



Synthesis and Characterization of Unconversion Nanomaterials

*To be submitted as the Major Project under the partial fulfillment of the
requirement for the degree of*

Master of Technology
In
Nano Science and Technology

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CERTIFICATE

This is to certify that the dissertation entitled on “**Synthesis and Characterization of Upconversion Nanomaterials**” submitted to Delhi Technological University (formerly Delhi College of Engineering) by **Mr. Manish Kumar (2K15NST03)** in the partial fulfillment of the requirements for the award of the degree of **Master of Technology in Nano Science and Technology (Applied Physics Department)** is a bona fide record of the candidate's own work carried out under the supervision of **Dr. A. Srinivas Rao**. The information and data enclosed in this thesis is original and has not been submitted elsewhere for honoring any other degree.

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Candidate Declaration

I hereby declare that the work which is being presented in this thesis entitled **“Synthesis and Characterization of Upconversion Nanomaterials”** is my own work carried out under the guidance of **Dr. A. Srinivas Rao**, Associate Professor, Department of Applied Physics, Delhi Technological University, Delhi.

I further declare that the matter embodied in this thesis has not been submitted for the award of any other degree or diploma.

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ABSTRACT

New generation fluorophores, also termed upconversion nanoparticles (UCNPs), have the ability to convert near infrared radiation with lower energy into visible radiation with higher energy via a nonlinear optical process. Recently these UCNPs have evolved as alternative fluorescent labels to traditional fluorophores, showing great potential for imaging and biodetection assays in both the *in vitro* and *in vivo* applications. UCNPs exhibit unique luminescent properties, including high penetration depth into tissues, low background signals, large Stokes shifts, sharp emission bands and high resistance to photo bleaching, making UCNPs an alternative source for overcoming current limitations in traditional fluorescent probes. Generally to synthesize UCNPs Rare Earth doped elements are used, because of their very low phonon energies and high chemical stability. In the proposed work wet chemical route is used to synthesize $\text{KLaF}_4 \text{ Yb}(15\%) \text{ Er}(3\%)$ and in experiments as a resultant α -phase (cubic phase) UCNPs attained.

The structural properties, morphology and composition of synthesized material was studied by X-Ray Diffraction (XRD), Transmission electron microscopy (TEM) Fourier Transform infrared spectroscopy (FTIR) and upconversion spectra. The obtained results show the formation of UCNPs of $\text{KLaF}_4 \text{ Yb}^{+3} \text{ Er}^{+3}$.

Chapter 1

Introduction

Optical imaging is a facile way to investigate tissue. For improving this optical labelling and imaging both the signal as well as spatial resolution, various optical probes have been developed in the past decades, to pinpoint the exact location of prescribed biomolecule tissues. Especially, the classic categories of fluorescent probes, such as fluorescent dyes, fluorescent proteins, and quantum dots (QDs), have drawn a great attention from both the scientists of chemistry and biology areas. Thanks to these fluorescent probes, some secrets of life from downward at the single molecular scope to upward at the in vivo tissue level are able to be visualized. However, these well-established fluorescent probes are experiencing certain incompetence when tackling the puzzles with ever-elevating difficulties and complexities in life science. For instance, a single molecular study is severely limited by the problems of insufficient intensity and fast photobleaching of fluorescent probes, while in vivo fluorescent optical imaging suffers from a strong background of autofluorescence and light scattering as well as a limited imaging depth. The demands for new fluorescent probes with higher brightness, photostability, and spectral distinguishability for bioimaging never end.

Lanthanide-doped upconversion nanoparticles (UCNPs) are emerging as a new class of optical probes, which hold great promise to overcome the inborn shortcomings associated with dyes, fluorescent proteins, and QDs. The emission phenomenon from UCNPs is, by appearance, a little similar to multiphoton-excited fluorescence from conventional biolabels (such as dyes and QDs), since both of them are produced by converting long-wavelength excitation photons into shorter-wavelength emission photons. It is noted that simultaneous multiphoton excitation has been widely applied in fluorescent optical microscopy to show increased resolution, decreased specimen autofluorescence, as well as increased imaging depth. However, the low NIR absorption cross section of multiphoton labels requires this technique to subject to the use of high-peak-power ultrashort-pulsed laser. Moreover, the photobleaching and/or

photoblinking problem persists for dyes or QDs in multiphoton microscopy, and the high peak power of the femto or pico pulsed laser used can produce possible photodamage in biological specimens. Principally distinct from simultaneous multiphoton process in dyes and QDs, which involves the use of a virtual energy level, photon upconversion in UCNPs relies on the sequential absorption of low energy photons through the use of ladder-like energy levels of lanthanide doping ions. This quantum mechanical difference makes UCNPs orders of magnitude more efficient than multiphoton process, thus allowing excitation with a low-cost continuous-wave laser diode at low-energy irradiance; typically as low as $\sim 10\text{--}1\text{ W.cm}^{-2}$. UCNPs also have other superior advantages for probe uses in imaging. First, the intra f–f electronic transitions of Ln dopants produce a set of atomic-like line emission peaks from UCNPs. These sharp emissions are able to reduce the possibilities of spectra overlapping, and facilitate the retrieval of signal during signal screening process. Second, the parity-forbidden nature of intra f–f transitions produces a long UC luminescence decay (up to 10 ms), providing opportunities for time-resolved imaging, biosensing, and multiplexing. Third, the intra f–f electron transitions are well-shielded by the outer complete 5s and 5p electron shells, thus resisting oxidation-induced photobleaching that is often seen for electronic transitions of organic dyes. Fourth, due to a collective emission of abundant dopants within a single UCNP, luminescence from a single UCNP does not show the blinking behaviour, which is important for single molecule imaging experiments involving a long-time observation. These unique and fascinating properties of UCNPs will offer realistic resolutions to address the challenges met in single molecule level, as well as in deep tissue optical imaging level. It also inspires manipulation of various photochemical reactions in vivo using biocompatible and captivating NIR light in conjunction with the frequency converting ability of UCNPs.

