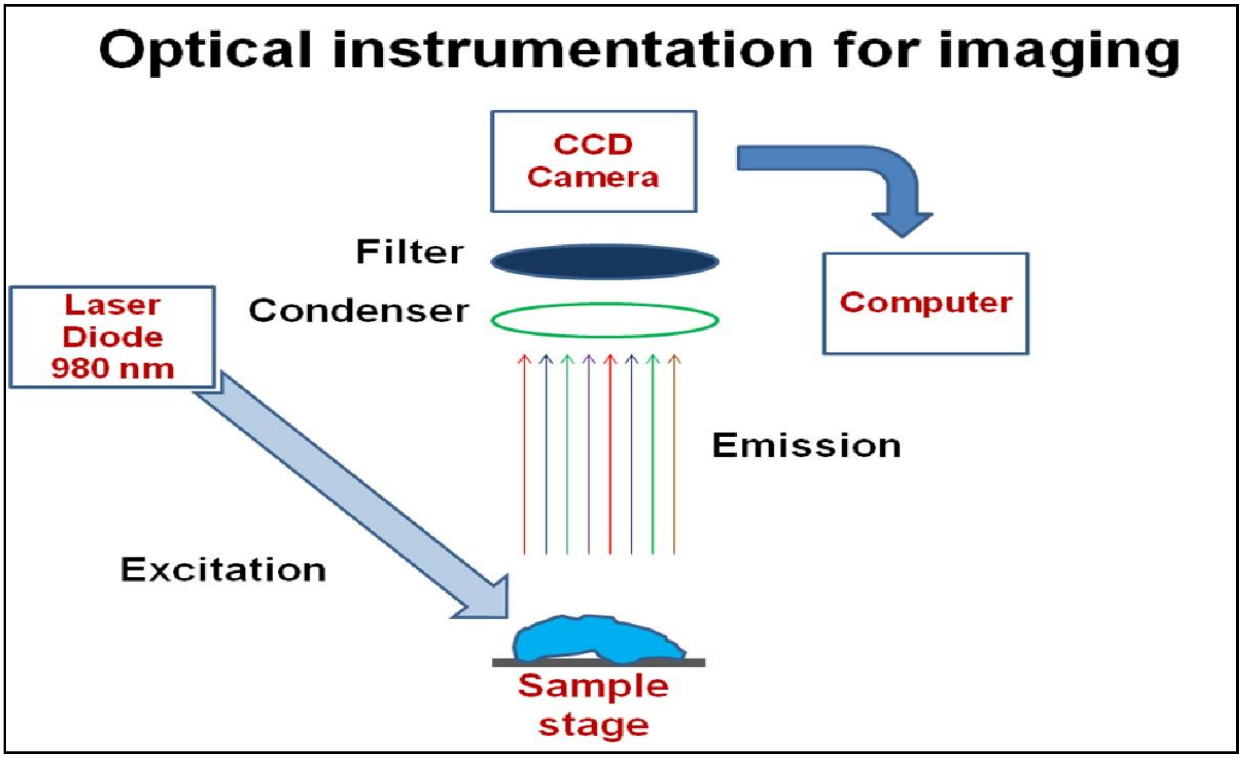

Figure 1.12: Optical instrumental setup for bioimaging

Under 980 nm infrared excitation, phosphors within the cell or tissue glow immediately and give the visible fluorescence from that particular cell or tissue which then can be captured by the CCD camera with sophisticated optical microscopy setup (Figure 1.12). Intense visible emission from these nanophosphors under near-infrared excitation makes them less harmful to biological samples and gives greater sample penetration depths compared to conventional ultraviolet (UV) excitation.

Upconversion nanoparticles exhibit anti-stokes emission upon low level of irradiation in the spectral region of near infrared, where biological molecules are optically transparent. These nanoparticles show a very sharp emission bandwidth, long lifetime, tunable emission, high photo stability and low cytotoxicity, which furnish them particularly useful for bioimaging applications [28].

1.7 Chromaticity

Measurement / Quantification of Colour

The measurement and quantification of a quality like colour seems to be abstract. However, there are standard procedures and methods to do the same. It is generally expressed in terms of a chromaticity diagram. Evidently, the specific property that is important for a phosphor is its colour. Colourimetry, which is the science and technology for quantifying colour physically as a human perception. The standards of measurement have been provided by the world governing body for colour and appearance measurement, called Commission Internationale de I'Eclarage or International Commission on Illumination [29].

