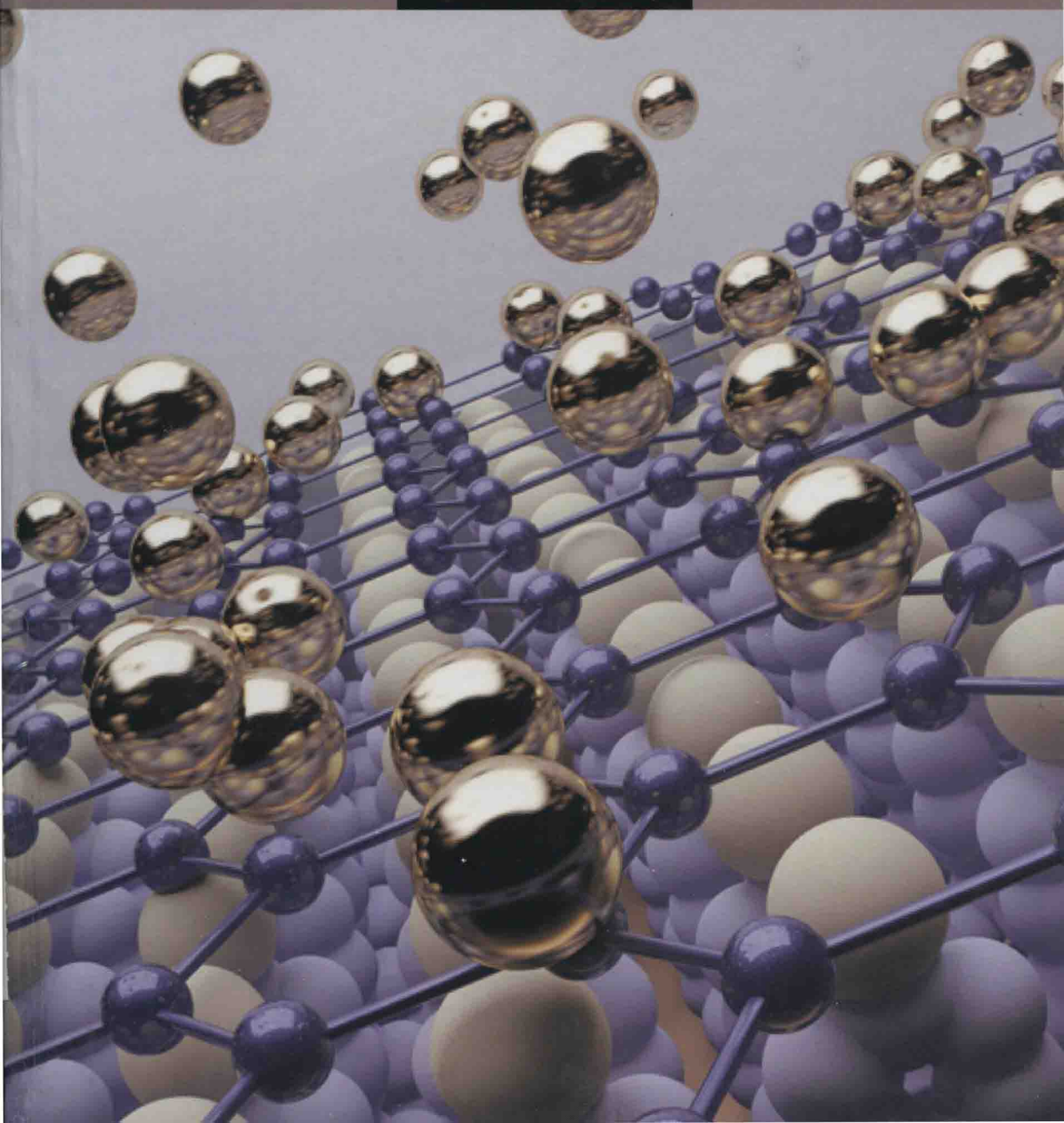


# NANOSCIENCE

## AN INTRODUCTION

Nishit Mathur



# **Nanoscience**

## **An Introduction**

*Er. Nishit Mathur*



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# **Nanoscience**

## **An Introduction**



# Preface

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Nanoscience, a field of science which has emerged during the last three decades, now-a-days comprises many different fields and starts to play an important role as key technology in application and business.