1.1 Phosphors

Phosphors is a substance which has the luminescence property which means it radiates luminescence when they are energised by an external light source. Light source can be ultraviolet light or an electron beam. Property of luminescence is shown by Phosphor because when these substances receive small wavelength energy

photons, they go to their excitation state and produce high wavelength energy light, or we can say luminescence.

Inorganic Phosphor generally has a host material doped with a small amount of activator ion. Host material can be any oxide, silicate, halide, nitride, or oxyhalide and activator ions can be rare-earth (RE) or transition metal ions [1]. Activators behave as luminescence centres and have energy levels that can be generated by direct excitation or indirectly by energy transfer [2].

There are some important things about phosphor materials. One is they should absorb incident energy and emits energy as fast as possible. So that the Quantum Yield QE can be high. Other important things are Colour point, the Lumen Equivalent, the Emission Spectrum and the Emission lifetime.

Because of the luminescence property conventional phosphors are used in various screens. But the advanced version that is upconversion Nanoparticles that is UCNP has attracted researcher's attraction because of their wide use in bio labelling and in Photo Dynamic Therapy. Conventional Phosphors work on Stoke Emission principal and they are down conversion particles as they absorb high energy photons and emit low energy photons that is why in bio labelling and imaging conventional phosphors are not used and more advanced UCNP particles are used.

In the area of semiconductor technology with the advancement in research work some very useful results got out of them Quantum Dots (QD) and UCNP are most useful because of their wide applications in imaging and bio labelling.

1.2 Quantum Dots

Quantum Dots popularly known as QDs are very small nano scale particles ranges from 2 to 10 nm in diameter. QDs are also known as the central particles of nanotechnology. Their emission of light is directly proportional to their size. Bigger the size of particle, the emission of light will be in Red region and smaller the size, emitted energy will be in blue light region. These QDs contain the movement of electrons in conduction band, holes in valance band and excitation of electrons and holes in both the conduction and valance band and binding of both the particles in both the bands in all three spatial directions.

The QDs have very good application in Fluorescence Resonance energy transfer (FRET) analysis, gene, cell labelling and tissue imaging by having nano scale size, fine fluorescence and broad UV excitation.

But with these very good applications of QDs, they also have some drawbacks like cytotoxicity and chemical instability. So it became necessary to develop more efficient particles to overcome the limitations of these QDs and improve the results. So as the result of research work is in the form of Upconversion nanoparticles that is UCNP.

1.3 UCNPs

UCNP stands for upconversion Nanoparticles. Due to enormous fine use of UCNPs, it has become a prime area of research in the field of Photo Dynamic Therapy. UCNPs are very tiny Nano scale particles ranges from 1 to 100 nm which shows the property of Upconversion. UCNPs are upgraded version of conventional Phosphors.

In mid of 1960s when using laser technology “Anti Stoke shift” is observed, it is named as upconversion. This experimental discovery is done by Francois Auzel [3]. Photon Conversion is the phenomenon in which two or more than two low energy photons incident on the host lattice and after absorbing these incident photons energies particles go to their excitation state and emit a high energy photon then the incident energy of photons. The incident energy is generally lies in Infrared region while emitted energy lies in visible or ultraviolet region.

For upconverting elements it is necessary to have optically active excited state for longer period. This is generally done by embedding an insulated host lattice by lanthanide ions. This upconversion is mainly observed in d-block and precisely in Rare Earth (RE) elements. These elements have normally +3 oxidation state. Like in Lanthanide Series Ln^{3+} ions exhibit f-f and f-d transitions because of their $4f^n 5d^0$ configuration [4]. For exhibiting the upconversion phenomenon 3 components are needed:

1. A host matrix
2. A sensitizer
3. An activator Ion

The Sensitizer is used for incidence the light on it and after getting energy it goes to its excitation state and transfer the excitation energy to the activator ion. This activator ion behaves as the luminescence centre. Sensitizer increases the luminescence efficiency.

The Yb^{3+} ion act as a sensitizer because it has a simple energy level structure and simultaneously Er^{3+} , Tm^{3+} , and Ho^{3+} ions works as UC Activator ions because their energy level structure is of ladder type. Both the sensitizer and activator ions mixed in different quantity [5]. Recently researches are going on surface modifications and applications of Liu's group Lanthanum doped NaYF_4 [5-8]. β NaYF_4 can be transformed from α NaYF_4 which is said more thermodynamically stable form but it is also observed that α phase of NaYF_4 is more stable than β phase because the

conversion of α NaYF₄ to β NaYF₄ is very high due to free energy barrier and thus it requires more transitional energy in cubic-to-hexagonal phase.

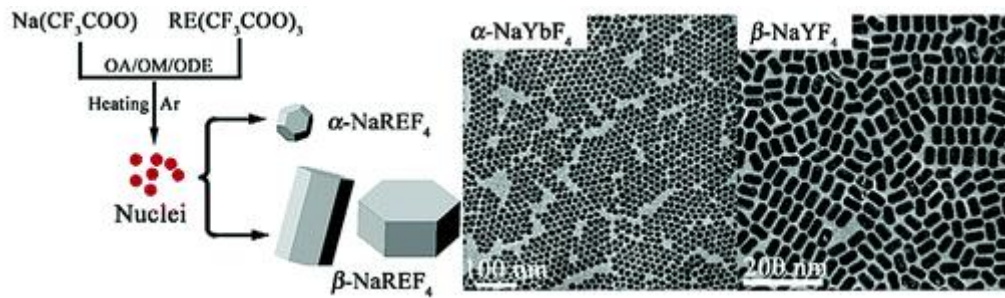


Figure 1.1: Synthesis of α -phase and β -phase NaREF₄ nanocrystals [9].

