CHAPTER-1

General Introduction
1A. General Introduction

1A.1 Nanoscience and nanotechnology

During the last decade, new direction in the materials research broadly defined as ‘nano scale science and nanotechnology’ have emerged. Nano scale science i.e. nanoscience is basically study of particles (metals, semiconductors, insulators etc.) with size in the range of 1 to 100 nm at least in one of the three dimensions. Nanotechnology on the other hand literally means any technology performed on a nanoscale that has applications in the real world. Nanotechnology encompasses the production and application of physical, chemical, and biological systems at scales ranging from individual atoms or molecules to submicron dimensions, as well as the integration of the resulting nanostructures into larger systems. Nanotechnology is likely to have a profound impact on our economy and society in the early twenty-first century, comparable to that of semiconductor technology, information technology, or cellular and molecular biology.1-4

The nanoparticles can be broadly divided according to their degree of confinement i.e. the degree of restriction of charge carriers (a) 1-dimension, e.g. thin films whose thickness is less than 100 nm, (b) 2-dimensions, e.g. Nanowires and (c) 3-dimensions i.e. confined in all three spatial dimensions, e.g. quantum dot. Because of this reduced size (> 100 nm) with any mentioned degree of confinement leads to increase in proportion of atoms in the surface and near surface layers thus quantum size effect.2,4,5-25 In this size regime the properties such as melting point, colour (i.e. bandgap and wavelength of optical transitions), ionisation potential, hardness, catalytic activity and selectivity,26-40 or magnetic properties such as coercivity, permeability and saturation magnetisation,41-48 which we are used to thinking of as constant, vary with size and shape. The optical bandgap and photoluminescence emission of binary II-VI semiconductors can be tuned in the entire visible range of light spectrum with the variation of size.12,49-60 Due to this variation in novel physical and chemical properties of nanoparticles with size will lead to unique applications. The idea of the limiting size scale of a miniaturized technology is fundamentally interesting for several reasons. As sizes approach the atomic scale, the relevant physical laws change.
from the classical to the quantum-mechanical laws of nanophysics. The changes in behaviour from classical, to ‘mesoscopic’, to atomic scale, are broadly understood in contemporary physics, but the details in specific cases are complex and need to be worked out. While the changes from classical physics to nanophysics may mean that some existing devices will fail, the same changes open up possibilities for new devices.

Nanoscale materials frequently show behaviour which is intermediate between individual atom/molecule and bulk solid system. Such behaviour of particles in the nanoscale range can be broadly divided into two types (a) *Scalable effects*: Surface atoms are different from bulk atoms. As the particle size increases, the surface to volume ratio decreases proportionally to the inverse particle size. Thus, all properties which depend on the surface to volume ratio change continuously and extrapolate slowly to bulk values and (b) *Quantum effects*: When the molecular electronic wave function is delocalised over the entire particle then a small, molecule-like cluster has discrete energy levels so that it may be regarded like an atom (sometimes called a super atom). The quantum effect is more pronounced with small particle system. The quantum size effect of nanoparticles can only be explained with the laws of quantum mechanics.4

In fact nanoparticles will be the next generation materials for the industrial and technological developments for the mankind. To quote few of the applications of nanoparticle in the technology include: Iron oxide nanoparticles can be used to improve MRI (Magnetic resonance imaging) images of cancer tumors. The nanoparticle is coated with a peptide that binds to a cancer tumor, once the nanoparticles are attached to the tumor the magnetic property of the iron oxide enhances the images from the Magnetic Resonance Imagining scan. Magnetic nanoparticles that attach to cancer cells in the blood stream may allow the cancer cells to be removed before they establish new tumours. Gold nanoparticles can be used for drug delivery and will be able to allow heat from infrared lasers to be targeted on cancer tumors.61-65 Titanium oxide nanoparticles are used for cleaning the drinking water.66 Gold nanoparticles combine with organic molecules to create a transistor known as a NOMFET (Nanoparticle Organic Memory Field-Effect Transistor). Zinc oxide nanoparticles dispersed in industrial coatings to protect
wood, plastic and textiles from exposure to UV rays. Silver nanoparticles in fabric can kill bacteria making clothing odour-resistant.3

1B. Synthesis methods of nanoparticles

Synthesis methods for nanoparticles are typically grouped into two categories: ‘top-down’ and ‘bottom-up’. The first involves division of a massive solid into smaller portions. This approach may involve milling or attrition, chemical methods, and volatilization of a solid followed by condensation of the volatilized components. The second, ‘bottom-up’, method of nanoparticle fabrication involves condensation of atoms or molecular entities in a gas phase or in solution. The latter approach is far more popular in the synthesis of nanoparticles. In this section some synthesis methods of later category will only be focussed for metal and semiconductor nanoparticles.