The term *nano*, derives from the Greek words nanos which means dwarf, designates a billionth fraction of a unit, e.g., of a mete. Thus, the science of nanostructures is often defined as dealing with objects on a size scale of 1-100 nm.

Nanoscience stands out for it's interdisciplinary character. Barriers between disciplines disappear and the fields tend to converge at the very smallest scale, where basic principles and tools are universal. Novel properties are inherent to nanosized systems due to quantum effects and a reduction in dimensionality: thus nanoscience is likely to continue to revolutionize many areas of human activity.

This book spans all fields of nanoscience, covering its basics and broad applications. After an introduction, coverage moves on to the adjacent fields of microscopy, nanoanalysis, synthesis, nanowires, nanomechanics, etc. Consequently, this broad yet unified coverage addresses research in academia and industry across the natural scientists. Didactically structured and replete with hundreds of illustrations, the book is aimed primarily at graduate and advanced-undergraduate students of natural sciences and medicine, and their lecturers.

Book writing-whether original or compilation is a complicated job requiring academic labour.

The present work is purely a research compilation based on authoritative publications/readings/excerpts/reviews/researches authored by eminent scientists.

Assistance has also been sought from Websites through Internet.

The author, humbly, acknowledges the contributions of all those eminent scientists alongwith their respective publishers and Websites in preparation of this book.

—*Er. Nishit Mathur*



# Contents

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<i>Preface</i>	(v)
<b>1. Introduction</b>	<b>1</b>
The History of Nanoparticles Research • The Science of Semiconductor Nanocrystals • Luminescence • Photoluminescence • Laser Induced Photoluminescence (Lip) Applications • Mechanism of Photoluminescence • Phosphors and their Applications • Luminescence of ZNO Phosphors • Theory of Luminescence • ZNO Nanostructures • ZNO Nanobelts	
<b>2. Legal Implications of Nanoscience</b>	<b>18</b>
Quantum Behaviour • Quantum Devices	
<b>3. Nanostructured Materials</b>	<b>45</b>
Introduction and Scope of the Review • Nanoclusters and Nanocrystals • Nanocluster Synthesis • Electronic Properties of Nanoclusters: Quantum Confinement and Single-electron Effects • Optical Properties of Nanoclusters • Magnetic Nanoclusters • Carbon-based Nanomaterials • Conclusions and Future Prospects	
<b>4. Nanoparticles</b>	<b>118</b>
Introduction • Preparation of Nanoparticles • Production of Nanoparticles using Supercritical Fluid Technology • Effect of Characteristics of Nanoparticles on Drug Delivery • Applications of Nanoparticulate Delivery Systems • Nanoparticles for Drug Delivery into the Brain • Conclusion	
<b>5. Quantum Dot</b>	<b>132</b>
Quantum Confinement in Semiconductors • Production • Optical Properties • Applications	
<b>6. Nanotubes and Nanowires</b>	<b>143</b>
Introduction • Experimental • Results and Discussion • Other Metal Nanowires and Nanotubes	



<b>7. Tools of the Nanoscience</b>	<b>160</b>
Tools for Measuring Nanostructures • Tools to make Nanostructures	
<b>8. Characterization Techniques</b>	<b>174</b>
X-ray Diffraction Techniques • Scanning Electron Microscope • Transmission Electron Microscopy	
<b>9. Surface Analysis Techniques</b>	<b>216</b>
Atomic Force Microscopy • Scanning Probe Microscopy • Scanning Tunneling Microscope • Nanoindentation	
<b>10. New Fields of Nanoscience</b>	<b>237</b>
Raw Materials of Nanotechnology	
<b>11. Nanosystems Intermolecular Forces and Potentials</b>	<b>250</b>
Introduction • Interatomic Potentials for Metallic Systems • Conclusions and Discussion	
<i>Bibliography</i>	<b>287</b>
<i>Index</i>	<b>289</b>

# Introduction

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The word 'nano' originates from Greek word 'dwarf' which is referred to the length scale of billionth of a meter. Thus nanoscience deals with the science of materials and technologies in the range of  $\sim 1\text{-}100$  nm. This means, the nanoscience deals with a few hundred to a few thousand atoms or atomic clusters, whereas the microscopic world is made of trillion of atoms or molecules. Presently, the nanoscience and nanotechnology represents the most active discipline all around the world and is considered as the fastest growing technological-revolution the human history has ever seen. The immense interest in the science of materials confined within the atomic scales stems from the fact that these nanomaterials exhibit fundamentally unique properties with great potential of bringing plethora of next-generation technologies in electronics, computing, optics, biotechnology, medical imaging, medicine, drug delivery, structural materials, automotives, aerospace, food, energy, etc: in almost all walks of life.

