

# CHAPTER-1

## Introduction and Review of Literature

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### 1.1 History of Nanomaterials

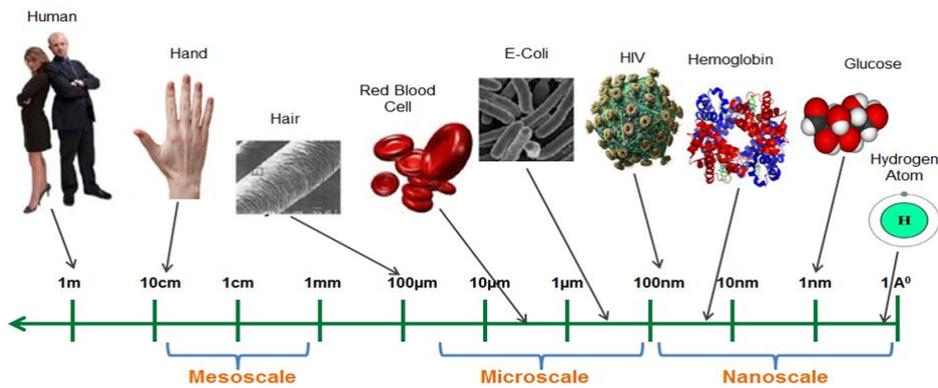
Richard Feynman gave a unique wonderful basic notion 'nano' in the year 1959 for first time in his noble talk, "There are plenty of rooms at the bottom" in a conference at Caltech, USA [1]. The word bottom related to the lower size dimensions which are measured in nanometer and angstrom. The prefix nano in the world of nanomaterials means a billionth  $10^{-9}$  of a meter. If size of a material lie in the nanometer (1-100 nm) range, at least in one dimension, then it is known as a nanostructured material or a nanomaterial. The existance of many varieties of functional devices and structures of nanometer dimensions is not a new thing. As an example, Roman glass art makers were involved to fabricate glasses which contains nanometer size metals in fourth century A. D. In the same period, gold and silver metal nanoparticles in Lycurgus cups had been seen in the British Museum, London. As the lights shine on it, the cup appears green and when light shines inside, it appears red. One more example is stained type glass art which flourish in 10<sup>th</sup> and 11<sup>th</sup> century, contain metal oxides nanoparticles that give color when glass is in molten state. In India, before 800 AD, a medicine Bhasma is being used in the traditional Ayurvedic system for healing, which also contains nanoparticles [2]. Further, in year 1857 Faraday has performed work on gold metal colloids for the first time. He had presented a purple color slide during his lecture in Royal Society at London. He postulated correctly how gold colloids change its color if salt is added [3]. In 1965, Gorden Moore gave the idea about reduction in size of silicon transistors have decreased from 10  $\mu\text{m}$  to 45-65 nm range up to year 2007. In 1976, nanomaterials prepared by popular inert-gas evaporation technique were reported by Granqvist and Buhrman [4]. Now a day, Maya blue-paint is found as a nanostructured hybrid material [5]. In 1980 Eric Drexler reinvents on nanotechnology and expanded this term into nanosystems like molecular machinery. In 1985, Tom Newmann gave a challenge that there was possibility of decreasing size of letters very small so that whole Encyclopedia able to fit on the head of a pin and he got prize for this claim. However, a regular study of these materials for potential applications is relatively new.

Nanomaterials are having the potential to be applied in many fields like bio-sensors [6], catalysis [7], light emitting devices [8], quantum devices [9, 10] etc.

## 1.2 What are Nanomaterials

The term nano means ‘dwarf’ which is a Greek word and used as a prefix with many words. Hence a nanometer is  $10^{-9}$  meters and a nanosecond is  $10^{-9}$  seconds [11]. One nm is approximately equal to 10 hydrogen atoms or 5 Si atoms arranged in a line. In nature many tiny objects are available which lie in nanoscale range. For example, our hair thickness is about 100000 nm, red cell of our blood is 5000 nm in length and DNA width is 2 nm. Nano crystalline material (1–100 nm) is extremely much strong, hard and ductile at high temperature, wear resistant, corrosion resistant, erosion resistant and chemically highly active.

Nanomaterials are those type of materials in which at least one dimension exist in the nanometer scale (1nm-100nm). Nanomaterials are in-between in size lying an isolated atom or molecule and bulk form material [12]. Nanostructured materials have large surface to volume ratio as compared to their bulk counterparts. Moreover, de-Broglie wavelength of electrons is comparable to the physical size of the nanomaterials. So the materials start showing strong quantum mechanical phenomenon when size of bulk material reduces to nanometer range. We say that it is the quantum size effect (QSE) in the field of nanoscience. In this nanometer range, physical properties have been found highly sensitive to their shape and size [13]. Here we also define nanotechnology, it is a combination field of research in physics, chemistry, biology, computer and material sciences which are also combined with engineering at the nanoscale (1-100 nm). This means that science and engineering are centered on fabricating the particles, things and useful objects at the atomic and molecular scale. Fig 1.1 shows size of the materials in microscale, mesoscale and nanoscale [14].



**Fig. 1.1: Dimensional scale of various materials.**

### **1.3 Classification of Nanostructured Materials**

A decrease in spatial dimension or more confinement of particles in a specific crystallographic orientation within a structure usually produces change in the physical behavior of the material. Hence, one way of classification of nanostructuring matter and its systems definitely depends on the number of dimensions that lies within nanometer range. Depending on their dimensions nanomaterials may be grouped as (i) zero-dimensional (ii) one-dimensional (iii) two-dimensional (iv) three-dimensional. All type of nanomaterials may be amorphous or in crystalline form and they may also be metallic, ceramic or polymeric, semiconductor and insulator etc. Silver nano particles made by sol-gel based technique are an example of metallic nanomaterials which are applicable in medical diagnosis [15]. In the present research work, we have studied about various properties of semiconducting nanomaterials.

#### **1.3.1 Zero dimensional nanomaterials**

In zero dimensional nanomaterials all three dimensions lie within nanometer range (1-100 nm). The material system is confined or restricted in three dimensions. For 0D nano form materials, the valence electrons behave comparable to atomic/molecular type energy states which are discrete states. Some examples of these nanomaterials are nanopowders, nanoparticles and quantum dots. A nanoparticle is a microscopic size particle and its size is measured in scale of nanometers that found all the dimensions smaller than 100 nm. Nanoparticles are formed by semiconducting materials also called as quantum dots [1]. These nanoparticals can be single crystalline or polycrystalline. They can exist singly or incorporated in a host matrix and existed in various shapes and forms. The size of a quantum dot is taken approximately 1-10 nm.

#### **1.3.2 One dimensional nanomaterials**

In one dimensional nanomaterial, any of the two dimensions exist in nanometer range (1-100 nm) and one dimension lie outside the nanoscale or we can say system is confined in 2D. Carbon nanotubes, nanowires, quantum wire, nanofibers are best examples. There exist many forms of nanowires like metallic (Ni, Au), semiconducting (Si, ZnO etc.) and insulating (SiO<sub>2</sub>, TiO<sub>2</sub>) etc. These nanomaterials may be existed in single or polycrystalline form and may be chemically these are pure or impure.

### 1.3.3 Two dimensional nanomaterials

In this case, one dimension exist in the nanometer range and two dimensions lie outside the nanometer scale e.g. nanofilms, coatings, quantum well and multilayers. In a quantum well when thickness approaches comparable with de Broglie wavelength of charge carriers (electrons/holes) then quantum confinement effects appear due to which discrete energy levels are formed. These nanomaterials are made up of many chemical compositions and very useful being as a single layer or multilayered structures. They are easily deposited on a substrate. Quantum well type semiconductor laser is found a most efficient laser system having nearly 30% efficiency.

### 1.3.4 Three dimensional nanomaterials

In this case system does not confine in any of the dimensions. All the dimensions are lying in more than 100 nm then they are called bulk nanomaterials [16]. The bulk nanomaterials can be formed different nano size crystals having different orientations. Three dimensional nanomaterials includes cluster of nanoparticles, bundles of nanowires and nanotubes. Nanocomposite materials are the example of these types of nanomaterials. According to Siegel [17], classification of the nanomaterials is shown in Fig.1.2.