1B.1 Synthesis of metal and metal oxide nanoparticles

Metal nanoparticles such as Fe, Co, Ni, Pd, Au, Ag etc. with good dispersibility have been synthesized through several methods, among which most adopted synthetic route is the reflux reduction of soluble metals’ salts in the presence of protecting polymers.67-71 The reducing agents commonly used are sodium borohydride, ascorbic acid, potassium bitartrate etc. In the reduction method of preparation the metal nanoparticles are obtained by refluxing the solutions of metal salt with reducing agent and capping agent for controlling the size of nanoparticles. In this process the solutions of metal salt and capping agent under stirring is heated at desired temperature and reducing agent is quickly added in order to hasten the reduction reaction. In the process the nucleation becomes faster and small nanoparticles are obtained. These nanoparticles are also can be prepared using organometalic precursors and other organic media. In such preparation, some typical high-boiling point organic solvents including oleic acid, trioctylphosphine, ethylene glycol, etc., are well introduced to reduce the reaction rate of the system, and limit mass transfer in both the initial nucleation and growth steps of the nanocrystals based on the solvents’ good viscous properties or low reducibilities.72-76 Normally in such process of nanoparticle synthesis the reaction
temperature exceeds 100 °C. Metal nanoparticles can also be prepared using polyvinyl pyrrolidone (PVP), thiols etc. as capping agents and by photochemical method. Metal oxides (Fe₂O₃, Fe₃O₄, etc.) and metal alloys (CoFe, NiCoFe, etc.) are also prepared using different capping agents such as oleic acid, ethylene glycol, sodium oleate etc.

**1B.2 Synthesis of binary semiconductor nanoparticles**

Nanoparticles and quantum dots of binary semiconductors are normally prepared using wet chemical method which is one of the easiest and cheapest methods of preparation. Generally, in this method, some organic capping agents are used during the reaction in order to control the particle size and its distribution. There are many reports of wet chemical method in aqueous medium to prepare the nanocrystals of this materials. In this method of preparation, the salts of cation and anion are made solutions in water. Then the solutions are slowly mixed together in the presence or absence of some organic compounds/solvents (capping agents). The organic compounds/solvents are used to control the growth of particle. By adding organic compounds/solvents a thin layer of organic compound is adsorbed/bonded on the surface of nanoparticles thereby agglomeration of particles is hindered. The commonly used organic compounds/solvents are L-Glutathione, α-methacrylic, mercaptoethanol, polyvinyl alcohol, sodium citrate, polyvinyl pyrrolidone, polynucleotide, thiophenol, etc. Another frequently adopted method of preparation is reverse microemulsion route for its simplicity of operation, the potential on controlling the number of nanocrystallines encapsulated and adjusting for the core size and the shell thickness. In this method the preparation is carried out in an isotropic liquid mixtures of oil, water and surfactant, frequently in combination with a cosurfactant. The two basic types of microemulsions are direct (oil dispersed in water, o/w) and reversed (water dispersed in oil, w/o). The commonly used surfactants are dioctyl sulfosuccinate sodium salt (AOT), Triton-X100, sodium dodecyl sulfate (SDS), cetyl trimethylammonium bromide (CTAB), etc. Sometimes sol-gel technique is also used for the preparation of semiconductor nanocrystals. In this process, the sol (or solution) evolves gradually towards the formation of a gel like network.
containing both a liquid phase and a solid phase. Typical precursors are metal alkoxides and metal chlorides, which undergo hydrolysis and polycondensation reactions to form a colloid.

Though above mentioned preparation techniques are simple, easy and cost effective, the frequent problems in controlling the desired particle size and size distribution lead to low photoluminescence (PL) quantum yield with broad emission peak. To overcome such problems Murray et al.\textsuperscript{12} in 1993 developed organomettallic route using long chain Tri-n-octylphosphine (TOP) and Tri-n-octylphosphine oxide (TOPO) as cappants and solvents to prepare high quality II-VI semiconductor quantum dots. Since then the high quality quantum dots of CdSe, CdS etc. have been prepared successfully.\textsuperscript{57,110-116} Quantum dots prepared using this route yields nearly monodispersed with desire size. And their optical properties can be tuned successfully with high quantum yield PL emission. The synthesis protocol of this route is as follows: Two stock solutions of cation and anion are made in TOP or TBP (tributyl phosphine). The cation containing stock solution is made hot with TOPO at 240-300 °C under inert atmosphere, then anion stock solution is swiftly injected and quickly withdrawn after desired duration of reaction. However, this synthesis route is very expensive due to costly solvents such as TOP/TBP and TOPO. In addition, TOP/TBP and TOPO are hazardous, not environment friendly solvent and unstable in open atmosphere which requires inert atmosphere during the preparation. Recently there are few reports of preparing high quality monodispersed nanoparticles of CdSe, CdS using cost effective and non toxic chemicals such as liquid paraffin and oleic acid as solvents and cappants.\textsuperscript{53,117-119} This method has the advantage over the former since the latter can be used to prepare in open to air atmosphere.

There are many techniques of thin films preparation of binary and ternary semiconductors such as RF-sputtering, sol-gel, pulse laser deposition, chemical vapour deposition, electrodeposition, spray pyrolysis, vacuum evaporation, laser ablation, molecular beam epitaxy, chemical bath deposition (CBD), successive ionic layer adsorption reaction (SILAR) etc.\textsuperscript{120-128} Among these methods, CBD is most commonly used technique for deposition of nanocrystalline binary and ternary thin films.\textsuperscript{122,129-137} This method easily gives nanocrystalline film with
ease. This method is simple and cost effective and can be carried out in open atmosphere in wide range of temperature. Essentially CBD process takes place through (i) ion by ion reaction which takes place by sequential ionic reaction, (ii) hydroxide (cluster) mechanism through either colloidal metal hydroxide or as an adsorbed species on the substrate but not in the bulk of the solution.