Although the research in present day of nanomaterials is based largely on the curiosity of investigating fundamental properties of matter in nanoscale regime, however, the timely attention and efforts are essential for the transformation of these new findings into technologies-products so that the well-assumed technological revolution can become day-light reality. By now, a variety of chemical, biological as well as physical processes have been established for the preparation of different kinds of nanoparticles, systems and the groundbreaking inventions such as *scanning tunneling microscope* (STM), *atomic force microscope* (AFM), etc, together with the conventional *high resolution transmission electron microscope* (HRTEM) have made the characterization and atomic scale manipulation of nanoscale materials a practical reality.

This chapter is aimed at providing a general overview of important concepts that are needed for understanding the research work done in the thesis. It is by no means a complete overview, many books are also available which provide a comprehensive introduction to this interesting field. This chapter also presents the lucid way to define the quantum confinement effect in small sized particles. Time resolved spectroscopy and lifetime measurements with lasers have been described in second chapter.

## **THE HISTORY OF NANOPARTICLES RESEARCH**

The existence of nanoscience can be traced back both in the living as well as non-living things existing in nature since billions of years. For instance, living-cells are the glaring examples of multifunctional nano-machines. Similarly, nanomaterials cannot be viewed differently from the colloidal system occurring naturally or made synthetically. Thus, it is difficult to fix a date for origin of nanoscience. However, one of the historically important observations on the size dependent properties of materials came from the great scientist of 19th century, Sir Michael Faraday.

*On March 11, 1856, he wrote in his diary:*

- \* "... And then, put small pieces of gold above the convex surface of a rock crystal and pressed it by hand steadily, rocking it a little. The applied pressure converted the violet or dark colour of the place of contact into a beautiful green; far more beautiful than any I have ever seen in a gold leaf beaten. The effect was perfect".

Sir Faraday was trying to make bigger pieces of gold from small particles by pressing them together.

*As one expects from a great scientist, it is not surprising that diary continues with an accurate explanation of this phenomenon of colour change in fine gold particles under pressure,*

- \* "... Has the pressure converted the; layer of atoms into a continues layer by expansions and welding? I rather think it is. So, it appears that these different layers are all gold only, and own their different appearance not to composition but to physical difference in size".

Thus, Sir Faraday discovered that the colour or to be more precise, the electronic structure, of material can be size dependent. Probably, this was the first reported observation on the size dependence of fundamental properties of matter.

Many decades later, in 1926, the first laboratory test proof on the size dependency of electronics properties of semiconductors (CdS) had been published. The potential of these low-dimensional systems came into the notice of scientific community in 1959, when Richard Feynman predicted the potential applications of atomic-scale system through his famous lecture '*There is plenty of room at the bottom.....*'. Few years later, in 1963's Sandomirskii theoretically predicted that the energy band-gap of semiconductor thin films can be tunable with the film thickness and this was experimentally proved by Stasenko in 1968 and for the first time called it '*quantum size effects*'.

In the modern history of nanoscience, Ekimov and Onuschenko finding of the three dimensional quantum confinement of nanoparticals in 1981, is considered to be the beginning of the present- day nanotechnology revolution. Almost during the same time, Brus of AT&T Bell Labs had been given such needed quantitative explanation on the size dependency of electronic properties

of matter based on the quantum mechanical theory, who has derived the time independent Schrodinger equation for quantum confined systems.

## **THE SCIENCE OF SEMICONDUCTOR NANOCRYSTALS**

Almost all material systems including metals, insulators and semiconductors show size dependent electronic or optical properties in the quantum size regime. Among these, the modification in the energy bandgap of semiconductors is the most attractive one because of its fundamental as well as technological importance. Semiconductors with widely tunable energy bandgap are considered to be the material for next generation flat panel displays, photovoltaic, optoelectronic devices, lasers, sensors, photonic-bandgap devices, bio-photonics systems, etc. When dimension of a material is continuously reduced from macroscopic size to few nanometers, then the various physical, chemical and biology properties change drastically.