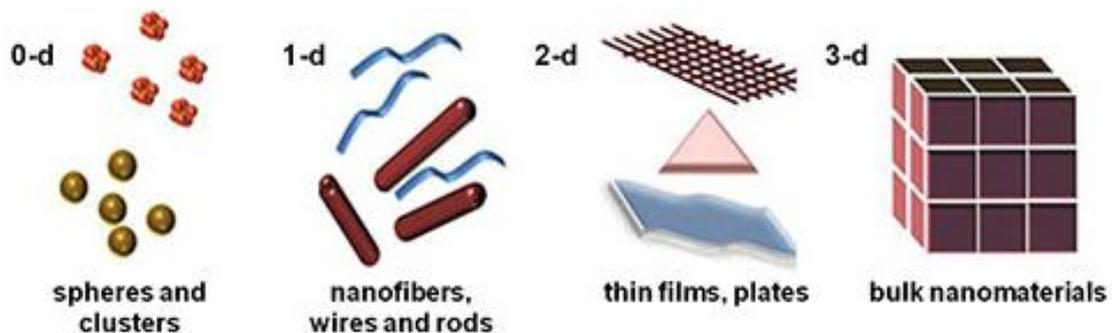


Fig. 1.2: Classification of nanomaterials.

## 1.4 Unique Properties of Nanomaterials

Nanomaterials exhibit their structural characteristics lying between those of atoms and bulk form of materials. All the micro-structured materials have almost same characteristic behavior as corresponding to their bulk form materials. The properties of

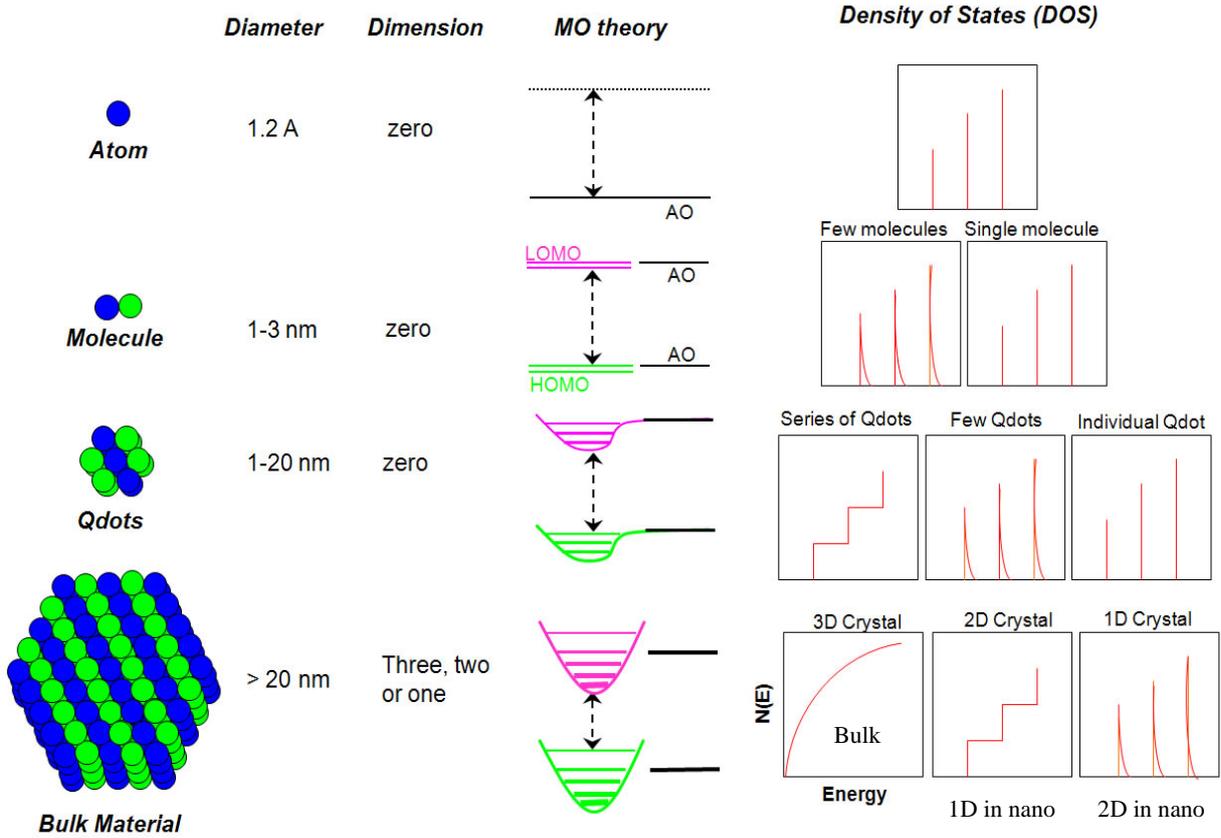
materials depending on the way of motion of electrons that can be executed, which further depending on the available space for their motion in the physical system. Thus, important parameters of a material are mainly determined by its length scale. When the size decreases from bulk to nano, these properties are changes mainly due to two reasons (i) surface effect: at the nanoscale surface to volume ratio increases, (ii) size effect: as size of the particle decreases, electron confinement increases and this type of confinement in 1, 2 and 3-dimensions also wonderfully affect the properties [18]. There are some properties which makes the nanomaterials unique that are listed below:

#### **1.4.1 Surface properties**

Chemical and physical properties of either a bulk or a nanomaterial depend largely on its surface properties. In case of nanoscale, surface atoms are increased as the size is decreased. The increase in surface area to volume ratio leads to increasing dominance of the behavior of atoms on the surface of nanomaterial over that the atom lying in the interior side of the system, thus altering the properties drastically of materials. The important properties like chemical reactivity of small particles are found very much different from the bulk form of material. Thus, energy at surface becomes high at the nanoscale size of material due to which atoms and molecules at the surface have greater tendency to agglomerate. So, the unique properties that depend on the surface effects also like melting point which becomes lower as we go from bulk to nanosize. This is because of the fact that surface atoms can be easily detached than bulk atoms, so energy needed to overcome intermolecular type forces that hold the atoms.

#### **1.4.2 Quantum size effects**

In a bulk form crystal, the properties of material are independent of its size and are dependent only on its chemical composition. With decrease of a crystal size in nanometer regime, its size dependent properties start to modify [19-21]. The electronic structure of material atoms changed from the continuous electronic bands into discrete or quantized electronic levels and become size dependent. Density of states changes as one goes from the bulk to quantum films that confined in 1-dimension to quantum wires confined in 2-dimension and finally the quantum dots that are confined in all the three dimensions (Fig. 1.3 and Fig. 1.4). If particle size reduces to Bohr's radius, then we can assume it as like a "particle-in-a box" problem.



**Fig. 1.3: Schematic illustration for change in density of quantum states with number of atoms in materials [22].**

The confinement effect on energy states may be expressed as

(i) Confinement in 3-dimensions (i.e quantum dots)

$$E_n = [\pi^2 \hbar^2 / 2mL^2](n_x^2 + n_y^2 + n_z^2) \quad (1.1)$$

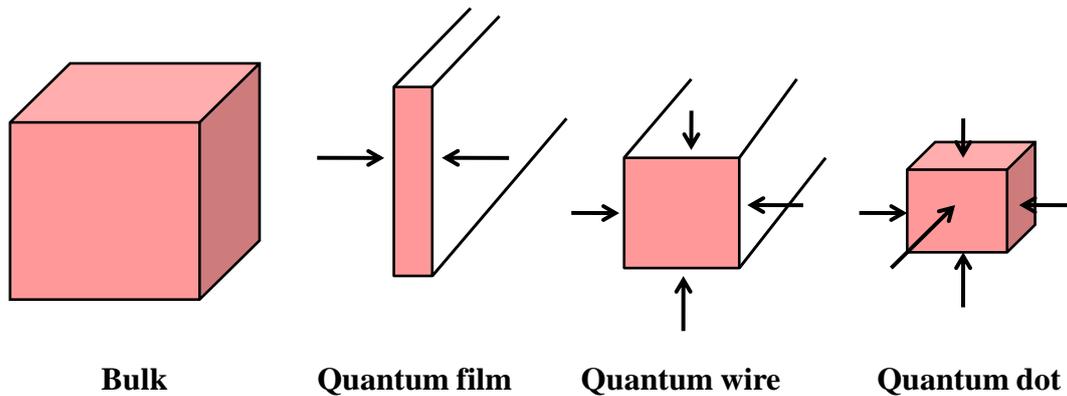
(ii) Confinement in 2-dimensions (i.e quantum wire)

$$E_n = [\pi^2 \hbar^2 / 2mL^2](n_x^2 + n_y^2) \quad (1.2)$$

(iii) Confinement in 1-dimensions (i.e quantum well)