The binary II-VI semiconductor quantum dots having different optical bandgaps and PL emissions of entire visible to near infra red (NIR) have been synthesized using the different mentioned routes. These binary semiconductors belong to both cubic zinc blende and wurtzite (hexagonal) structure. Figure 1 shows the typical unit cell of cubic zinc blende and wurtzite (hexagonal) structure. A brief list of their physical and structural properties is given in the Table I. With the successful synthesis of these semiconductor nanoparticles they will be useful in many promising applications in display devices and photovoltaic and solar cells. However, they have the limitations is display applications due to very short luminescence lifetime. The lifetime of these nanoparticles ranges from several nanoseconds to 1 μs. Again, the Cd based semiconductor nanoparticles

Figure 1 Typical unit cell of cubic zinc blende (left) and wurtzite (hexagonal) structures (right) of CdS and CdSe respectively.

which are very useful for photovoltaic, light emitting diodes for flat panel displays and solar cells applications have environmental concerns due to their toxicity. Despite the optical tunability of these luminescent quantum dots there is frequent problem of quenching the luminescence due to surface defects and dangling bonds. Thus surface atoms are not fully coordinated and eventually low quantum yield. The use of long chain organic compounds with strong coordinating ability with surface atoms can passivate the surface defects to certain extent resulting
decrease in non-radiative recombination confining wavefunction of electron hole pairs to the interior of the crystal. More efficient ways of increasing the luminescence quantum yield include (a) adding a small amount of second component during the synthesis of the nanoparticles. For instance, doped nano-

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Bandgap (eV)</th>
<th>Type</th>
<th>Emission wavelength region (nm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe</td>
<td>1.74</td>
<td>Direct</td>
<td>450-650</td>
<td>It is an n-type, use in optoelectronics. Tested for high-efficiency solar cells.</td>
</tr>
<tr>
<td>CdS</td>
<td>2.42</td>
<td>Direct</td>
<td>400-450</td>
<td>Used in photoresistors and solar cells; CdS/Cu$_2$S was the first efficient solar cell. Used in solar cells with CdTe. Crystals can act as Electroluminescent.</td>
</tr>
<tr>
<td>CdTe</td>
<td>1.49</td>
<td>Direct</td>
<td>520-700</td>
<td>Used in solar cells with CdS. Used in thin film solar cells and other cadmium telluride photovoltaics. Fluorescent at 790 nm.</td>
</tr>
<tr>
<td>ZnSe</td>
<td>2.7</td>
<td>Direct</td>
<td>370-420</td>
<td>Used for blue lasers and LEDs. Common optical material in infrared optics.</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.5/3.9</td>
<td>Direct</td>
<td>--</td>
<td>Bandgap 3.5 (cubic), 3.9 eV (hexagonal). Common scintillator/phosphor when suitably doped.</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.37</td>
<td>Direct</td>
<td>--</td>
<td>Window layer coatings transparent in visible and reflective in infrared region and as conductive films in LCD displays and solar panels as a replacement. Resistant to radiation damage. Possible use in LEDs and laser diodes. Can have the novel magnetic properties as well as photocatalytic properties.</td>
</tr>
</tbody>
</table>

particles such as ZnS:Mn$^{2+}$ show an increase in luminescence quantum efficiency, (b) epitaxially growing an inorganic shell of material with larger bandgap over a smaller bandgap core which is known as core shell. In these core shell nanoparticles, the hole is confined to the core of the particles surface while the electrons can travel over the whole particle. Because of the absence of hole at the particle surface the quantum yield is increased. The later method proves to have dramatic improvement in the luminescence quantum yield.
of II-VI semiconductors nanomaterials such as CdS/Cd(OH)$_2$, CdSe/ZnSe, CdSe/ZnS, CdSe/CdS etc.

In thin film form the II-VI semiconductors are quite useful many optoelectronic and solar cell applications. $n$-type semiconductors CdSe and CdS is useful in solar cells as window layer by making $p$-$n$ junction with $p$-type CdTe because near lattice match. Transparent ZnO can replace indium tin oxide (ITO) which is a transparent conducting oxide. CdS and CdSe thin films will be quite useful for transistors, electronic switches and optical detectors.