The NaREF₄ is an effective host matrix for upconversion emission in RGB scale with appropriate doping. The selection of host matrix of upconversion particles is justified by its low photon energy and multisite characteristic. So we can say that UC efficiency affect in two things one by the phonon dynamics and other is by the local crystal field.

There are three type of UCNP conversion mechanism.

1. Excited State absorption
2. Energy TransferUpconversion
3. Photon Avalanche

UCNPs are unique because of their some unique optical properties like quick luminescence, deep penetration to the tissues without damaging cells, excellent contrast agent in vivo and vitro applications and have very high resistance to photo bleaching. That is why they have a very good scope in biological applications. They are biocompatible and can be coagulated in bio molecules and can help in making various biological bio detector assays and therapeutic modalities [10].

1.4 Difference between QDs and UCNPs

QDs and UCNPs have a very fine difference in applications like as follows [11]:

Table 1.1: Comparison of QDs and UCNPs [11]

Property	QDs	UCNPs
Toxicity	It has a tendency of toxicity because of having lead and cadmium, and if they are covered with sell protection then also they show toxicity if they are used for a long term.	These are not toxic as they do not have such elements which create toxicity.
Lifetime and durability	Prone to get effected by oxidation so shall layer required which enhances its	These are made of oxides so oxidation is not a problem. So they are easy to handle,

	complexity and operating cost.	give high productivity and do need much surface modifications. As they do not need so much modifications in their natural structure, so minimum manufacturing defects occur.
Solubility	They are bad solvent in water. They need additional treatment for having hydrophilic surface. So they are not so much suitable for biological applications.	These are hydrophilic particles.
Size Vs. Color	The emitted colour is totally size dependent. Emitted colour is in blue region if size is small and in red region if size is big.	Particle size does not matter and by using same different biological applications can be done.
UV Absorption	UV light absorption is in broad region.	Here it is a narrow band.
Excitation	Because of Broad UV region, absorption occur at the same time.	Simultaneous excitation.
Synthesis	It is complicated as various steps involved.	Easy processing of synthesis which helps in great production.
Functioning	For adding multiple functional groups so many steps are required.	Here it is very easy to add functions and these are available with or without carboxylic functionalities.

Ideal fluorescent probe should be ultrasensitive, resistant to photo-bleaching, bio-compatible and non-toxic and should possess high fluorescent efficiency and superior chemical and physical stability. While QDs have low light penetration depth inherited to the short wavelength excitation light. They possibly damage or even death of bio-molecules by long term irradiation, and have a low signal to noise ratio due to significant auto fluorescence from biological samples in the UV short wavelength regions.

1.5 Anti Stoke Emission

It is named after Irish physicist George G. Stokes [12]. It means when a molecule or atom absorbs a photon, it gains energy and enters an excited state. If the emitted photon has more energy than the incident photon, the energy difference is an Anti Stoke shift. This extra energy comes from dissipation of thermal photons in a crystal lattice, cooling the crystal in the process. This anti stoke emission is backbone in

research of upconversion of nanoparticles. Stoke fluorescence is the emission of a longer wavelength photon by a molecule than that has absorbed a photon of shorter wavelength.

1.6 Upconversion Mechanism

Upconversion mechanism can be broadly characterized and explained via given three mechanisms:

1. Excited State Absorption
2. Energy Transfer Upconversion
3. Photon Avalanche

1.6.1 Excited State Absorption (ESA)

It is a key phenomenon in optical limitation of telecommunication. It is a sequential absorption of two pumped photons. This model is proposed by Bloembergen in late 1950s [13]. In ESA, absorption of photons is takes place by a single ion because of the ladder like structure. In three level system as shown in figure 1.2 when a photon get absorbed in ground state of the ion, it goes to energy level 1 and here the second photon is get absorbed and jump to the next energy level that is E_2 and after reaching at level 2 it emits higher energy photons and again come back to Ground state or E_0 . The first photon absorption is known as Ground state absorption and after second photon absorption, ion goes to its optical transition and hence upconversion emission takes place.

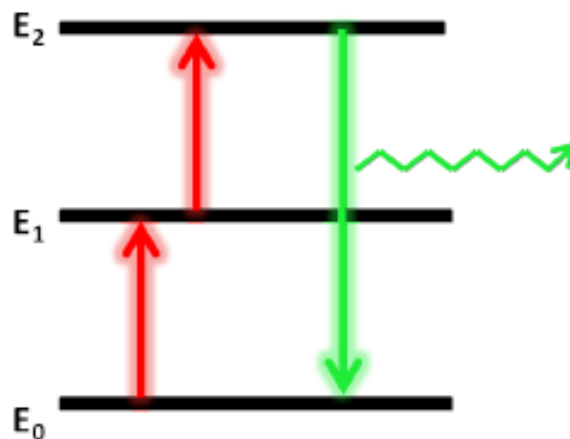


Figure 1.2: Excited State Absorption process

1.6.2 Energy Transfer Upconversion (ETU)

Energy transfer upconversion involves two ions. One is Sensitizer or donor and other is Activator or acceptor ion. This phenomenon is exhibited in those materials which have high doping ion concentration. In ETU sequential absorption of two photons is used to populate the Meta stable level. Here the electron transfer happens in two ways:

1. Resonant non - radiative transfer (RNRT): It is exhibited when the distance between the neighboring ions is very small and energy level of both the sensitizer and activator is nearly equal. Energy gets transferred from donor to acceptor and simultaneously exciting activator from its ground state to excited state before sensitizer emits photons.
2. Phonon- assisted non- radiative transfer in two ion involved system.