Historically, it dates bake to 1931 when CIE gave the basis for colourimetry. It proposed three primary colour in terms of these three primary colours. The standard primary colours proposed were blue (435.8 nm), green (546.1 nm) and red (700 nm) [29]

These primaries, in appropriate proportions can reproduce a full range of colours. These amounts are represents as set called "Colour Matching Functions" denoted by $\bar{x}$, $\bar{y}$ and $\bar{z}$. They are also called "Tristimulous Response Functions". These standard colour primaries proposed by CIE, also known as standard CIE observer model. The response of three types of photo-receptors in the retina of the human eye to a particular colour [30]. These three human receptors have specific spectral response curves over the visible range which are known as “Tristimulous Response Curves”, as shown in figure 1.13.

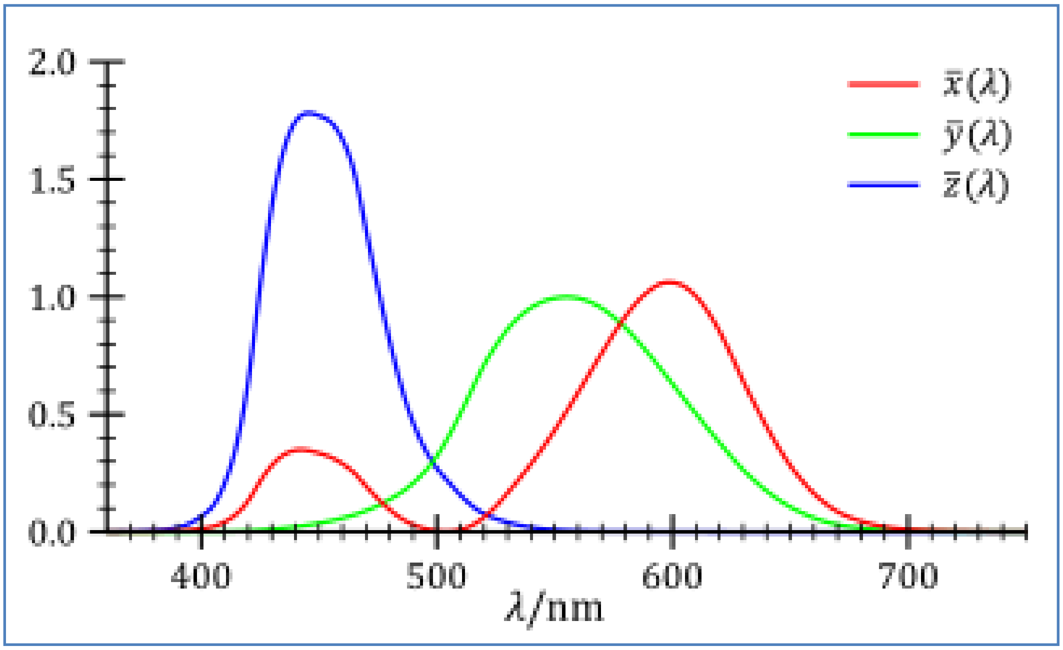

Figure1.13: Tristimulous Response Curves

These may be also called the finalized response curves for the standard observer. It can be seen from figure 1.13 that the tristimulous vale $\bar{x}$ representing red colour has some amount of blue as well. This is to duplicate the response of the red receptor in the retina of the eye.

The tristimulous response curves are used to find the colour represented by a given spectrum in a diagram called Chromaticity diagram. Since the energy of any spectral curve S (λ) is defined as summation of intensities times wavelengths, the spectral curve is overlapped on the tristimulous response curves and the energy (intensity) of the spectral curve S (λ) is multiplied with the vales of tristimulous response $\bar{x}$ (λ), $\bar{y}$(λ) and $\bar{z}$(λ) at the same wavelengths. The summation of the products give the “Tristimulous Values” X, Y and Z.

$$X = k \int_{380}^{780} S\,(\lambda)\,\overline{\mathrm{x}}\,(\lambda)\,\mathrm{T}\,(\lambda)\,\mathrm{d}\lambda$$

$$Y = k \int_{380}^{780} S\,(\lambda)\,\overline{\mathrm{y}}\,(\lambda)\,\mathrm{T}\,(\lambda)\,\mathrm{d}\lambda$$

$$Z = k \int_{380}^{780} S\,(\lambda)\,\overline{\mathrm{z}}\,(\lambda)\,\mathrm{T}\,(\lambda)\,\mathrm{d}\lambda$$

Where k is a normalizing factor given by $\frac{100}{\int_{380}^{780} S\,(\lambda)\,\overline{\mathrm{y}}\,(\lambda)\,\mathrm{d}\lambda}$

S (λ) is the relative spectral power distribution of the illuminant and T (λ) is the spectral transmittance of the colour object [31].