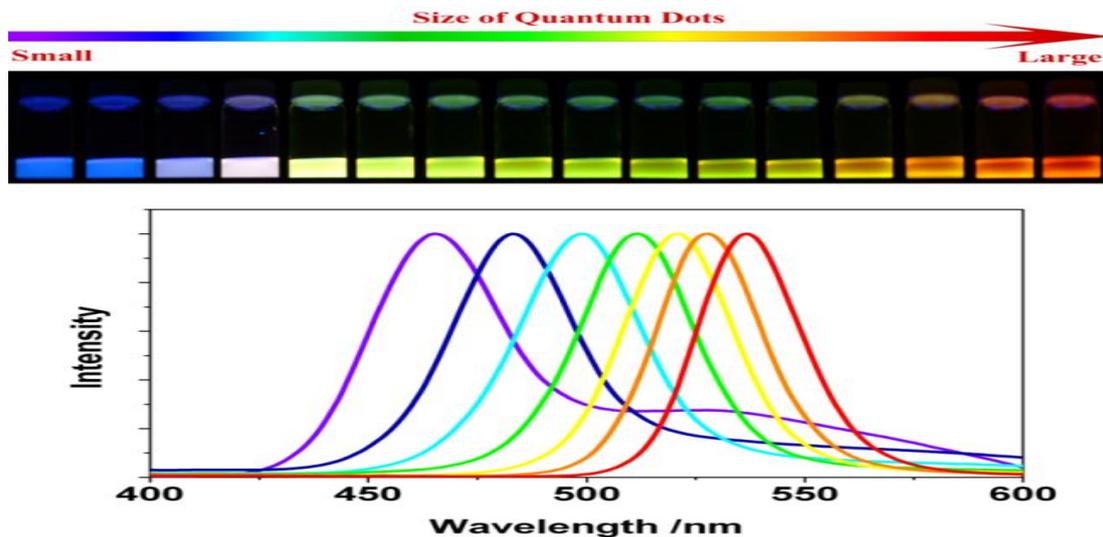
$$E_n = [\pi^2 \hbar^2 / 2mL^2](n_x^2) \quad (1.3)$$

As  $E_n$  is depends on number of conducting electrons in each type of dimensional materials. This means that number of electrons  $dN$  with in a narrow energy range  $dE$  which is represented by density of states,  $D(E)=dN/dE$ . So density of states as a function of energy  $E$  is different for quantum dot, quantum wire and quantum well and bulk form of material in which no confinement [16].



**Fig. 1.4: Dimensionality of bulk solid, quantum film, quantum wire and quantum dot.**

Fig. 1.5 shows optical absorption spectra and colors of different sized CdSe nanoparticles or quantum dots (QDs). Optical properties of the semiconducting nanomaterials changes with their size as an example color of CdSe nanoparticle changes from red to blue as the size changes from 5.5 nm to 2.3 nm when excited by a ultraviolet light.



**Fig. 1.5: Emission of colors from small size (blue) to large size (red) CdSe quantum dots.**

### 1.4.3 Electrical properties

Electrical properties of nonmaterials discuss about the basis of electrical conductivity in all nanostructures materials like nanofilms, nanotubes, nanowires, quantum-dots etc. Electronic behavior of such system changes when the length-scale is decreased which is mainly due to the influence of wave like properties of electrons. As, size becomes comparable with de Broglie wavelength of electrons or holes, the periodic boundary

conditions of crystalline particle are destroyed and discreteness of the energy states starts and this discreteness increases as the confinement occur along all the three dimensions [23]. For some cases, conducting materials become insulators as the length scale reduces below a certain value because energy bands cease to overlap.

#### **1.4.4 Mechanical properties**

The mechanical properties of the materials also affected as their size approaches to the nanoscale. Copper nanoparticles that are less than 50 nm in size have exhibited different malleability and ductility than bulk copper. The mechanical properties of a nanomaterial may be increased with a decreasing size. There are mainly two possible mechanisms that have been suggested for improved strength of nanowires. Smaller is the cross section of nanowires then less is the possibility of finding any imperfections and impurity precipitates. Another one is side faces of nanowires becomes perfect. Usually small sizes of particles have less surface deformation [24-25].

#### **1.4.5 Optical properties**

Nanocrystalline particles have large attraction and interest for their novel optical properties that differ amazingly from their bulk form crystals. HOMO and LUMO have been affected significantly due to reduction in size dimension at nano scale level. These two states are responsible for emission and absorption type transitions. Semiconductors and many metals show large changes in optical properties as the size of materials is reduced to nano scale like emission color changes with the size. For example, gold nano particles of very small size (in nano) have dark red color but when the particle size increases they become gradually more yellow. Silver particles at size range 40 nm exhibit blue color otherwise it is of silver color in bulk form. There are other properties like photocatalysis, photoconductivity, photoluminescence and electroluminescence that have changed by decrease in dimensionality [26]. For example, in a semiconductor nanomaterial absorption peak shifts towards a shorter wavelength side due to an enlarged band gap. Further, metal nanoparticles are used in biomedicine, energy and environment protection due to surface plasmons [27].

### **1.5 Applications of Nanomaterials**

**Nanomedicine:** Nanomaterial's size is similar to that of most bio molecules. In nanomedicine field, nanorobots are used that are introduced into the body to detect damages, infections and tumour and can repair them. Carbon is used mainly to form

nanorobots because of its inherent strength and various forms of carbon. Cancer can be cured very effectively by using these nanorobots. Nanorobots when injected into blood, identifies and separate the cancer cell and thus problem is detected, then these nanorobots would destroy only these cancer cells without affecting the healthy cancer cells.

**Nanoelectronics:** The main applications of nanoelectronics are in computer chips, information storage and sensors. The new information and communications systems (ICT) are more economic, small and reliable. Silicon has been used almost in all the computer chips. Only nanotechnology and nanomaterials of semiconductor can fundamentally modify ICT systems to continuously obey the Moore's law. Further, electronic miniaturization is a true driving force for research and technology [28]. Nanotechnological approach is expected to enable for the production of smaller and cheaper devices with high efficiency and stability. All semiconductor nanomaterials are highly useful in nanoelectronics.

**Recycling of batteries:** By the availability of portable electronic equipments like mobile phones, laptop, computers and remote sensors, there is a great requirement for lightweight batteries. Relatively low energy storage by batteries their operating time is less limited and hence a replacement or recharging is required. Further, by using nanomaterials based battery disposal problem could be easily solved.

**Sunscreens and cosmetics:** A sunscreen lotion made by mineral nanoparticles such as titanium dioxide, protects our skin from the UV rays. In some lipsticks nano iron oxide is present. Hence, by using nanoparticles in the field of cosmetics has increased by a number of ways for consumer safety.

**Paints:** Nanoparticles present in the paints can also enhance their performance. For examples, a very thin paint coating used in aircraft decrease their weight that is useful to our environment. Mostly, quantum well type nanomaterials are used in these types of paints [29].

**Displays:** Nanomaterials of ZnSe, ZnS, CdS and PbTe synthesized by different methods are potentially applicable for the next generation light-emitting nanophosphors.

**Catalysis:** Nanoparticles are very proficient catalyst in many chemical reactions. Platinum nanoparticles are useful to the incoming generation for automotive catalytic

converters. By using nanomaterials some chemical reactions are also carried out conveniently.

**Aerospace:** By the help of nanotechnology lighter and stronger materials have been used in aircraft manufacturing and thereby fuel expenditure decreased.