1B.3 Synthesis of lanthanide ions doped rare earth vanadate nanoparticles

Rare earth vanadates such as GdVO$_4$, YVO$_4$, LaVO$_4$ etc. are useful host materials for many applications in laser, cathode ray tubes and display devices when doped with lanthanide ions (trivalent lanthanide ions emission will be discussed later). With the evolution of nanoscience and nanotechnology and owing to their promising applications there has been great interest in the synthesis and luminescence studies during the last decade or so. Several synthesis methods have been utilized during the last decade for preparation of nanoscale lanthanide ions doped rare earth vanadate (rare earth vanadate means doped with lanthanide ions in the remaining part of the chapter otherwise stated). Earlier, nanoparticles were made via solid state reaction at high temperature of 1000 °C or more. This method of synthesis has the drawback of producing aggregated bigger size of nanoparticles as well as not soluble in organic solvents due to absence of solubilising agents on the surface of particle. In this method of reaction stoichiometric amounts of rare earth oxides or oxalates and lanthanide oxides with V$_2$O$_5$ or NH$_4$VO$_3$ are thoroughly mixed together and fired at $\sim$1000 °C for several hours. In recent times ‘bottom up’ approach using several chemical methods have become more popular which includes sol-gel, hydrothermal, polyol method using urea or sodium hydroxide (NaOH) as hydrolyzing agent, precipitation, etc. In sol-gel method of preparation, stoichiometric amounts of precursors are dissolved in water-ethanol mixture using chelating agents such as citric acid or sodium citrate or acetic acid with a cross linking agent like polyethylene glycol (PEG). The reaction solution which can be in either acid or basic solution is
stirred for few hours. The solution first forms the sol showing complete mixing of precursors and eventually to gel. The gel is finally separated for the characterization. Hydrothermal technique is one of the versatile methods for the preparation of crystalline nanoparticles which are dispersible in organic solvents. In the hydrothermal process, the crystallization of particle takes place under high temperature and vapour pressure. In a typical synthesis, required precursors are dissolved in water and put in a tightly closed teflon lined stainless autoclave and maintained at desired temperature for different durations of time. Thus crystallized rare earth vanadates are obtained. Another very simple and cost effective chemical method of synthesis is polyol method. In this method cost effective ethylene glycol/glycerol which have very short chain is used both as capping agent and reaction solvent. Urea or NaOH can be used as hydrolyzing agent. Short hydrocarbons which can control the nanoparticle size is very important for luminescence since very long hydrocarbon capping agents have high tendency of quenching the luminescence efficiency. The synthesis protocol is very simple which consists of putting altogether the requisite precursors of rare earth, lanthanide ions and vanadate sources in the ethylene glycol/glycerol and reflux at 130-160 °C with urea/NaOH for 3-4 hrs. The precipitate formed is separated with centrifugation for characterization.

Both GdVO\(_4\) and YVO\(_4\) belong to zircon type tetragonal structure having space group \(I4_1/amd\). Figure 2 shows the typical unit cell of YVO\(_4\) crystal.

![Figure 2 Typical unit cell representation of YVO\(_4\) crystal](image-url)
Similar atomic positions exist with the replacement of Y by Gd in the GdVO₄ tetragonal crystal. Single crystal and polycrystalline form of GdVO₄ and YVO₄ are important host material for laser applications. Most commonly use vanadate crystal laser is YVO₄:Nd or GdVO₄:Nd or LuVO₄:Nd.¹⁶³-¹⁶⁸ There are also vanadate crystals doped with other rare earth ions, e.g. with ytterbium, erbium, thulium or holmium etc. Due to similar size, yttrium, gadolinium or lutetium ions can be replaced with laser-active rare earth ions without strongly affecting the lattice structure. This is important e.g. for preserving high thermal conductivity of the doped materials. Moreover, vanadate crystals are naturally birefringent, which eliminates thermally induced depolarization loss in high-power lasers. Also, the laser gain is strongly polarization dependent. Another most important application of rare earth vanadate crystals is use as host material for lanthanide ions emission. The lanthanide ion emissions in the visible light spectrum are used in many applications (which are already mentioned above). Crystalline GdVO₄ and YVO₄ have the advantage of excellent chemical and thermal stability. The most important factor of using these materials as host materials is their ability to act as both holding the activators (lanthanide ions) as well as sensitizing the luminescence by energy transfer. In the process most of the absorption energy from vanadate is transferred to the excited states of lanthanide ions along with the vanadate emission.

1C. Luminescence of materials

A material can become a generator or origin of light (radiation) after absorbing suitable extraneous primary energy by two processes. In one process the absorbed energy is converted into low quantum energy heat that diffuses through the material and emits as thermal radiation. In the other process an appreciable amount of absorbed energy is temporarily localized as relatively high quantum energy excitation of atoms or small group of atoms which then emit non thermal radiation called luminescence. The current investigation will only be dealt with the later emission process of material. There are various types of luminescence according to mode of excitation (Table II).¹⁶⁹,¹⁷⁰

Fluorescence and phosphorescence are particular cases of photoluminescence.
Table II Various types of luminescence with their respective mode of excitation

<table>
<thead>
<tr>
<th>Luminescence phenomenon</th>
<th>Mode of excitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photoluminescence</td>
<td>Absorption of light (photons)</td>
</tr>
<tr>
<td>Radioluminescence</td>
<td>Ionizing radiation (X-rays, α, β, γ-rays)</td>
</tr>
<tr>
<td>Cathodoluminescence</td>
<td>Cathode rays (electron beams)</td>
</tr>
<tr>
<td>Electroluminescence</td>
<td>Electric field</td>
</tr>
<tr>
<td>Thermoluminescence</td>
<td>Heating after prior storage of energy (e.g. radioactive irradiation)</td>
</tr>
<tr>
<td>Chemiluminescence</td>
<td>Chemical process (e.g. oxidation)</td>
</tr>
<tr>
<td>Bioluminescence</td>
<td>Biochemical process</td>
</tr>
<tr>
<td>Triboluminescence</td>
<td>Frictional and electrostatic forces</td>
</tr>
<tr>
<td>Sonoluminescence</td>
<td>Ultrasounds</td>
</tr>
</tbody>
</table>

Figure 3 Schematic illustrations of: (a) photoluminescence; (b) electroluminescence; and (c) Cathodoluminescence.