If one dimension is reduced to nanometer range while other two dimensions remain large, then one obtains a structure known as quantum well. If two dimensions are reduced and one remains large, the resulting structure is referred as quantum wire. The extreme case of this process of size reduction in which all three dimensions reach to few nanometers is called a quantum dot. The word quantum is associated with these three types of nanostructures because the changes in properties arise from quantum mechanical nature of physics in ultra small domain. In quantum dot the surface to volume ratio is large and surface effects dominate. Every film, wire or particle will not be quantum structure, word quantum wire, quantum well and quantum dot can be used when specific dimensions should be equal to or less than Bohr exciton radius of the material.

## **LUMINESCENCE**

Luminescence, the emission of light by a material, after it has been exposed to ultraviolet radiations, electron bombardment, X-rays or some other method of excitation, has fascinated people since ancient times.

*Even as late the yearly 1900s Thomas Edison and E.D Nicholas concluded that*

- \* "Unless someone discovers a means of making luminescent bodies that are vastly brighter than the best known now, luminescence may be excluded altogether as a factor in artificial lightning."

Luminescence is a phenomenological term describing the process in which energy is emitted from a material at a different wavelength from that at which it is absorbed. Luminescence is a non-equilibrium process which requires an excitation source, such as a UV lamp or a highly intense monochromatic laser. Luminescence is divided broadly in two categories, intrinsic luminescence and

extrinsic luminescence. The intrinsic luminescence is due to host material or is also defined as luminescence of its own on excitation with a suitable radiation source. The intrinsic luminescence is further classified into two categories such as band-to-band and exciton.

The band-to-band luminescence is generated due to recombination of electron in conduction band with a hole in the valance band in high purity semiconductors, whereas this luminescence at low temperature is replaced by exciton luminescence.

Extrinsic luminescence is generated due to impurities, called activators, incorporated at the lattice sites of the host semiconductor material. The extrinsic luminescence is further subdivided into two categories such as localized and unlocalized luminescence. Luminescence can also be categorized into various subcategories on the basis of emission life time and source of excitation.

On the basis of emission lifetime luminescence is subdivided into two categories, fluorescence and phosphorescence. Fluorescence is the phenomenon in which de-excitation of electrons occurs almost spontaneously and the luminescence ceases on removal of excitation source. Fluorescent material has same spin for both excited and ground electronic states. So, this process is a spin or electric dipole-dipole allowed transition leading to a very fast decaying radiation having life time of the order of nanoseconds. Phosphorescence is a phenomenon in which de-excitation of electrons occurs with some delay. This is a long period emission process which is due to spin or electric dipole-dipole forbidden transition but allowed by a magnetic dipole-dipole transition.

This delay is due to different spins of the excited and ground states due to which the delayed emission from metastable state to ground state takes place. The clear distinction between fluorescence and phosphorescence is described in figure.