## **1.6 Science of Semiconducting Nanomaterials**

Semiconductor nanomaterials are very small in size due to which their electronic, optical, and physical properties deviate significantly from their bulk form of materials. Therefore, it is essential to recognize the basic physics behind the semiconductor nanomaterials. The electronic structures of these semiconductors lying in transition region between molecular and bulk limits. The radical changes in properties are found in the nano regime. In semiconducting materials, electrical conductivity exists between conductivity of a good conductor and insulator. These materials have CB and VB bands which are separated with an energy gap ( $E_g$ ) or regions where 'no wave of electron orbital exist' [30]. When a photon of energy greater than  $E_g$  excite electrons from the valence band then leaves a hole behind it. The negatively charged electron and positively charged hole may be mobilized in the presence of an electric field to give up electric current, but electron hole bound in their lowest energy state by columbic attraction force, called the exciton. By de-excitation, the excited electrons go to the valence band there by annihilates the exciton with emission of a photon in visible region, known as radiative recombination. We know it very well that below critical nanosize characteristics of every nanomaterial like physical/chemical properties get change radically. In a semiconductor, Bohr exciton radius has critical size diameter 1-10 nm [31]. Due to decrease in size, confinement in dimensions starts *e.g.* in 1D like thin films and quantum well, in 2D like nanorods or nanowires and in 3D in quantum dots [32-34]. Here, D is for the dimension of material/particle. Thin films and nanoplatelets are the similar structures. The exciton energy increases by decrease of crystal size in nano range and thus blue shift occurs in absorbance and emission of exciton in the semiconductor nanomaterials.

## **1.7 II-VI Semiconducting Nanomaterials**

A number of semiconducting materials are available but out of them silicon has widely been used because it's huge production than all other semiconductors. Silicon is an elemental (composed of single element) semiconductor and it exists in group IV of

periodic table. The semiconducting parameters of a material are having relation with its crystal structure and number of valence electrons. Large number of semiconductor materials are made by IIIrd and Vth group elements like GaAs, GaP, InGaAs alloys etc. Based on such combinations, semiconductor laser works in regular wave mode with their emitted wavelength that are found normally within 630-1600 nm range. But recently GaN semiconductor lasers generate 410 nm blue light at room temperature. Now a days semiconductor laser which give blue green light is required. So this condition is fullfilled by using the second (Cd and Zn) and sixth (S, Se and Te) group elements. The laser works on the principle of recombination radiation. The II-VI semiconductors are formed from the elements of group IIB and VIA of the periodic table like CdS, CdSe, CdTe, ZnS, ZnSe, PbS, and HgS etc. These semiconductors which exist in II-VI group are known as binary semiconductors. Group VIA can also be combined with beryllium, calcium, barium, magnesium and strontium. We also have some others binary semiconductors from the group of III-V elements, i.e. InP, GaN, InAs etc. The group II atoms can make covalent bonds with group VI atoms and in a similar way group III atom with group V atoms. These materials are also found comparatively easy to mix in a very well manner in any proportion of their synthesis. Moreover, these types of materials are having high absorption and emission of electromagnetic radiation for device fabrication. As an example, for device fabrication n and p-type junctions are formed from II and VI type semiconductors. For the point of view of optical properties, semiconductors are having their special importance. The binary II-VI type materials, ternary compounds like  $Zn_{1-x}Cd_xS$  and  $ZnS_xSe_{1-x}$  and quaternary materials like  $Zn_{1-x}Cd_xS_ySe_{1-y}$  alloys are highly important optical materials [35].

### **1.7.1 Binary semiconductors**

An alloy is a combination of either solution or solid compound which is prepared by two or more elements. The resulting alloy substance usually has characteristics different from constituents. Binary semiconductors are made by combining the cation from group IIB ( $Zn^{2+}$ ,  $Cd^{2+}$  and  $Hg^{2+}$ ) with the anion of group VIA (i.e  $S^{2-}$ ,  $Se^{2-}$ ,  $Te^{2-}$ ). For example CdS, CdSe, CdTe, ZnS, ZnSe, PbS and HgS etc. All these materials are wide energy band gap materials which can accomodate a number of dopants and give excellent luminescence properties. They possess highly increased charges and good photoconductivity. Their crystal and band structure is changed by introducing some

impurities. Among them CdS and ZnS are most important materials which are widely applicable in optical and electronic devices.

**Cadmium sulfide:** It is a compound with formula CdS made by Cd and S ions having yellow color [36]. It exists in nature as two different forms, with stable hexagonal wurtzite structure [37] and cubic or zinc blende form. CdS is a direct band gap semiconductor ( $E_g=2.42$  eV) and has many applications for example in light detectors, solar energy cells, green light lasers, photoconductors and LED [38,39]. With the addition of CdTe and HgS in CdS, colors found between deep red to yellow. As CdS is the first semiconductor used in thin size transistors.

**Zinc sulfide:** The ZnS was discovered by a French chemist Theodore Sidot in 1886. It exists in more stable cubic and hexagonal form having either yellow white color [40]. This is also a wide band gap semiconductor having energy 3.54 eV at 300 K in cubic form and its hexagonal structure has a band gap of 3.91 eV but normally its value is to be taken 3.68eV [41]. ZnS semiconductor is found very much useful in photonics. By doping with Mn, it exhibits high luminescence efficiency due to increase in optically active sites within the band gap. Moreover, ZnS is used to facilitate optical pump in lasing action [42].

### 1.7.2 Ternary semiconductors

Ternary semiconductor is an alloy which is made by three different chemical elements, normally two cations and an anion. Ternary alloys of compound semiconductors can be prepared by substituting an element Zn for the homologous element CdS to form  $Cd_{1-x}Zn_xS$ . The alloy of such semiconductors are ternary consisting three elements two out of them in either cation or anion site i.e CdZnS, CdZnSe, CdZnTe, HgCdTe and HgZnTe etc. Almost all the II-VI semiconductors have zinc blende type or wurtzite structure. These are wide direct band gap semiconductor materials due to which they are used in optoelectronic devices. Ternary compounds have one important option that their band gap can be varied in a continue manner up to wide energy. Its band gap variation is depending on the materials and its growth techniques.

**Cadmium zinc sulphide,** (CdZnS or CZS) is a material or an alloy of two cation Cd, Zn and anion sulphur. Being a direct band-gap semiconductor its band-gap is lying in between the CdS (2.24eV) and for ZnS (3.68eV) which depends on the composition Cd/Zn ratio. The structure of CZS is wurtzite or in hexagonal phase and in some cases

it exists in cubic phase [43,44]. The introduction of Zn can result to enhance in photocurrent through a match in electron affinities of these two considered materials instead of individual CdS. In our present thesis work we choose  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  as a base material. It is highly useful semiconductor which is mostly being used in optoelectronic devices like LED, photodetector, display devices etc.

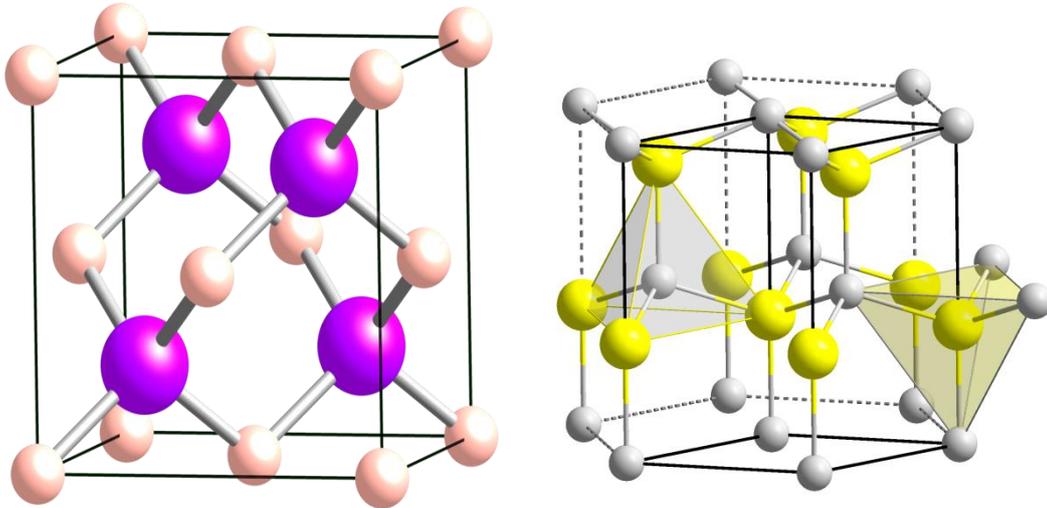
### 1.7.3 Crystal structure of semiconductors

The II-VI type semiconductors almost form wurtzite (W hexagonal phase) and ZB cubic phase crystal structure. Both the materials namely CdS and ZnS exhibit cubic zinc blende structure along with hexagonal wurtzite structure similar to all II-VI chalcogenides. Such structures are made by intogether of tetrahedrally  $sp^3$  bonded lattice sites with the outermost cations d states. These energy states lying very close to the energy of valence states. Such types of lattice sites have been found generally if electrons have the tendency to share among the atoms. These structures are described as follows.