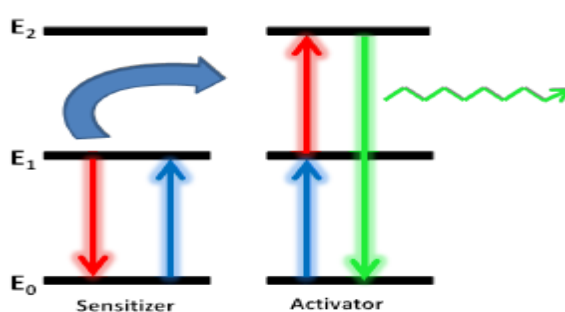
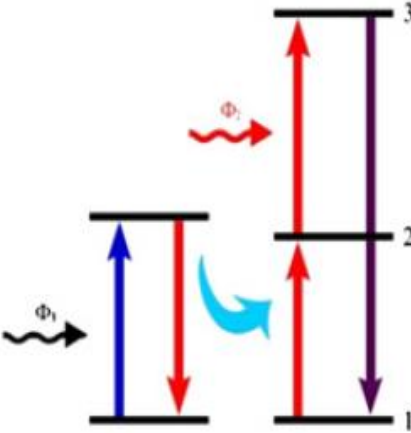
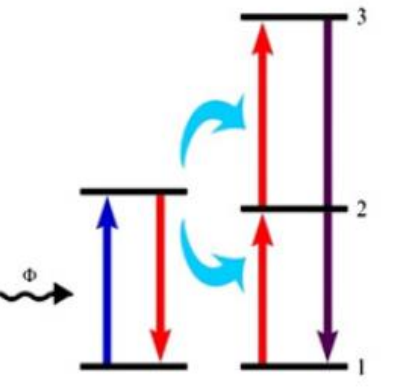
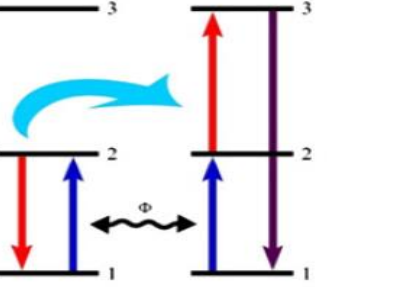
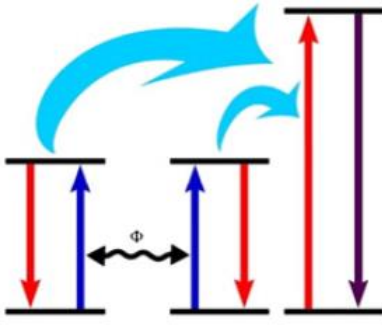
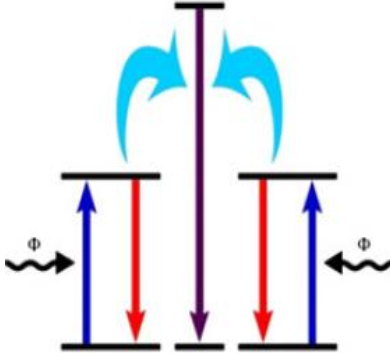


Figure 1.3: Upconversion process in ETU.

There are various ways to do Energy Transfer Upconversion, like Successive Energy Transfer (SET), Cross Relaxation (CR), Co-Operative Sensitization (CS) and Co-Operative luminescence(CL) as shown in table 1.2:

Table 1.2: Various Processes of Energy Transfer upconversion [14]

Type	Schematic of Strategies	Remarks
EFE		<p>Energy is transferred from donor when it is in excited state to the acceptor ion by an ET for activating the acceptor ion for its energy state 2 and in next process the acceptor ion is promoted to its energy level 3 through an ESA process</p>
SET		<p>The acceptor ion in E_1 is promoted to E_2 by an ET. In next process the acceptor ion is promoted to E_3 by a second ET. Here only the donor ion absorbs the incident photon.</p>
CR		<p>Here both the ions are identical and energy of incident photon is absorbed by both the ions for promotion of these ions in E_2. Next ET promotes the accepting ion to its E_3 whereas the donor ion goes to its ground state.</p>

CS		<p>Here two donor ions are used and their cumulative energy of excitation level is transferred to a single activator ion for promoting the acceptor ion to its higher energy level.</p>
CL		<p>Here the emission takes place in single process when one photon is used by two excited ions which act as both the acceptor and donor ion.</p>

1.6.3 Photon Avalanche (PA)

This is also known as absorption avalanche [15]. This is considered the most efficient process of upconversion. As in figure 1.4 the excitation is generally starts with a little higher energy then E_2 level.

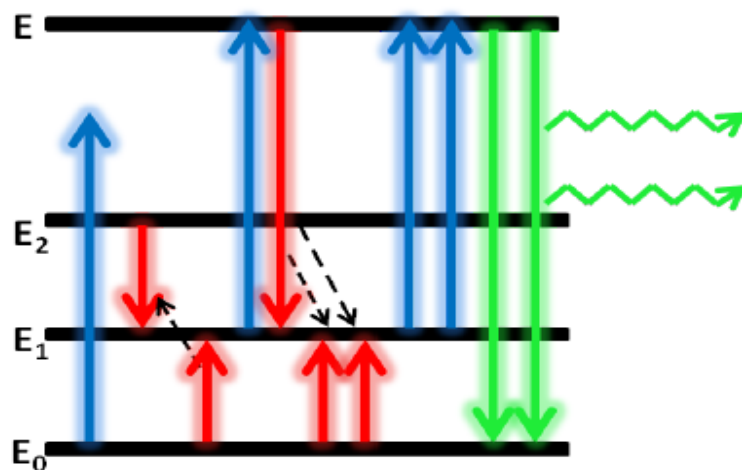


Figure 1.4: Photon Avalanche

Here the intermediate ion acts as a storage reservoir for energy so that an avalanche of the ion population at energy level E_2 can be established. Energy transfers between the

second state electron and ground state electron. This leads to formation of two electrons in the first state. Out of these two, one absorbs the excitation wavelength and gets excited to the E state where after interacting with ground state electron, energy transferred from these first state electrons. In this state excitation is resonant with absorption transition from first state to E state. Having the same process again and again the electron density in E state increases and when these E state electrons go back to their ground state, very high energy photons get emitted.