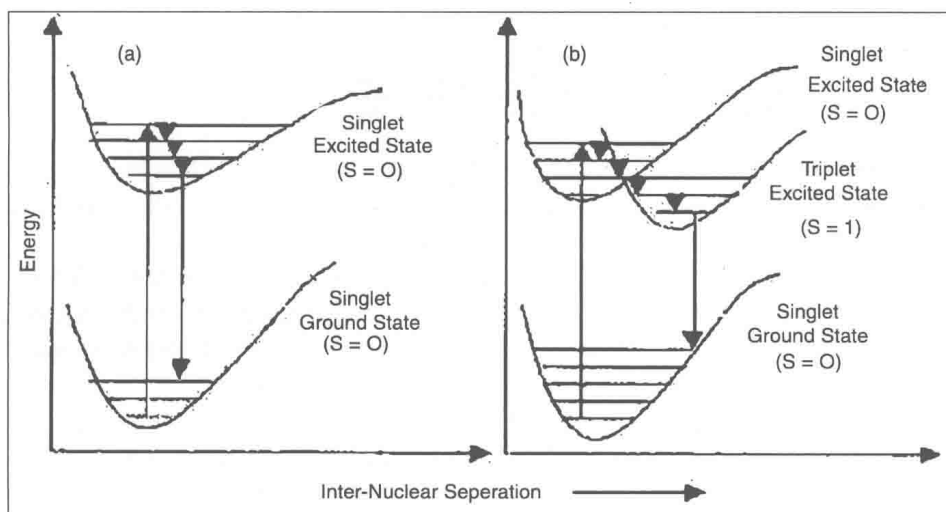


Fig. (a) Fluorescence (b) Phosphorescence

Several other categories of luminescence are characterized according to the process of excitation and named accordingly *e.g.* when photons generally in UV or visible region, excite the material, the luminescence observed afterward is termed as photoluminescence. Similarly the excitation source for cathodoluminescence, bioluminescence, electroluminescence, chemiluminescence and sonoluminescence, are electrons, biological process, stationary electric field, chemical reactions and acoustic wave respectively, whereas, a material put under external mechanical stress exhibits the phenomenon of triboluminescence. Whenever a phosphorescent material is heated, the excitation of energy level takes place due to random motion of electrons, due to which this material shows luminescence, this category of luminescence is called thermoluminescence. Radioluminescence is observed in some materials, whenever bombarded with some radioactive energy.

## **PHOTOLUMINESCENCE**

Photoluminescence is a process in which a semiconductor compound absorbs a photon with a wavelength in the UV or visible range of electro-magnetic radiations, thus making transition to a higher electronic energy state, and then radiates a photon back at higher wave length, after returning to a lower energy state.

The period between absorption and emission is, extremely short, typically of the order of a few nanoseconds. Under special circumstances, however, this period can be extended into minutes or hours. The simplest photoluminescence processes occur due to resonant radiations in which a photon of particular wave length is absorbed and an equivalent photon is immediately emitted. *Laser induced photoluminescence* (LIP) spectroscopy is a contactless and nondestructive method for probing the electronic structure of materials. Coherent, monochromatic and intense laser light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called photo-excitation. Some part of this excess energy can be dissipated by means of lattice vibrations within the material and remaining through the emission of visible light.

Photoluminescence emission intensity and other spectral contents are a direct measure of various important material properties. Photo-excitation cause electrons within the material to move into permissible excited states. When these electrons return to their equilibrium states, the excess energy is released and may include the emission by a radiative or a nonradiative process. The energy of the emitted light relates to the difference in energy levels between the two electron states involved in the transition between excited and the equilibrium states. The quantity of light emitted is related to the relative contribution of the radiative process occurring inside the materials due to various traps present in the band gap.

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## **LASER INDUCED PHOTOLUMINESCENCE (LIP) APPLICATIONS**

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### **BAND GAP DETERMINATION**

The most common radiative transition in semiconductors is between the lowest state in the conduction band and upper state of valence band, with the energy difference being known as the bandgap. Bandgap determination is particularly useful when working with new synthesized semiconductor compounds. If a semiconductor compound is irradiated with the energy equal to or greater than its band gap, it shows luminescence. Luminescence obtained from the semiconductor compound may be due to the band edge emission from where its bandgap can be estimated.

### **IMPURITY LEVELS AND DEFECT DETECTION**

Some pure semiconducting materials are non-luminescent in nature. As soon as some amount of impurity is doped in the semiconductor material, it becomes luminescent due to impurity level embedded in the band gap of the material. When excited with suitable radiation, the doped materials give luminescence depending on the energy levels introduced in the bandgap. Radiative transitions in the semiconductors also involve localized defect levels. The photoluminescence energy associated with these levels can be used to identify specific defects and the intensity of photoluminescence can be used to determine their concentration.

### **RECOMBINATION MECHANISM**

When the electrons from excited state return to ground state the excess energy is released due to process known as 'recombination', which can involve both radiative and non-radiative processes. The intensity of photoluminescence emission helps to understand the underlying physics of the recombination mechanism.

### **MATERIAL QUALITY**

In general, nonradiative processes are associated with localized defect levels whose presence is determined by material quality and subsequent device performance. Thus, the material quality can be measured by quantifying the amount of radiative recombination. Luminescence mechanism involves the emission corresponding to the bandgap of the semiconductor compound or defects present in the material.

These emission characteristics determine the quality of the synthesized product. Environmental conditions, synthesis technique and external physical strains on the material can change its material quality permanently e.g. ZnO sintered at higher temperature under the free flow of nitrogen gas, creates



interstitial defects in its wurtzite crystal structure due to which the luminescence observed is in green region. However, defect free zinc oxide semiconductor compound shows luminescence in ultraviolet region corresponding to the exciton formed in its band-gap.