**Cubic zinc blende structure:** If base triangles of a tetrahedran are parallel but rotated through 60 degree about the normal to each other, cubic structure is formed. Cubic structure or ZB has the combination of tetrahedral sites with two interpenetrating cubic closed packed lattices (ccp) displaced by 1/4 of the body diagonal and with  $(\sqrt{3}/4)a$  as the nearest neighbour separation. The arranged sequence in lattic is ABCABCABCABC type. In this case, four atoms per unit cell of type II is tetrahedrally coordinated with the four atoms of type VI and vice versa as shown in Fig.1.6.

**Hexagonal wurtzite structure:** Hexagonal crystal structure are formed when the base triangles of interpenetrating tetrahedra are parallel and lined up to one another [13]. Four atoms of each sub lattice of group VI surround the four atoms of other kind of group-II and vice versa, which are arranged at the edges of a tetrahedron. In hexagonal structure two interpenetrating closed packed hexagonal (hcp) lattices displaced with the nearest neighbour distance  $(\sqrt{3}/8)a$  and  $u=3/8=0.375$  c along the hexagonal c axis with respect to each other, having  $c/a$  ratio equal to  $\sqrt{8/3}=1.633$ , where u is the bond length parallel to the c-axis, in units of c. The pictorial representation of hexagonal wurtzite structure is given in the Fig.1.6. Both the materials CdS and ZnS and also CdZnS form almost hexagonal wurtzite structure in the nanoscale region, however, it is not stable in

bulk state. It is reported that CdS, CdSe and other II-VI semiconductors are more stable at wurtzite structure when an appropriate technique of synthesis is adopted. Wurtzite structure has space group P63mc. The stacking sequence in the crystal structure is ABABABABAB type and represent planes along the c direction where A and B represents the constituents of the crystallite.



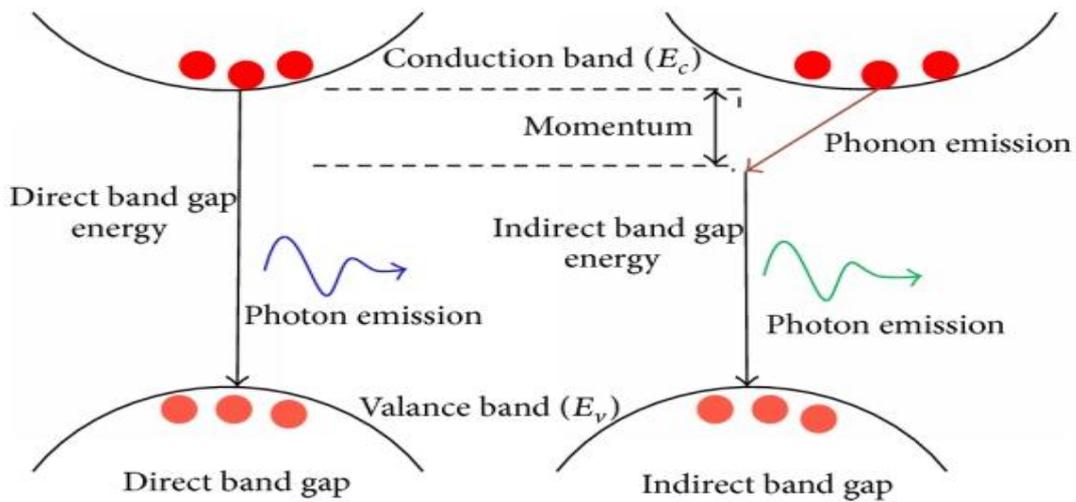
**Fig. 1.6: Zinc Blende (Cubic)**

**Wurtzite (Hexagonal)**

#### **1.7.4 Band structure of direct and indirect band gap semiconductors**

Energy bands have been formed in crystalline semiconductor materials with a large number of nearly spaced energy levels. In case of II-VI materials, valence electrons are very important that interact with optical wavelength of photons. It can also be possible to design a complex material system, utilizing the different conduction band minima and valence band maxima of various semiconducting materials to channelize or trap the charge carriers, resulting in interesting potential applications. The band structure,  $E(k)$  of a crystal has a relation of energy of an electron under a periodic potential to its wave vector  $k$  in  $k$ -space. For a direct energy band-gap semiconducting material, both valence band maximum and conduction band minimum occur at the same  $k$ -value normally at  $k=0$  for ZB structure. Thus, in direct energy band gap semiconductors momentum remains conserved. However, for indirect energy band gap semiconductors CB and VB extrema occur at different  $k$ -values not at  $k=0$  in the  $k$  space. For example GaP, Si and Ge are indirect energy bandgap semiconductors. This case has an interband transition that must involve a phonon (either absorption or emission) to conserve momentum during transition of an electron. So there exist a less probability of an

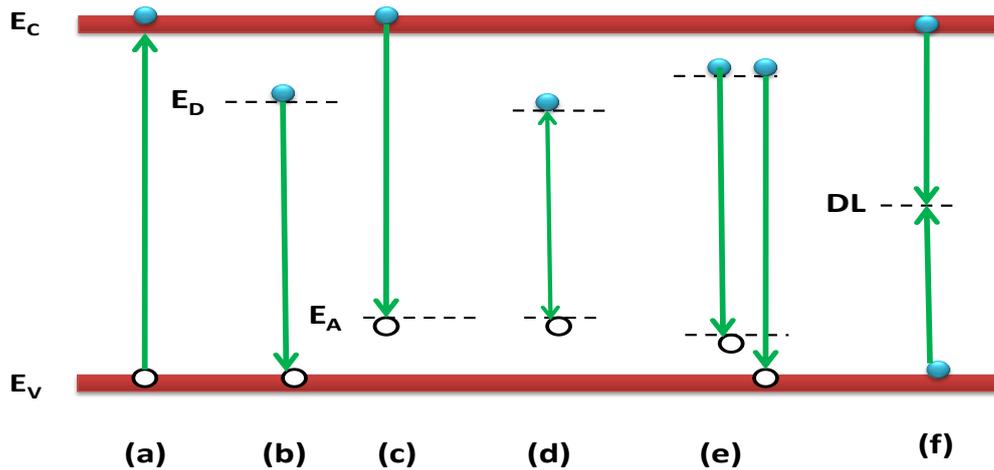
electron to make transition. In contrast, in a direct energy band-gap semiconductors optical transitions are very strong due to that such semiconductor materials are highly useful in optoelectronic devices [45]. Moreover, all semiconductor materials have been used in LED and semiconductor diode lasers; must have direct band gap materials because they are efficient emitters of light. The semiconductors of II-VI group have direct band gap except the CdO which have very small (0.8eV) and indirect type band gap. Fig.1.7 describes the E(k) diagram of a direct and indirect band gap semiconductors.



**Fig. 1.7: Band structure in direct and indirect band gap materials.**

### 1.7.5 Recombination mechanism

As the electron excited from valence band to the conduction band by absorbing some photon of energy greater than the band gap energy then the electron returns back to its original state by releasing energy radiatively or non-radiatively. By the addition of impurities in semiconductor material discrete energy states are formed within forbidden energy gap. The donor levels are existed as the levels just below the conduction band, whereas, shallow acceptor levels are defined as energy levels just above valence band. These donor or acceptor energy levels trap an electron which can work as recombination centers for transitions within the band gap of materials. The nature of such trap levels give knowledge about the impurity or defect levels introduced by any dopant or other impurities. Fig.1.8 describes the energy band diagram of a semiconductor. These transitions are discussed below.



**Fig. 1.8: Radiative and non-radiative transitions observable with photoluminescence.**

- ❖ **Band-to-band transition:** These types of transitions take place from conduction energy band to valence energy band and vice-versa. These transitions are known as radiative band-to-band or direct recombination type (Fig.1.8. (a)), that dominate at room temperature and have been used to estimate band-gap energy ( $E_g$ ) of the material. These types of transitions are mainly functions of the number of electrons and holes available in the bands and probability which is directly proportional to the absorption coefficient. In indirect band gap semiconductors, band-to-band type recombination takes place that occurs with a phonon involvement.
- ❖ **Free to bound transition:** Free electrons may recombine radiatively and sometimes non-radiatively with the holes shown in Fig.1.8(c) which are trapped on acceptors or holes in the valence band that can recombine with the trapped electrons on the donor level, shown Fig.1.8(b). Such transition concerning free electron and bound hole, are known as free-to-bound transition. These transitions occur at sufficiently low temperatures. In Fig 1.8, (d) and (e) shows the donor- acceptor pair transition and excitonic transition respectively.