1.7 Synthesis and Formation Mechanism of RE Doped UCNPs

There are various kinds of synthesis processes available for RE- doped UCNPs like:

1. Co precipitation Method
2. Thermal Decomposition method
3. Hydrothermal / Solvothermal Method
4. Sol-gel Processing
5. Combustion Synthesis

1.7.1 Co Precipitation Method

This method is first reported by Yi GS, Lu HC, Zhao SY, et. al. [16] in which they have done synthesis on $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ UCNP. Conversion of phosphor is done from Infrared to visible region. In this method Yi et al. have injected Re-EDTA complex into a NaF solution and stirred the complex solution very well. After this process as a result α - $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ UCNP formed in a homogenous nucleation process. Annealing treatment is used to enhance fluorescent intensity as intensity of α - $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ UCNPs are not up to the mark. This resulted in transition of phase from cubic to hexagonal, but after annealing particles become larger in size so their applications get limited at high temperature.

So for overcoming this problem improvement in the same method is done by adding EDTA Complex [17]. After adding of EDTA a change in morph structure of nanoparticles.

In co precipitation method annealing is typically required for increasing intensity and if EDTA added it results in decrement in hydrophilicity of nanoparticles which again needs surface modifications using silica coating.

So collectively we can say that co precipitation method is not as efficient as required in biological applications.

1.7.2 Thermal Decomposition Method

This is the easiest method for synthesis of KYF_4 up converted nanoparticles. It is easy because of metallic tri-fluoroacetates. As these elements have a property of thermal

decomposition in their metal fluorides. As reported by Mai et al. [17] for synthesizing a high quality $K\text{ReF}_4$ nanoparticles by using procurers as $\text{K}(\text{CF}_3\text{COO})$ and $\text{RE}(\text{CF}_3\text{COO})_3$. These two solvents are made up of co-ordinating and non-co-ordinating solvents. For giving high temperature, 1-octadecene is used as the non-co-ordinating solvent, and for co-ordinating solvents Oleic acid and leyamine is used. These prevent from agglomeration. α and β KYF_4 can be obtained from Oleic Acid-Oleyamine-1-octadecene and Oleic acid-1-octadecene respectively. αKYF_4 is obtained in mild conditions while βKYF_4 is obtained in harass conditions, means in obtaining αKyF_4 nanoparticles low K/RE ratio is used at low temperature and the reaction time is short, while in obtaining βKYF_4 nanoparticles high K/RE ratio is used at very high temperature and the duration of reaction is longer. By this method high quality UCNPs are obtained.

A new method for synthesizing nanoparticles by using thermal decomposition is given by Shan et al. [18] in which only one solvent that is trioctylposphine oxide is used. This solvent works for controlling Crystalline growth and to give high temperature for obtaining β -UCNPs. In this method obtained particles are small in size with high efficiency. By using this method energy barrier in converting cubic- to -hexagonal shape also get reduced. Here they reported that there are two stages for obtaining β -UCNPs: first is a precipitation method which is Kinetic controlled which yields α -UCNPs. Second is for obtaining β -UCNPs diffused growth and a controlled size stage. Here they reported their intensity of UCNP is directly proportional to the size of β -UCNPs.

Thermal decomposition method is an effective method for obtaining monodisperse pure α and β UCNPs, which are single crystalline but it also have some drawbacks like it needs high temperature environment and the medium should be oxygen free so that oxidation should not get happen. The metals used for this process also have toxic property as well as the chemical reactions with aiding agents also make UCs surface hydrophobic, which limit their biological applications.

1.7.3 Hydrothermal Method

The aqueous/solvothermal strategy alludes to a substance combination strategy inside a fixed situation under high weight and temperature (regularly over the basic purpose of the dissolvable). This is another decomposition technique which normally requires very low temperature then any other methods. This method is used to obtain mono disperse Lanthanide doped NaYF_4 upconversion particles which are in small in size, shape and phase.

For getting this method done a special arrangement get done in which the reaction vassals, are made of very thick steel wall, seals are hermetic in nature and the protective inserts are of corrosion resistive materials like Teflon or titanium. So because of all kind of isolation inside the vassals it is not possible to view the particles in reaction.

In this method both the pressure and temperature are more than the critical temperature and pressure point of solvent. For increasing the solubility of materials for increasing the reaction performance temperature in vassals is more than critical or in supercritical region.

The fabrication of β UCNP both tested by using hydrothermal and solvothermal method in various solvents like distilled water, acetic acid using CTAB and EDTA for tuning the crystal morphology and size of particles.

In the presence of CTAB synthesis in acetic as well as alcoholic medium, the size of the particles is generally bigger while in EDTA the order of nanoparticles is in range of 20-30nm if the medium is acetic and in range of 50nm if the medium is alcoholic. It is noted that when we use EDTA the morphology of particles can be controlled as well as tuning of size of NaYF₄ nanoparticles can be controlled. If the ratio of EDTA v/s Ln³⁺ ions is low, the respective size of particles will be bigger and vice versa.

For preparing water soluble NaYF₄: Yb³⁺, Er³⁺ UCNP with an outer layer of organic polymer use a rare earth stratus popularly use ((C₁₇H₃₅COOH)₃RE), sodium fluoride and various different polymeric organic substances as capping legends. Further these materials get wetted with water and ethanol for reaction for one day at a temperature of 180 degree centigrade. The UCNP obtained from this process are hexagonal crystals with a uniform size of 40nm.