The mode of excitation is absorption of a photon, which brings the absorbing species into an electronic excited state. The emission of photons accompanying deexcitation is then called photoluminescence (fluorescence, photoluminescence or delayed fluorescence), which is one of the possible physical effects resulting from interaction of light with matter. Figure 3 shows the schematic representations of (a) photoluminescence; (b) electroluminescence; and (c) Cathodoluminescence. Fluorescence is the emission of light by a substance that has absorbed light or
other electromagnetic radiation of a different wavelength. The time between initial absorption and return to the ground state takes place in the order of $10^{-8}$ sec. Quantum mechanically, fluorescence occurs between singlet states. However, phosphorescence is a transition between triplet state in the excited state and singlet ground state. Normally, phosphorescence takes longer time and continues to emit light for few microseconds, milliseconds, seconds, minutes, or even hours.

1D. Luminescence emission from lanthanide ions

The rare-earth elements usually comprise 17 elements consisting of the 15 lanthanides from La (atomic number 57) to Lu (atomic number 71), of Sc (atomic number 21), and of Y (atomic number 39). The electronic configurations of trivalent rare-earth ions in the ground states are shown in Table III. As shown in the table, Sc$^{3+}$ is equivalent to Ar, Y$^{3+}$ to Kr, and La$^{3+}$ to Xe in electronic configuration. The lanthanides from Ce$^{3+}$ to Lu$^{3+}$ have one to fourteen $4f$ electrons added to their inner shell configuration, which is equivalent to Xe. In the ground state, electrons are distributed so as to provide the maximum combined spin angular momentum ($S$). The spin angular momentum $S$ is further combined with

<table>
<thead>
<tr>
<th>Atomic number</th>
<th>Ions</th>
<th>Corresponding element</th>
<th>$4f$ electrons</th>
<th>S</th>
<th>Σs</th>
<th>L</th>
<th>ΣL</th>
<th>$J(L+S)$</th>
</tr>
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<tbody>
<tr>
<td>21</td>
<td>Sc$^{3+}$</td>
<td>Ar</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>39</td>
<td>Y$^{3+}$</td>
<td>Kr</td>
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<tr>
<td>57</td>
<td>La$^{3+}$</td>
<td>Xe</td>
<td></td>
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<tr>
<td>58</td>
<td>Ce$^{3+}$</td>
<td>Xe</td>
<td>$\uparrow$</td>
<td>1/2</td>
<td>3</td>
<td>5/2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>Pr$^{3+}$</td>
<td>Xe</td>
<td>$\uparrow$ $\uparrow$</td>
<td>1</td>
<td>5</td>
<td>4</td>
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<tr>
<td>60</td>
<td>Nd$^{3+}$</td>
<td>Xe</td>
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<td>3/2</td>
<td>6</td>
<td>9/2</td>
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<tr>
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<td>Pm$^{3+}$</td>
<td>Xe</td>
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<td>6</td>
<td>4</td>
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<td>62</td>
<td>Sm$^{3+}$</td>
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<td>5</td>
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<tr>
<td>63</td>
<td>Eu$^{3+}$</td>
<td>Xe</td>
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<td>3</td>
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</tr>
<tr>
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<td>Xe</td>
<td>$\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$</td>
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</tr>
<tr>
<td>65</td>
<td>Tb$^{3+}$</td>
<td>Xe</td>
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<td>3</td>
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<tr>
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<td>Dy$^{3+}$</td>
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<td>$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$</td>
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<td>15/2</td>
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<td>67</td>
<td>Ho$^{3+}$</td>
<td>Xe</td>
<td>$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$</td>
<td>2</td>
<td>6</td>
<td>8</td>
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</tr>
<tr>
<td>68</td>
<td>Er$^{3+}$</td>
<td>Xe</td>
<td>$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$</td>
<td>3/2</td>
<td>6</td>
<td>15/2</td>
<td></td>
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</tr>
<tr>
<td>69</td>
<td>Tm$^{3+}$</td>
<td>Xe</td>
<td>$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$</td>
<td>1</td>
<td>5</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>Yb$^{3+}$</td>
<td>Xe</td>
<td>$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$</td>
<td>1/2</td>
<td>3</td>
<td>7/2</td>
<td></td>
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<tr>
<td>71</td>
<td>Lu$^{3+}$</td>
<td>Xe</td>
<td>$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$</td>
<td>0</td>
<td>0</td>
<td>0</td>
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</tbody>
</table>
the orbital angular momentum ($L$) to give the total angular momentum ($J$) as follows $J = L - S$, when the number of $4f$ electrons is smaller than 7, $J = L + S$, when the number of $4f$ electrons is larger than 7. An electronic state is indicated by notation $^{2S+1}L_J$, where $L$ represents $S, P, D, F, G, H, I, K, L, M, \ldots \ldots \ldots \ldots$, corresponding to $L = 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, \ldots \ldots \ldots \ldots$, respectively.