## 1.8 Potential Applications of II-VI Semiconducting Nanomaterials

The II-VI type semiconductors ZnO, ZnS, ZnSe, ZnTe, CdO, CdS, CdSe, and CdTe are highly useful mainly in optoelectronic and semiconductor based device applications.

- (i) The II-VI materials have wide energy band gap property due to which they can serve as efficient light emitting agents and they can replace III-V materials particularly for GaN type light emitters diodes. Doping of transition metal ions ( $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{3+}$ ,  $\text{Co}^{2+}$ ) and rare earth ions ( $\text{Ce}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Gd}^{3+}$ ) may affect the characteristics of the semiconducting materials.
- (ii) The CdTe, CdSe, CdS, ZnSe and ZnTe doped with these transition ions have been used widely in photovoltaic solar cells. Some semiconductors like ZnSe, CdSe and CdS may be easily doped only with n-side and ZnTe doped on p-side. Due to this unique property of these materials, it is useful in making homo and heterojunction devices. Optical properties are also affected by different preparation methods of doped semiconductor nanocrystals. Consequently, increase in quantum efficiency, surface effect, band gap, photoconductivity, current density and fluorescence intensity of these materials have been found very useful for fabrication of optoelectronic devices [46-47].
- (iii) Mixed ternary and quaternary type semiconductors like  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ,  $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ ,  $\text{CdSe}_{1-x}\text{Te}_x$ ,  $\text{In}_{1-x}\text{Ga}_x\text{Sd}_{1-y}\text{As}_y$  have been found potentially applicable in making of photoconductive, photovoltaic and solar cells in the field of electronic and optoelectronic devices [48-53]. Silver (Ag) ion may be incorporated as an acceptor in the II–VI semiconductors like CdZnS, since it affect greatly the electrical conductivity and optical properties of such type of materials [50].
- (iv) Further, CdZnS doped with copper ion is a highly important semiconductor because it has high water dispersability and stability due to that it has a promising application for biolabelling [51]. Furthermore, the binary CdS semiconductor can be replaced by higher energy band gap of ternary  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  that has led to a decrease in window absorption loss and enhancement in current which is valuable in CdS based solar cells.
- (v)  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  and other similar type compounds are also having applications for high density optical recording and for blue or UV semiconductors laser diodes whose absorption edges can be changed from green region to UV [52]. During 1980s, performance of diode laser has been improved with the help of active quantum well material. Moreover, the quantum well semiconductor laser is an economical, reliable and high performance device.

It is very difficult to synthesize 1D (quantum wires) and 0D (quantum dots) laser diodes as an active gain medium. However zero dimensional systems have potential benefits in laser physics. Just only one electron-hole pair per quantum dot is sufficient to achieve threshold inversion and contribute to the optical gain. So, quantum well as an active medium is one of the semiconductor laser give high performance. Further, luminescence properties of a core-shell QDs can be easily tuned.

## 1.9 Literature Review

Nanomaterials such as quantum well, quantum wire, quantum dot and carbon nano tubes have been investigated in detail by many researchers. All these types of nanomaterials have potential use for different types of device fabrication. By adopting many methods of synthesis like sol gel [54], co-precipitation [55], spray pyrolysis [56] chemical bath deposition [57] etc. these materials may be synthesized. In our present thesis work CdS, ZnS and their alloy have been prepared successfully by using co-precipitation method [58]. Doping of many transition metal ions like Cu and Mn in these type of materials give a different idea to the research of nanomaterials. The II–VI compounds, CdS and ZnS are very useful for making of a wide variety of optoelectronic devices.

In 1994 Bhargava et al [59] have published that Mn doped ZnS nanocrystalline materials show enhanced luminescence intensity than the intrinsic ZnS. It can be observed that on decrement of the particle size, enhancement in the PL intensity and shortening of life time takes place. The  $Mn^{2+}$  ions has d 5 configuration and it is most useful dopant ion for  $Zn^{2+}$  and  $Cd^{2+}$  and other related compounds. Moreover, the chemical properties such as ionic radii, valence state of  $Mn^{2+}$  are found well matched with the host cations. High efficiency in PL and its stability have been shown by the core-shell nanoparticles. These nanocrystals are applicable in target orientation processes in diagnosis and LEDs based on quantum dots of CdSe/ZnS [46], nanowires of Si/CdS and quantum rods of CdSe/CdS, [60]. Many reports have been published on rare earth ions ( $Tb^{3+}$ ,  $Sm^{3+}$ ,  $Eu^{3+}$  and  $Er^{3+}$ ) doped chalcogenides [61,62]. However, because of their different chemical characteristics than host cations, successful incorporation of such type dopants has not yet to be achieved. It is observed in some reports that luminescence intensity of CdS nanomaterials can be enhanced by doping of

Eu<sup>3+</sup> ions [63]. Reisfeld et al. formed CdS quantum dots in ZrO<sub>2</sub> films with addition of lanthanide ions (Eu<sup>3+</sup> and Tb<sup>3+</sup>) [64]. Rastogi et al. have reported that ZnS nanocrystals exhibit yellow emission at 591 nm by the <sup>4</sup>T<sub>1</sub> - <sup>6</sup>A<sub>1</sub> of Mn<sup>2+</sup> transition [65]. In case of undoped ZnS the emissions at 350 nm are produced by recombining of electrons at donor level of the sulfur vacancy. A. Vanaja et al. synthesized Co doped ZnO nanoparticles by sol-gel method and observed that such nanomaterials may be used in optoelectronics and thermally stable devices [66]. Khosravi et al. have synthesized ZnS:Mn nanoparticles which are useful in catalysts [67]. Further, Dontas et al. synthesized Cd<sub>1-x</sub>Mn<sub>x</sub>S NCs with controlled Mn<sup>2+</sup> ion diffusion grown on a glass template by the method of fusion and observe a blue shifting in absorption spectra by the addition of Mn ion [68]. Son et al. have also synthesized ZnS:Mn nanomaterials by using a liquid-solid-solution method [69]. The effect of doping concentration for optimum luminescence properties was also investigated. It was observed that annealing at 450°C, enhances the photoluminescence properties by addition of 1.0 % Mn dopant. Y.L. Gayou et al also reported the FL analysis; with the addition of yttrium as a dopant in ZnS nanomaterials, the FL intensity signal increases by 6-7 times in magnitude as compared to the uncapped ZnS nanomaterials [70].

A lot of research has been done on these ternary semiconducting nanomaterial and its applications in optoelectronic devices [71-75]. By using ternary semiconductor materials, optical properties like band energy can be tuned from UV to near infrared region [76]. Yakoubi et al. have also synthesized CdZnS:Cu quantum dots and observed that by changing the Cu<sup>2+</sup> ion concentration, reaction time and Cd/Zn ratio, optical parameters of these quantum dots can be controlled. Further, by using the capping agent PL lifetime and PL quantum efficiency can be increased up to 42% via the reduction of non- radiative recombination center's density [51]. Spray pyrolysis method has been used by Narasiman et al. to synthesize CdZnS thin films on glass substrates at temperature 400°C. It has been observed that doping up to 6 wt.% of Zn concentration increases transparency to exhibit a highest transmittance of nearly 90% in the visible region. By the increase in Zn dopants, band-gap was also found blue shifted that is associated with the Moss-Burstein (MB) effect [56]. Further, P. Zhou et al. observed successful incorporation of Mn<sup>2+</sup> ion in the ZnCuInS colloidal solution. He has also published that the temperature-dependent PL spectra give a red shift with