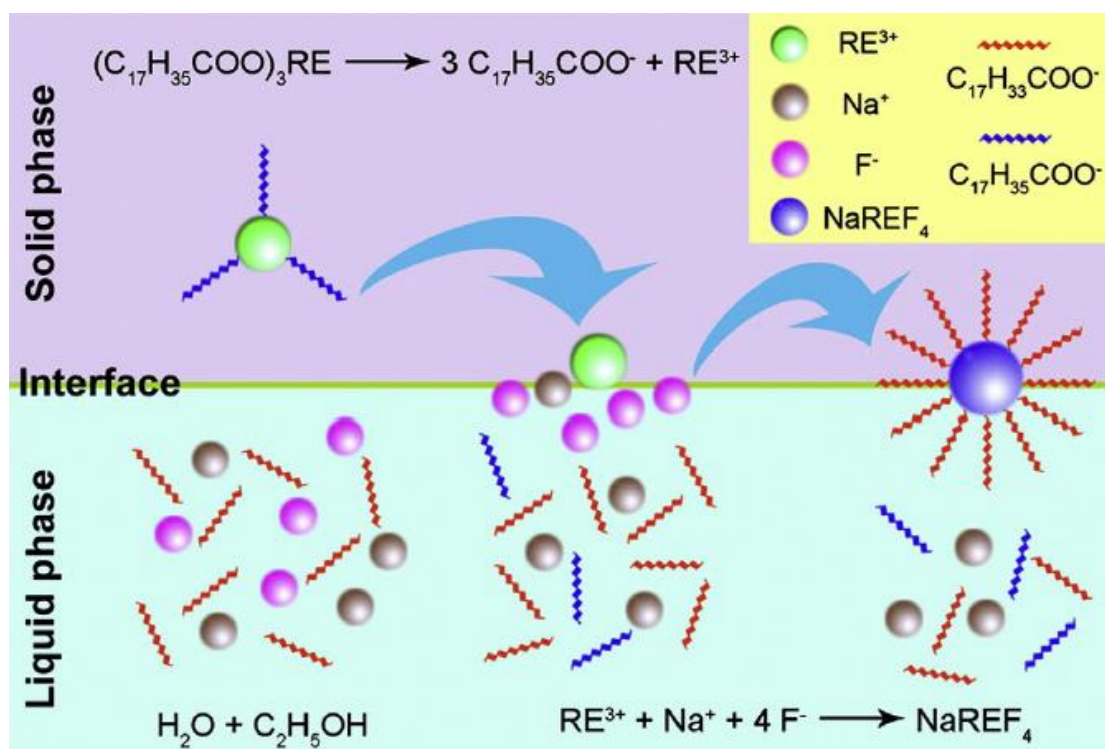


Figure1.5: Synthesis Mechanism using Solvothermal Method

The benefits of embracing an aqueous/solvothermal strategy for blending excellent UCNP incorporate (1) a high level of item immaculatness, (2) simple control of

size, structure and morphology of the NPs, (3) generally bring down response temperatures (when all is said in done underneath 200°C), [27] and (4) utilization of basic hardware and straightforward general process. In any case, in most cases the hydrophilicity of UCNPs arranged utilizing the aqueous/ solvothermal technique was not adequate due to the nearness of hydrophobic natural ligands, (for example, OA) on the surface of the NPs. Thusly, to enhance the water-dissolvability furthermore, biocompatibility of the UCNPs, surface alterations are a high need.

1.7.4 Other Methods

Polyols, which have high breakingpoints and great water solubility, have been utilized broadly as solvents to get ready assortments of NPs, including metals, oxides and phosphates. Wei et al [28] announced a polyol strategy for get ready NaYF₄:Yb³⁺,Er³⁺/Tm³⁺ UCNPs. In their reviews, three sorts of polyols, which include dethylene glycol, diethyleneglycol and glycerol, were utilized not just as solvents additionally as topping ligands to constrain the development of NPs and balance out them from conglomeration. After the solvothermal methodology, the period of the UCNPs was changed over from the α -stage to β -stage, bringing about an improvement of the fluorescent force. Since polyols are water dissolvable, the as prepared UCNPs could be very much scattered in water. Different sorts of fluorides, for example, NH₄Y₃F₁₀ and YF₃ were additionally combined utilizing this polyol-interceded method. Li et al revealed a straightforward strategy for the amalgamation of β -NaYF₄:Yb³⁺,Er³⁺/Tm³⁺ UCNPs with upgraded fluorescence. This framework has two noteworthy strides: 1) nucleation at room temperature(25°C) and 2) molecule development at hoisted temperatures (300°C).

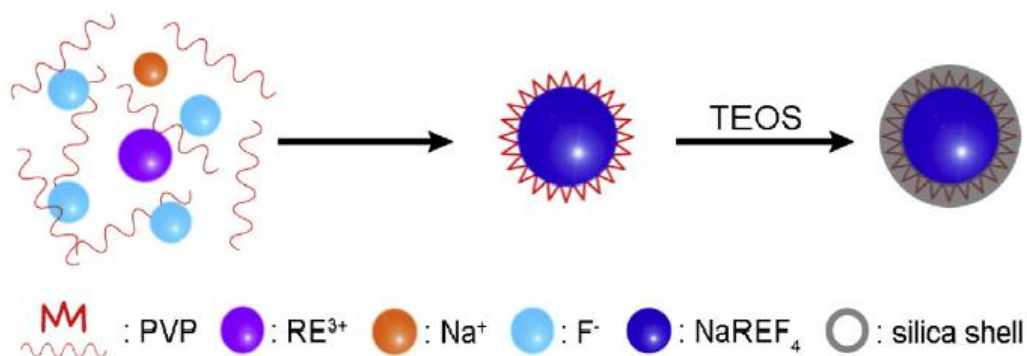


Figure 1.6: Surface Silica coating

OA and Tribute were utilized as a part of this strategy to give a high temperature condition for the cubic-to-hexagonal stage move. Here, utilization of metal trifluoroacetates was kept away from to restrict the lethality of fluorine species. Notwithstanding, thorough engineered conditions including anhydrous and sans oxygen situations were moreover required. Heer et al [30] announced a three-stage blend of NaYF₄:Yb³⁺,Er³⁺/ Tm³⁺ UCNPs utilizing N-(2-hydroxyethyl)-ethylenediamine (HEEDA). This strategy included the arrangement and response of two educt-arrangements (containing Na⁺ and RE³⁺ cations, and F⁻ anions,

individually) in HEEDA. The subsequent UCNPs were scattered in dimethyl sulfoxide (DMSO) to frame a straight forward colloidal arrangement. This strategy is the primary detailed combination of $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}/\text{Tm}^{3+}$ UCNPs.