## **LIFETIME MEASUREMENTS**

Time resolved laser induced photoluminescence is an effective tool to find the lifetime of the excited states present within the forbidden gap of the semiconductor material. Excited state lifetime values are helpful in determining the values of trapdepth, decay constants, oscillator strengths, dipole moments, integrated cross-sections values etc. due to the radiative transition from impurity or defect related levels. The indistinguishable properties such as high intensity and short pulse width of lasers, operating in UV region such as N<sub>2</sub>, excimer and He- Cd lasers, make these light sources very important excitation sources. Pulsed nature of N<sub>2</sub> laser, having very high peak power per pulse, makes it unique source for excitation of some doped materials of shallow luminescent centers.

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## **MECHANISM OF PHOTOLUMINESCENCE**

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Exposing semiconductor material with ultraviolet light leads to absorption of the energy and results in one or more of the electrons of an atom to shift into a higher energy state, which here can be envisioned as moving to an orbit farther away from the nucleus. All such excited electronic states are unstable, and sooner or later the electron will lose its excess energy and fall back to its original orbit. This excess energy can be dissipated in several ways, the most common being simply to increase lattice vibrations of the material but some materials also emit some of the energy as light called photoluminescence.

## **ACTIVATORS**

The fluorescence of many semiconductor compounds is not only due to the host material itself but to some chemical impurity or a defect in its crystal structure. The impurity added to the semiconductor compound in this way is said to be an activator or dopant responsible for luminescence decay curves. The decay curves can also be employed to study the trapping levels and the distribution of trapping levels introduced by the activators in the forbidden gap of the semiconducting material.

## **KILLER OR QUENCHER IMPURITIES**

Some chemical impurities deter luminescence by promoting radiationless transitions causing a given substance to lose energy by processes that do not involve the emission of light. Typically the energy is dissipated as lattice



vibrations. Among minerals the most notorious poisoners of fluorescence are iron, cobalt and nickel. For example, a ruby crystal containing 1% chromium will probably fluoresce bright deep red but if it also contains 1% iron it probably will not fluoresce at all. The photoluminescence mechanism involves luminescence due to levels of free or bound excitations, electron to acceptor or hole to donor, donor to acceptor and from the other internal impurities causing defect transitions. The schematic representation of mechanism involved for luminescence is shown in figure.

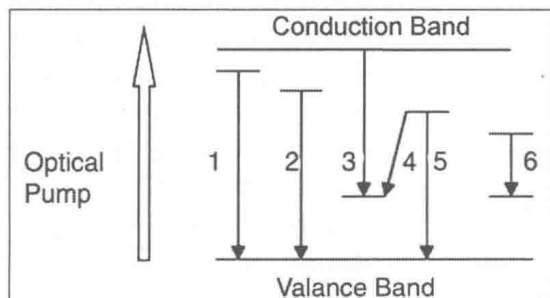


Fig. Photoluminescence Mechanism

## **PHOSPHORS AND THEIR APPLICATIONS**

Sustained glowing without further stimulus is known as phosphorescence and phosphor is a substance that exhibits this phenomenon. A very important application of the phosphors is as a coating material for cathode ray tubes used for computer and TV screens. The light that comes from these devices is emitted by tiny phosphor dots that are coated inside the screen, and are excited by a stream of electrons emitted by a cathode ray tube. Three colours of dots blue, red, and green are used in most computer monitors. In fluorescent tube ionization of gases generates UV light which further falls on the coated material and due to down conversion phenomena visible emission takes place.

All laundry detergents contain a fluorescent dye that emit strongly the blue light when exposed to sunlight. The blue region counteracts the yellow tinge of old or incompletely cleaned clothes and thus makes them to appear cleaner than these really are. The dye is designed to fluoresce in daylight. Phosphors play a major role in applications such as display, diagnostic, sensing, and illumination technologies. For fast and efficient phosphor development, the emphasis is given to the materials having higher quantum yield, fast decay, higher stability and operating at low voltage for various applications *e.g.* ZnO for green, ZnS: Cd for red, ZnS for blue colours etc. For low operating voltage applications, ZnS is used for green and blue, and yttrium oxide for red colours. Zinc oxide operating in green region has a luminescence of 10-12 lm/W.