decreasing intensity at low temperature (20–300 K) for these samples [77]. Furthermore N.X. Ca et al. have made CdS, CdS/ZnSe core/shell (C/S), core/intermediate/shell (C/I/S) nanoparticles and then studied their Raman, UV and PL properties. They have observed some unusual result in the Raman spectrum that is due to compressed strain shell parts and surroundings. It has also been indicated that the intermediate layer found between core and shell can reduce lattice-strain, and improves PL emission intensity [78]. N. Safta has calculated electronic properties of  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  quantum dot for Zn composition ranging from Zn=0 to 1 or CdS to ZnS. It is also observed that  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  QD's can show a superlattice behavior at composition  $x = 0.4$  [79]. Moreover, Chawla et al. reported the Cu doped  $\text{Zn}_{1-x}\text{Cd}_x\text{S}$  by chemical precipitation route [72]. A decrease in energy band-gap is observed in sample  $\text{Zn}_{0.9}\text{Cd}_{0.1}\text{S}$  with the increase in copper concentration. In PL spectra, a green emission at 526 nm was observed due to the transition from sulfur vacancy to  $t_2$  level of  $\text{Cu}^{2+}$  ion. CdS nanorods [80] were prepared by solvo-thermal method at 160°C, have a diameter 22 nm and thickness 85 nm. The PL spectra of these two nano slabs CdS/ZnS shows emission at 420-484 nm and 530-544 nm in blue and green region respectively. As like given above many other researchers have investigated for different characteristics of II-VI group semiconductors. They have used a variety of techniques to prepare these nanomaterials. In the present thesis work, we have successfully synthesized the ternary alloy quantum dots by using co-precipitation method. By using transition metals ( $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ) as a dopants, their structural and optical properties have been investigated which gives very interesting and fruitful results. Our reported experimental data may be useful for device fabrication and further research.

## **1.10 Objectives and Organisation of Thesis work**

As our aim is to synthesize some II-VI semiconducting nanomaterials by using a well known co-precipitation method and characterization of their structural and optical properties. In present course of thesis work, desirable samples of  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  and doped  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  nanomaterials have been successfully synthesized and characterized as per proposed research work under the synopsis. Further, transition metal ions (Cu, Mn) were introduced in nano CdZnS to investigate its structural change and also explored the possibilities for some important applications. Furthermore, the temperature effect on structural aspect and optical properties of prepared samples has also been

investigated. As the size dimension of these particles reduces into nanometre size scale, the surface area enhances greatly, resulting in novel phenomena. The results of the entire research work of various samples and their interpretation have been compiled in the form of this thesis. The chapter wise classification of the thesis work is as follows:

The **first chapter** consists of the general introduction on nanomaterials and classification of nanomaterials. Review of literature, unique properties and applications in different fields of these nanomaterials have been described. The outline of II-VI semiconducting nanomaterials, with their properties, structure and band structure has been explained. In the last, aim of the present research work has also been included under this chapter.

The **second chapter** describes about the synthesis method and different structural and optical characterization techniques used. Among the synthesis techniques, co-precipitation was used for the present work and it has also been discussed in detail. Moreover, these synthesized nanomaterials were also characterized by XRD, FTIR, AFM, SEM, TEM, UV-visible, and Photoluminescence (PL) methods. Details of these techniques like principle, working and instrumentation set up were also described under this chapter.

In the **third chapter**, preparation and characterization of Cu doped CdZnS samples using co-precipitation technique are discussed. In view of this, the aim was to explore the possibilities of this method with regard to materials preparation and control of their chemical composition and particles size. Further, interesting aspects of the prepared quantum dots have been investigated by many complementary techniques such as XRD, FTIR, TEM, AFM, EDX, UV, PL, thermo gravimetric and differential analysis (TG-DTA). The results obtained from these characterization techniques have been compiled, discussed, interpreted and coincided.

The **fourth chapter** describes the preparation of Cu,Mn codoped CdZnS nanopowders using co-precipitation technique. The structural and optical properties have also been studied by using the XRD, FTIR, TEM, AFM, UV, PL and TG-DTA experimental techniques. The important findings have been interpreted and discussed in detail by comparing the work carried by other researchers.

The **fifth chapter** deals with the preparation of samples by changing the dopant's (Cu,Mn) concentration from 1M% to 5M% in the base Cd<sub>0.7</sub>Zn<sub>0.3</sub>S nanopowders. Further, the prepared samples were characterized by XRD, SEM, EDX, TEM, UV and PL methods experimentally.

Moreover, temperature dependent properties of prepared samples have also been presented under the **sixth chapter**. Thus prepared samples were characterized by using XRD, FTIR, TEM, UV and PL techniques. In the **seventh chapter**, conclusions and future perspectives have been drawn from the obtained results.

## References

- [1] M. Sylvain, Nanotechnology, Sarup and Sons, ISBN: 81-7625-666-8 (2006).
- [2] T. K. Bhowmick, A. K. Suresh, S. G. Kane, A. C. Joshi, J. R. Bellare, J. Nanopart. Res. **11** (2009) 655.
- [3] Nanoyou Teachers Training kit [http://nanoyou.eu/attachments/188\\_Module-1-chapter-3-proof read.pdf](http://nanoyou.eu/attachments/188_Module-1-chapter-3-proof%20read.pdf).
- [4] C.G. Granqvist, R.A. Buhrman, J. Appl. Phys. **47** (1976) 2200.
- [5] M. Jose-Yacamán, L. Rendon, J. Arenas, M.C.S. Puche, Science **273** (1996) 223.
- [6] M. Bruchez J., M. Moronne, P. Gin, S. Weiss, A. P. Alivisatos, Science **281** (1998) 2013.
- [7] Z. Xu, F. S. Xiao, S. K. Purnell, O. Alexeev, S. Kawi, S. E. Deuth, B. C. Gates, Nature **372** (1994) 346.
- [8] V.L. Colvin, M.C. Schlamp, A.P. Alivisatos, Nature **370** (1994) 354.
- [9] B.O. Dabbousi, M.G. Bawendi, O. Onitsuka, M.F. Rubner, Appl. Phys. Lett. **66** (1995) 1316.
- [10] D.L. Klein, R. Roth, A.K.L. Lim, A.P. Alivisatos, P.L. McEven, Nature **389** (1997) 699.
- [11] J. Dutta and H. Hoffman, Nanomaterials, (2005) 8.

- [12] C.P. Poole, Jr., F.J. Owens, Introduction to Nanotechnology, John Wiley & Sons (2003).
- [13] D.R. Vij., N. Singh, (Eds) Luminescence and related properties of II-VI semiconductors Nova science pub. Inc., New York, (1998) ISBN 1-56072-433-1.
- [14] N.T. Nguyen, S.A.M. Shaegh, N. Kashaninejad, D.T. Phan, Advanced drug delivery reviews (2013)
- [15] D.S. Ahlawat, R. Kumari, Rachna and I. Yadav, Int. Journal of Nanosci. **13** (1) (2014) 1450004, DOI: 10.1142/S0219581X14500045.
- [16] M.F. Ashby, P.J. Ferreira, D.L. Schodek, Nanomaterials, nanotechnologies and design: an introduction for engineers and architects, Butterworth-Heinemann, (2009).
- [17] P.R. Sajanlal, T.S. Sreeprasad, A.K. Samal, T. Pradeep, Nano Rev. **2**(1) (2011) 5883.
- [18] G. Cao, Nanostructures and Nanomaterials, Imperial College Press, London, UK, (2004).
- [19] S. Wu, M.A. Vddin, S. Nagamine, E Sasaoka, Fuel **83** (2004) 671.
- [20] J. Rowland, K.H. Kim, R.E. Humme, P. Holloway, Electrochim. Solid State Lett. **8** (2005) 36.
- [21] R.N. Bhargava, D. Gallagher, T. Welker, J. Lumin. **60** (1994) 275.
- [22] [http://www.nanowerk.com/nanotechnology/ten\\_things\\_you\\_should\\_know\\_3.php#ixzz20C7npM00](http://www.nanowerk.com/nanotechnology/ten_things_you_should_know_3.php#ixzz20C7npM00).
- [23] G. Schmid Nanoparticles: From Theory to Application (Weinheim: Wiley-VCH) (2004)
- [24] V.G. Lyuttsau, Yu.M. Fishman, I.L. Svetlov, Sov. Phys. Crystallogr, **10** (1966) 707.
- [25] A. Nohara, Jpn. J. Appl. Phys. **21** (1982) 1287.
- [26] Nanomaterials and its properties <https://shellzero.wordpress.com/nano-materials-and-its-properties> (2012).
- [27] M. A. Garcia, J. Phys. D: Appl. Phys. **44** (2011) 283001.