Table 1.3: Comparison of different synthesis processes

Techniques		
Method	Hosts	Remarks
Co-precipitation	LaF_3 NaYF_4 LuPO_4	Fast growth treatment with cheap equipments
Thermal Decomposition	LaF_3 NaYF_4 GdOF	Expensive, air sensitive precursors. Monodisperse NC. Toxic byproducts
Solvothermal Synthesis	LaF_3 YVO_4	Cheap raw materials. Excellent control over particle size
Sol-gel	ZrO_2 TiO_2 BaTiO_3	Cheap raw materials, Calcination at high temperature required
Combustion Technique	Y_2O_3 Gd_2O_3 La_2O_3	Energy economic. Time savvy. Particle aggregation
Flame Synthesis	Y_2O_3	Time efficient.

1.8 Upconversion Multicolour Tuning

The capacity to move upconversion outflow shading is very pivotal for their application in natural naming and barcoding.

1. By changing the relative measure of dopant particles and host material, we can change the outflow wavelength and their relative intensity.[31]. The coupling between f-f move furthermore, the nearby precious stone field of the host cross section is very frail and thus can be misused to get change in relative outflow power. Be that as it may, phonon dispersion from the host grid and surface ligands can deliver a noteworthy change in the populace thickness between two firmly divided vitality level of a given lanthanide particle.

2. Estimate subordinate radiance property comes about because of surface impacts rather than quantum impacts as a result of little span of the exciton in the lanthanide-doped nanocrystals. As the span of nanoparticle gets diminished, the grouping of surface dopant particles is relentlessly expanded. The outflow range of the nanocrystals is an aggregate of emanations from dopant particles at the surface and in the inside of the particles. Size of the nanocrystals can be controlled to direct the centralization of surface dopant particles, prompting a progressive change in the shading delivered.

3. The relative measure of the dopant particles and the normal separation between neighbouring dopant particles impacts the optical properties of the nanocrystals[32]. For instance, an increment in the convergence of Yb^{3+} in $\text{Y}_2\text{O}_3:\text{Yb}^{3+}/\text{Er}^{3+}$

nanoparticles achieves an improved back-vitality exchange from Er^{3+} to Yb^{3+} , along these lines prompting a relative increment in power of red outflow of Er^{3+} [33].

4. It is currently realized that various surface and mass deformities could exist as a result of the low-temperature combination and the high surface territory of nanoparticles.[34]. Few imperfections could prompt arrangement of nonradiative recombination focuses which comes about in extinguishing of energized Er^{3+} states[35]. With increment in temperature the states of UCNPs turn out to be increasingly regular[36].

1.9 Potential Applications of Upconversion Nanoparticles

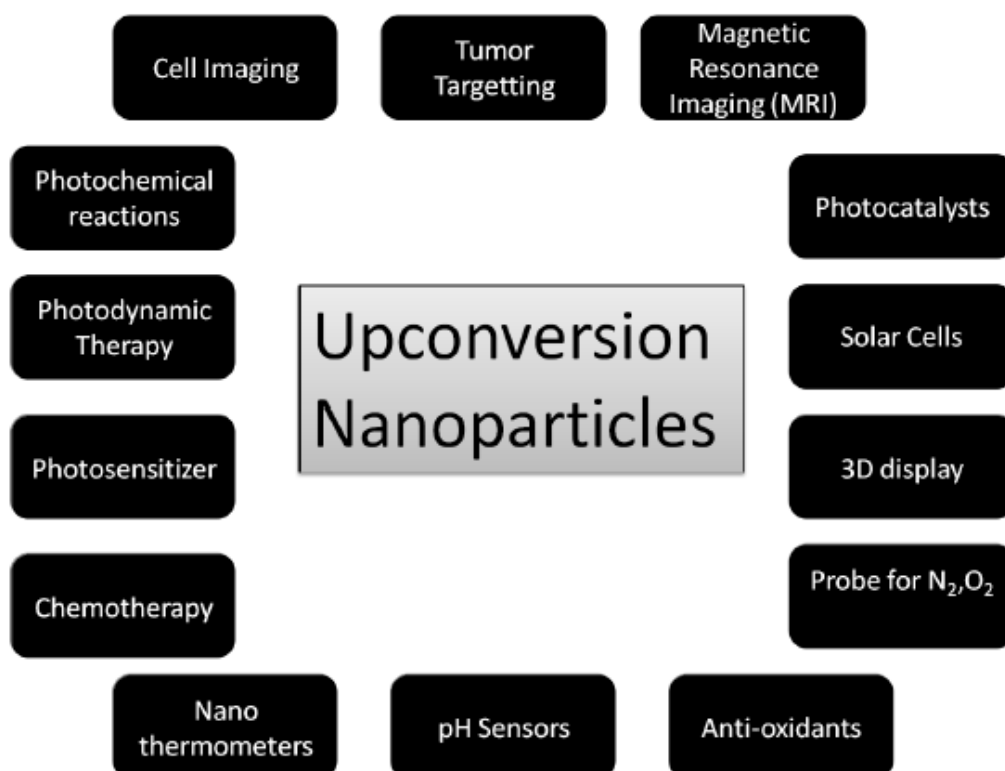


Figure 1.7: Potential Applications of UCNPs

1.9.1 Biological Applications

In DNA Sampling Assays

RE doped UCNPs are useful in DNA pattern detection by using two Approaches: First is to use DNA- Sensitive nano-particles and second is to use nano-particles for labelling DNA parts.