Figure 4 Energy level diagram of $4f^n$ states of lanthanide ions.
More accurately, an actual electronic state is expressed as an intermediate
coupling state, which can be described as a mixed state of several $2S-1L_J$ states
(Russel-Saunders notation) combined by spin-orbit interaction. Ions with no 4$f$
electrons, i.e., Sc$^{3+}$, Y$^{3+}$, La$^{3+}$, and Lu$^{3+}$, have no electronic energy levels that can
induce excitation and luminescence processes in or near the visible region. In
contrast, the ions from Ce$^{3+}$ to Yb$^{3+}$, which have partially filled 4$f$ orbitals, have
energy levels characteristic of each ion and show a variety of luminescence
properties around the visible region. Many of these ions can be used as
luminescent ions in phosphors, mostly by replacing Y$^{3+}$, Gd$^{3+}$, La$^{3+}$, and Lu$^{3+}$ in
various compound crystals.

The current investigation will focus on the luminescence of some of the
lanthanide ions (Dy$^{3+}$, Eu$^{3+}$, Sm$^{3+}$ and Tm$^{3+}$) in GdVO$_4$ and YVO$_4$ nanoparticles.
The 4$f$ electronic energy levels of lanthanide ions are characteristic of each ion.
Since 4$f$ electrons are shielded by the outer 5$s^2$ and 5$p^6$ electrons, the levels are not
affected much by the environment or crystal field. The transitions within the 4$f$
state are parity forbidden. Figure 4 presents the 4$f^m$ energy levels of lanthanides.\textsuperscript{171}
Though the transitions are forbidden, due to the mixing with allowed transitions,
like 4$f$-5$d$ transitions, can occur. As a result of the forbidden nature, the absorption
cross section is small with long luminescence lifetimes ranging from
microseconds to several milliseconds. Each energy level designated by J in Figure
4 can split into a number of sublevels by the Stark effect due to crystal field. The
number of split sublevels is at most $(2J+1)$ or $(J+1/2)$ for $J$ of integer or $J$ of half
integer. Electrons in the excited states always relax via two competitive pathways:
one by light emission and other by phonon emission. The rate of phonon emission
$w$ depends on the number of phonons emitted simultaneously to bridge the energy
gap and is expressed as,$^\text{169}$

$$w = \exp\left(-\frac{k\Delta E}{h\nu_{\text{max}}}\right)$$

(1)
where $\Delta E$ is the energy gap to the nearest lower level and $h\nu_{\text{max}}$ is the maximum
energy of phonons coupled to the emitting states.

Luminescence originating from 4$f$ levels of lanthanides is predominantly due
to electric and magnetic dipole interactions with the wavefunctions of higher and
lower energy levels. Electric dipole $f$-$f$ transitions in free $4f$ ions are parity-forbidden, but become partially allowed by mixing with orbitals having different parity because of an odd crystal field component. The selection rule for transition is $\Delta J = \pm 2, \pm 4$ and $\pm 6$. Magnetic dipole $f$-$f$ transitions are not affected much by the site symmetry because they are parity-allowed. The selection rule for transition is $\Delta J = 0, \pm 1$ (except $0 \rightarrow 0$).\textsuperscript{172,173} For example, Eu$^{3+}$ emission in GdPO$_4$ occurs with the dominant emission due to magnetic dipole transition, $^5D_0 \rightarrow ^7F_1$. This is because of the fact that Eu$^{3+}$ occupies in a crystal site having inversion symmetry, however, the emission due to electric dipole transitions of Eu$^{3+}$ is is forbidden. In a crystalline site without inversion symmetry, the electric dipole transition $^5D_0 \rightarrow ^7F_2$ is dominant because transition with $\Delta J = \pm 2$ is hypersensitive to small deviations from inversion symmetry. For instance Eu$^{3+}$ emission corresponding to electric dipole transition is dominant in crystalline GdVO$_4$ or YVO$_4$.

Since the absorption cross section of the lanthanide ions (activators) is small due to forbidden nature of $f$-$f$ transitions ($\alpha = 0.1$-$10$ cm$^{-1}$), it is required to sensitize for obtaining efficient emission from them such as by vanadate ion whose absorption cross section is large ($\alpha = 10^3$-$10^5$ cm$^{-1}$). Essentially there are two types of sensitization: impurity-sensitization and host-sensitization. Among these types of energy transfer only later type will be briefly discussed. Resonant energy transfer can be obtained between allowed transition in the sensitizer and forbidden activators (lanthanide). In general the transition in the host will be allowed electric dipole transition. So, the transfer mechanism from sensitizer to sensitizer will usually be dipole-dipole ($dd$) process. Depending on the degree of forbiddenness of the transition in activator, the transfer mechanism is either a $dd$ process, a competition between dipole-quadrupole ($dq$) and exchange, or exchange from sensitizer to activator.\textsuperscript{174} The probability per second of energy transfer from sensitizer to activators is given by,\textsuperscript{169,174}