The tristimulous values XYZ can be used to define a colour. However to visualize the colour, the chromaticity diagram is needed. This chromaticity diagram is constructed by calculating the chromaticity coordinates x, y and z using the tristimulous values X, Y and Z.

$$x = \frac{X}{X + Y + Z}$$

$$y = \frac{Y}{X + Y + Z}$$

$$z = \frac{Z}{X + Y + Z}$$

Where x + y + z = 1.

Hence it is sufficient to compute only two coordinates. The CIE 1931 model used (x,y) coordinates [31] and the diagram appears as shown in the figure 1.14 below:

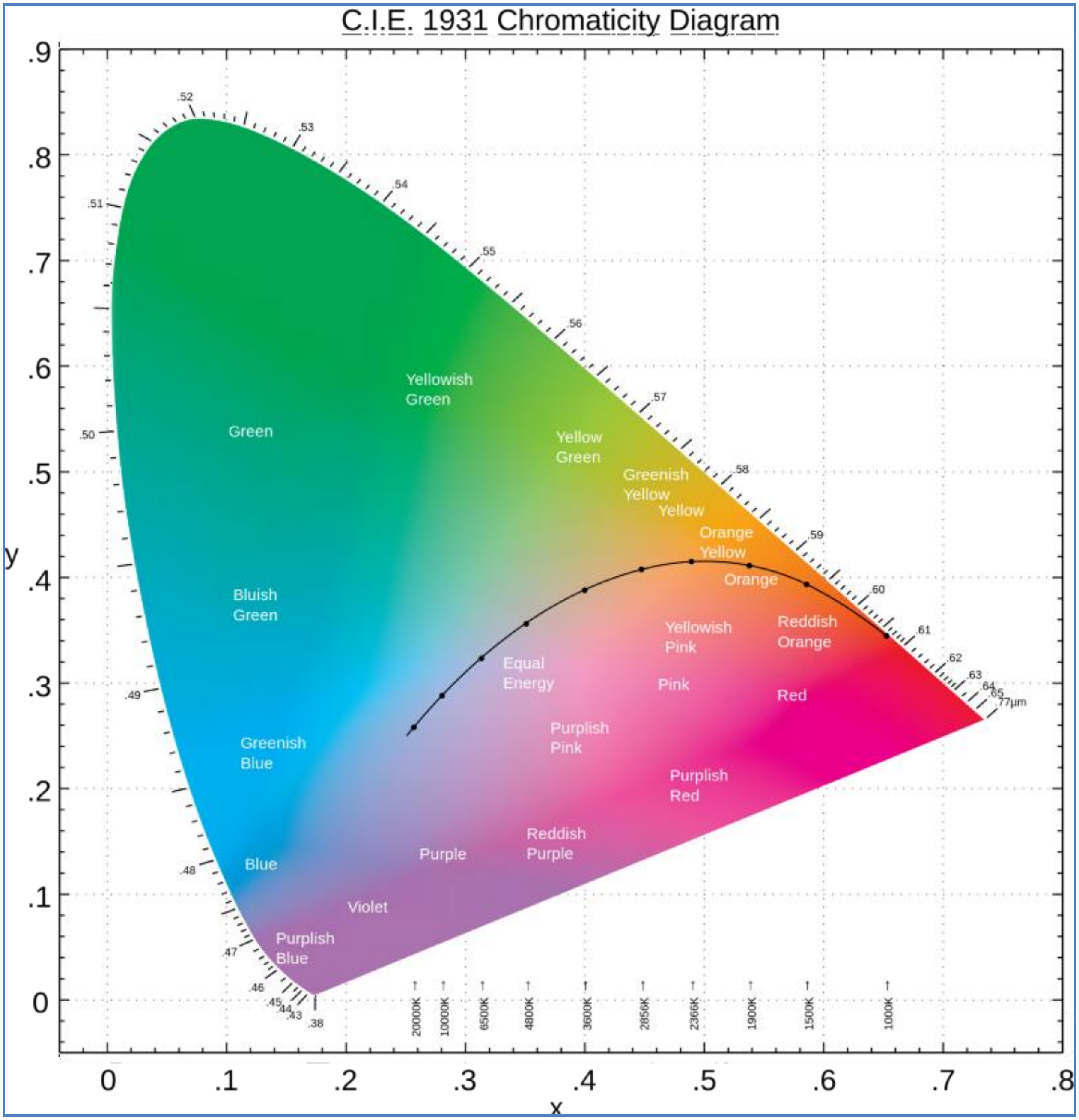

Figure 1.14: CIE 1931 Chromaticity Diagram

{Courtesy: CIE 1931 color space – Wikipedia}

Hence, chromaticity coordinates are the ratio of the intensities of the three primary lights that appear identical to a series of monochromatic lights of equal energy in the visible region.

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