- [28] NanotechApplications <http://www.nanocompositech.com/nanotechnology/nanotechnology-applications.htm>.
- [29] K. Arivalagan S. Ravichandran, K. Rangasamy and E. Karthikeyan, *Int.J. Chem.Tech. Res.* **3** (2) (2011) 534-538.
- [30] C. Kittel, *Introduction to Solid State Physics*, 5<sup>th</sup> Ed. Wiley, New York (1976) .
- [31] L. E. Brus, *J. Chem. Phys.* **80** (1984) 9.
- [32] S. Ithurria, M. D Tessier, B. Mahler, R.P Lobo, B. Dubertret, A.L. Efros, *Nat. Mater.* **10** (2011) 936-41.
- [33] D.V. Talapin, E.V. Shevchenko, C.B. Murray, A. Kornowski, S. Förster, H. Weller, *J. Am. Chem. Soc.* **126** (2004) 12984-12988.
- [34] E. Groeneveld, et al., *Nano Lett.* **12** (2012) 749-757.
- [35] B. G. Yacobi, “Semiconductor Materials: An Introduction to Basic Principles”, Kluwer Academic Publishers, (2004).
- [36] Pradyot Patnaik, *Handbook of Inorganic Chemicals*. McGraw-Hill. ISBN 0070494398(2002).
- [37] B.S. Rao, B.R. Kumar, V.R. Reddy, T.S. Rao, G.V. Chalapathi, *Chalcogenide Letters* **8** (2) (2011) 53–58.
- [38] J.C.Lee, N.G.Subramaniam, J.W.Lee, T.W.Kang, *Appl. Phys. Lett.* **90** (2007) 262909.
- [39] A. M. Acevedo, *Solar Energy Materials and Solar Cells* **90** (2006) 2213.
- [40] A. F. Wells, *Structural Inorganic Chemistry* (5th ed.), Oxford: Clarendon Press, ISBN 0-19-855370-6 (1984).
- [41] J. X. Ding, J. A. Zapien, W. W. Chen, Y. Lifshitz, S. T. Lee, X. M. Meng, *Appl. Phys. Lett.* **85** (2004) 2361.
- [42] J.A. Zapien, *Applied Physics Letters* **84** (7) (2004) 1189-1191.
- [43] T. Vijaya, S. Ram Mohan Rao, M. Nagabhushanam, S. Srinu Naik, B. Rajam, *International Journal of Engineering Research & Technology (IJERT)* **5**(9) (2016) DOI:<http://dx.doi.org/10.17577/IJERTV5IS090358>.

- [44] R. Mariappan, M. Ragavendar, V. Ponnuswamy, *Journal of Alloys and Compounds*, **509** (2011) 7337–7343.
- [45] J. Singh, *Smart Electronic Materials: Fundamentals and Applications*, Cambridge University press, United Kingdom (2005).
- [46] H. Huang, A. Dorn, V. Bulovic, M.G. Bawendi, *Appl. Phys. Lett.* **90** (2007) 023110.
- [47] M. Shakir, Siddhartha, G. Bhagavannarayana, M.A. Wahab, *Chalcogenide Letters* **8** (7) (2011) 435 - 440.
- [48] B. Chen, D. Yang, P. A. Charpentier, S. Nikumb, *Solar Energy Materials and Solar Cells* **92** (9) (2008) 1025-1029.
- [49] S. Figge, T. Bottcher, J. Dennemarck, R. Kroger, T. Paskova, B. Monemar, D. Hommel, *Journal of Crystal Growth* **281** (2005) 101-106.
- [50] N.A.Shah, W.Mahmood, *Thin Solid Films*, (2013), doi.org/10.1016/j.tsf.2013.03.088.
- [51] A. Yakoubi, T. B. Chaabane, A. Aboulaich, R. Mahiou, L. Balan , G. Medjahdi, R. Schneider, *Journal of Luminescence* **175** (2016) 193–202.
- [52] Kasim Uthman Isah, *Materials Sciences and Applications* **4** (2013) 287-292.
- [53] M. A. Hines, P. Guyot-Sionnest, *J. Phys. Chem.* **100** (1996) 468-471.
- [54] S. K. Ma, J. T. Lue, *Solid State Commun.* **97** (1996) 979.
- [55] A. Roosen, H. Hausner, “Ceramic Powders.” Elsevier, Amsterdam, (1983).
- [56] V.Narasimman, V.S. Nagarethinam, K. Usharani and A.R.Balu, *Int. J. Thin. Fil.Sci.Tec.* **5** (1) (2016) 17-24.
- [57] T.A. Abbas, J.M Ahmad, *J. of Electron Devices* **17** (2013) 1413-1416.
- [58] I. Yadav, D.S. Ahlawat, R. Ahlawat, *Applied Physics A* **122** (2016) 245.
- [59] R.N. Bhargava, D. Gallagher, X. Hong , A. Nurmikko, *Phys. Rev. Lett.* **72** (1994) 416.
- [60] Z. Wan, W. Luan, S. T. Tu, *Journal of Colloid and Interface Science* **356** (2011) 78–85.

- [61] S. Rai and L. Bokatial, *Bull. Mater. Sci.* **34** (2) (2011) 227–231.
- [62] S. Rai, L. Bokatial, P. J. Dihingia, *Journal of Luminescence* **131** (2011) 978–983.
- [63] J. Mu, L. Xu, X. Li, Z. Xu, Q. Wei, H. Sun, S. Kang, *J. Disper. Sci. Technol.* **27** (2006) 235.
- [64] R. Reisfeld, M. Gaft, T. Saridarov, G. Panczer, M. Zelner, *Mater. Lett.* **45** (2000) 154.
- [65] C. K. Rastogi, C. S. Tiwary, P. Kumbhakar and A. K. Mitra, *Asian Journal of Chemistry* **21** (10) (2009) S039-042.
- [66] A. Vanaja, K. Srinivasa Rao, *Advances in Nanoparticles* **5** (2016) 83-89.
- [67] A.A. Khosravi, M. Kundu, B.A. Kuruvilla, G.S. Shekhawat, R.P. Gupta, A.K. Sharma, P.D.Vyas, S.K. Kulkarni, *Appl. Phys. Lett.* **67** (1995) 2506.
- [68] N.O. Dantas, E.S. Freitas Neto, R.S. Silva, F. Chen, M.A. Pereira-da-Silva, V. Lopez-Richard, G.E. Marques, *Solid State Communications* **152** (2012) 337–340.
- [69] D. Son, D.R. Jung, J. Kim, T. Moon, C. Kim, B. Parka, *Applied Physics Letters* **90** (2007) 101910, DOI: 10.1063/1.2711709.
- [70] V. L. Gayou, B. S. Hernández, M. Rojas-López, C. Z. Islas, J. A. Ascencio, *Journal of Nano Research* **9** (2010) 139-143.
- [71] C. Jin, W. Zhong, X. Zhang, Y. Deng, C. Au, Y. Du, *Crystal Growth and Design* **9** (2009) 4602-4606.
- [72] A.K. Chawla, S. Singhal, S. Nagar, H O Gupta, R. Chandra, *J Appl Phys* **108** (2010) 123519-7.
- [73] R. Shrivastav, S.C. Shrivastav, R.S. Singh, A.K. Singh, *Indian J. Phys.* **89** (2015) 1153.
- [74] K. Hadasa, G. Yellaiah, M. Nagabhushanam, *Bull. Mater. Sci.* **37** (2014) 53-60.
- [75] T. D. Dzhafarov, F. Ongul, I. Karabay, *Journal of Physics D:Appl Phys* **39** (15) (2006) 3221.
- [76] J. A. Rojas, A. I. Oliva, *Materials and Manufacturing Processes* **30** (2015) 785–792.

- [77] P. Zhou, X. Zhang, Li. Lan, L. Xiaojuan, L. Yuan, X. Zhang, *Optical Materials Express* **5** (9) (2015) 2069, DOI:10.1364/OME.5.002069.
- [78] N.X. Ca, N.Q. Bau, T.L. Phan, V. T. K. Lien, N.T.T. Lieu, N.X. Nghia, *Journal of Alloys and Compounds* **697** (2017) 401- 408.
- [79] N.Safta A. Sakly, H. Mejri, and Y. Bouazra, *Eur. Phys. J. B* **51** (2006) 75–78.
- [80] Zinki Jindal, N.K.Verma, *Physica E* **43** (2011) 1021–1025.