\begin{equation}
P_{dd}(R) = \frac{3c^4\hbar^4\sigma_A}{4\pi^5n^4\tau_D R^6} \int \frac{f_D(E)F_A(E)}{E^4} dE \tag{2}
\end{equation}

and

\begin{equation}
P_{dq}(R) = \frac{135\alpha c^8\hbar^6\sigma_A}{4\pi^3n^6\tau_D\tau_A R^8} \int \frac{f_D(E)F_A(E)}{E^8} dE \tag{3}
\end{equation}
with $\alpha = 1.266$. Here, $R$ is the separation between sensitizer to activator, $n$ is the refractive index of the crystal (host), $\alpha_A$ is the absorption cross-section of activator, $\alpha_D$ and $\alpha_A$ are radiative lifetime of sensitizer and activator. $f_D(E)$ and $f_A(E)$ represent the shape of the emission and absorption spectra from sensitizer and activator respectively, which are normalized. The integrals of above two equations are, therefore, the overlapping ratios of these two spectra, which is a measure of the resonance condition. Figure 5 shows the typical energy transfer mechanism from vanadate ($\text{VO}_4^{3-}$) excited states to excited states of lanthanide ions ($\text{Eu}^{3+}$).\textsuperscript{175,176} It is highly important to transfer some excited electrons to the excited states of the lanthanide ions. Sensitizing elements such as Ce, Yb etc. are used in many cases. But host material sensitized phosphors have advantage for their ease in preparation. In this regard, GdVO$_4$ or YVO$_4$ are good choice as host materials for lanthanide ions emission. They also have similar ionic radii and making ease in replacing the lattice sites of Gd/Y by lanthanide ions. In these systems there is strong absorption due to charge transfer from oxygen ligands to the central vanadium atom inside the $\text{[VO}_4^{3-}\text{]}$ ion which has $T_d$ symmetry with V-O distance.

![Figure 5 Energy transfer scheme from vanadate (VO$_4^{3-}$) to Eu$^{3+}$ in YVO$_4$:Eu$^{3+}$](image)
of 1.72 Å. According to the molecular orbital theory, this excitation band arises from the \(^1A_2(1T_1)\) ground state to the \(^1A_1(1E)\) and \(^1E(1T_2)\) and relaxes nonradiatively to the lowest excited state \(^1A_1(1A_1)\).\(^{175}\) Most of these electrons at the lowest excited state are transferred to the excited states of lanthanide ions.

1E. **Luminescence quenching processes**

As already mentioned in the above, there are various mechanisms which compete with radiative transitions of excited states to the ground states of lanthanide ions. It is important to discuss at least some of the mechanisms for better understanding of the luminescence of lanthanides.

1E.1 **Cross-relaxation**

This process is fundamentally the same as energy transfer, however after the energy transfer process both ions are in excited states. But not all excited energy is transferred, if only part of it is transferred, is called cross-relaxation.\(^{176-179}\) Thus this quenching mechanism is associated with exchange interaction between lanthanide ions. Such luminescence quenching occurs when the concentration of lanthanide ions is large. Figure 6 shows the typical quenching mechanism due to cross-relaxation. For example if the Eu-Eu distance is shorter than 5 Å, exchange

Figure 6 Energy level schemes of Eu\(^{3+}\) and Sm\(^{3+}\) showing possible pathways of \(^{2}D_2, \, ^{2}D_1\) emission of Eu\(^{3+}\) and \(^{4}G_{5/2}\) emission of Sm\(^{3+}\) due to cross-relaxation.
interaction becomes effective. In case of Sm\(^{3+}\) also \(^4\)G\(_{5/2}\) emission can be transferred by exchange interaction to the low lying energy levels of another ion so that orange emissions from \(^4\)G\(_{5/2}\) are quenched. Similar mechanism is also prevailed in Dy\(^{3+}\) emissions. The following cross-relaxations may occur in Eu\(^{3+}\) and Sm\(^{3+}\) to quench the higher energy level emissions due to high doping concentration.\(^{176,177}\)

\[
Eu^{3+}(^5D_0) + Eu^{3+}(^7F_0) \rightarrow Eu^{3+}(^5D_0) + Eu^{3+}(^7F_3) \\
Sm^{3+}(^4G_{5/2}) + Sm^{3+}(^6H_{5/2}) \rightarrow 2Sm^{3+}(^4F_{9/2})
\]

### 1E.2 Multi-phonon emission

Luminescence emissions of lanthanide ions can also be quenched due to non-radiative transition processes due to phonon vibrations of surroundings which often refer to phonon emission. The non-radiative return to the ground state is possible if certain conditions are fulfilled, viz. the energy difference/gap \(\Delta E\) is equal to or less than 4-5 times the vibrational frequency of the surroundings. In such case, this amount of energy can simultaneously excite a few high-energy vibrations, and is often lost for the radiative process. This non-radiative process is called multi-phonon emission.\(^{176,177-182}\) The rates of multiphonon emission for rare earths in crystals and oxide glasses have been found to exhibit an approximately exponential dependence on energy gap \(\Delta E\) to the next lower level of the form,\(^{181,182}\)

\[
W_{MP} = W_0 \exp(-\alpha\Delta E)
\]

where \(W_0\) and \(\alpha\) are phenomenological parameters. Although the energy gaps of Eu\(^{3+}\) is large between the emissive \(^5\)D\(_0\) level of 12150 cm\(^{-1}\), but still these ions are substantially quenched when the environment of ions are surrounded by water of its fourth overtone vibration (vibrational energy of OH, 3500 cm\(^{-1}\)). However, quenching effect is less in Tb\(^{3+}\) whose energy gap is large, 15000 cm\(^{-1}\) because its fifth overtone of OH bond vibration is required for extensive quenching of Tb\(^{3+}\) emission in water. Phonon vibration of host lattice also plays a role in the luminescence quenching mechanism. For example in classic oxide glasses the rare
earth ions do not emit efficiently, since their high vibrational frequency (≈1000-1200 cm⁻¹) surrounds the rare earth ions. Such luminescence quenching of host lattice vibrations are only important when the energy gap is less than about five times the highest vibrational frequency of the host lattice and it is independent of the concentration of activators.

1F. Luminescence from binary semiconductors

Luminescence from the binary semiconductors comes when exited electrons are relaxed radiatively at some lower energy states. The electrons from the valence band are excited through the bandgap by absorption with a suitable energy at the empty quantum states of conduction band. In photoluminescence, excitation is through light photon absorption. In the process, electron and hole possess high energies due to transitions from ground state to an excited state and forms exciton. The electron may recombine with the hole and relax to a lower energy state, ultimately reaching ground state. The excess energy resulting from recombination and relaxation may be either radiative (emits photon) or non-radiative (emitting phonons or Auger electrons). Figure 7 depicts the two recombination processes. Some of the radiative recombination processes consisting of band edge or near band edge transitions, or from defect and/or activator quantum states is discussed.

![Diagram showing radiative and non-radiative processes](image)

Figure 7 Radiative and non-radiative processes occur during photoluminescence (e: electron, h: hole)
1F.1 Band edge or near band edge emission

Band edge or near band edge (exciton) emission is the most common radiative relaxation process in the intrinsic semiconductors and insulators. The recombination of an excited electron in the conduction band with a hole in the valence band is called band edge emission (Figure 7A). Electron and hole is bound by few meV to form exciton. So, radiative recombination leads to near band edge emission at slightly lower than bandgap. Depending on the path required to relax, radiative emission may also be characterized as either fluorescence or phosphorescence. In a typical PL process, an electron in a phosphor is excited by absorption of an electromagnetic wave, $h\nu$ from its ground state to an excited state. Through a fast vibrational (non-radiative) process, the excited electron relaxes to its lowest energy excited vibrational state. For electronic relaxation in molecules, nanoparticles or bulk solids, the emitted photon is red shifted relative to the excitation photon energy/wavelength (i.e. Stokes shift as discussed below) because of the presence of vibrational levels in the excited state as well as the lower energy (e.g. ground) states (Figure 7A).

1F.2 Defect emission

Radiative recombination may also occur at the localized impurity/defect and/or activators quantum states in the bandgap (Figure 7B). Defect state can act as a donor (has excess electrons) or an acceptor (has a deficit of electrons) which is dependent on the type of defect or impurity. These defects states can be categorized into either shallow or deep levels, where shallow level defect states have energies near the conduction band or valence band edge. In most cases, a shallow defect exhibits radiative relaxation at temperatures sufficiently low so that thermal energies ($kT$) do not excite the carriers out of the defects or trap states. Deep levels, on the other hand, are so long-lived that they typically experience non-radiative recombination. Despite many passivation processes, in many cases of quantum dots these defect states are more due to large surface atoms. These surface states act as traps for charge carriers and excitons, which generally degrade the optical and electrical properties by increasing the rate of non-radiative recombination. However, in some cases, the surface states can also lead to
radiative transitions, such as in the case of ZnO which gives green/yellow-red emission due to oxygen related defects states.\textsuperscript{183,184-187}

1F.3 Activator emission

Luminescence from intentionally incorporated impurities (activators) is called extrinsic luminescence. These activators perturb the band structure by creating localized quantum states within the bandgap. The predominant radiative mechanism in extrinsic luminescence is electron-hole recombination, which can occur via transitions from conduction band to acceptor state, donor state to valance band or donor state to acceptor state. In some cases, this mechanism is localized on the activator atom center. In many cases, transition and lanthanide ions are doped in semiconductors for achieving different colours of luminescence.\textsuperscript{87,138}

1G. Outlook of the thesis

In the present investigation an effort has been made in the synthesis of lanthanide (Dy\textsuperscript{3+}, Eu\textsuperscript{3+}, Sm\textsuperscript{3+} and Tm\textsuperscript{3+}) doped GdVO\textsubscript{4} and YVO\textsubscript{4} nanoparticles through simple polyol method. The samples so prepared were characterized using X-ray diffraction, spectroscopy and electron microscopy. Photoluminescence and its decay process of the lanthanide ions emission in these nanoparticles have been discussed. PL behaviour of re-dispersible nanoparticles in polar solvents and incorporation polymer based films has been discussed. Quantum dots and thin films of CdSe and CdS binary semiconductors were prepared by chemical method and characterized.
References