$\text{LaF}_3:\text{Ce}^{3+}$, Tb^{3+} UCNPs are near to fifty nano meter in size with a polymer coating exhibits fluorescence property because of Tb^{3+} ion transitions. So this can be done with the help of DNA because it is also a nucleic acid. This is because there is a bonding of Hydrogen bonds in nucleic acid and carboxylic acid of nano-particles which helps in transfer of energy from the excited state of Tb^{3+} to De-oxi-nucleic acid. So by the emitted energy the intensity of fluorescence can be detected. This process can be done with the help of spectro-photo-meter.

These micro-arrays of DNA samples are very useful to get information of mRNA patterns. This is done with by doing hybridization of DNA coils taken as a sample for fluorescence by doing reverse transcription of extracted mRNA.

By analysing the quantity of fluorescence intensity it is easy to find complementary parts in each part.[37] Generally for this purpose Cy3 or Cy5 dyes are used. This conventional method is replaced by new method in which target DNA get biotinylation by doing labelling with coating of neutraviding. $\text{Gd}_2\text{O}_3:\text{Eu}$ or by $\text{Y}_2\text{O}_3:\text{Yb}^{3+}\text{Er}^{3+}$ UCNPs as shown in figure 1.8. By using this method a very low concentration up to 1 ng/ml can also be detected.

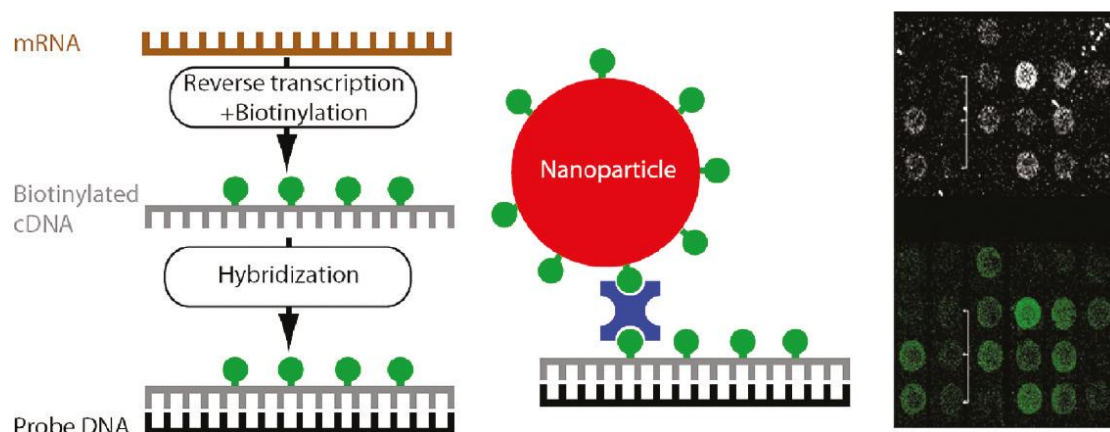


Figure 1.8: DNA detection process by using Upconversion nanoparticles

Detection of SNPs that is single nucleotide polymorphism is crucial for treating various diseases for example PKD that is polycystic kidney disease which is normally done by a time consuming calculation based reverse transcription polymer chain reaction method.

$\text{Fe}_3\text{O}_4/\text{Gd}_2\text{O}_3:\text{Eu}$ nanoparticles has core made of Fe_3O_4 with Er^{3+} ions and shows magnetism because of Fe_3O_4 which helps in detecting SNPs.

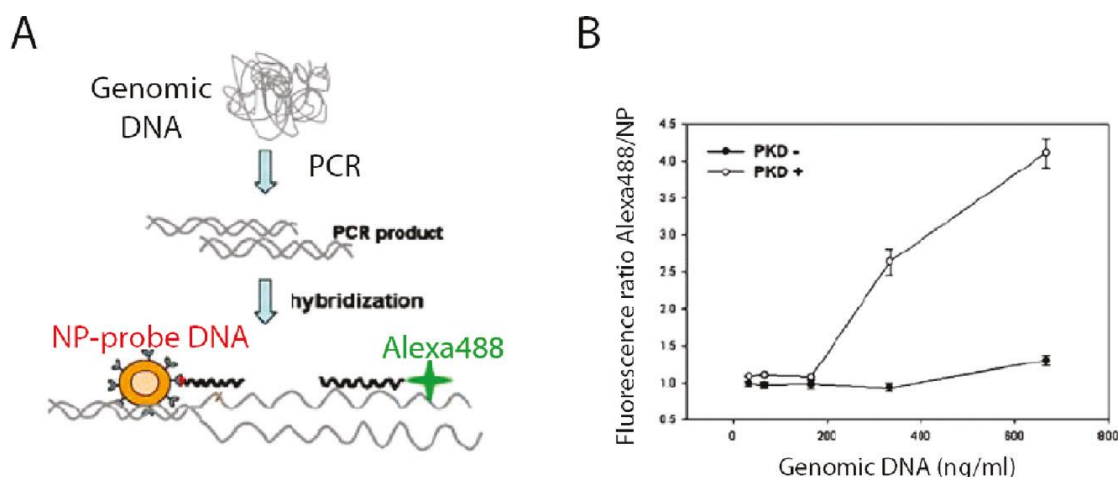


Figure 1.9: (A) Discovery of single nucleotide polymorphisms (B) FRET Signal as a function of nature E_2 concentration.

By doing neutravidin in nano-particles get functional and after that they are added to DNA fragments. After that genomic part of DNA is get extracted from the targeted tissue and then the region is get selected which has the polymorphism is collectively amplified by PCR. And then hybridisation is done with PKD with a complementary part of organic dye. When the part of DNA is coupled with nano-particles sample DNA, these are mixed that results in hybridization of mixture for preferred SNP. From this hybridized sample nano-particles are separated by using a magnet and then the luminescence ratio of Eu^{3+} and organic dyes gives information of presence of bounded DNA. And then the presence of polymorphism is detected by calculating fluorescence ratio. Both these ratios used for a basis to get yield of organic dye. It is the efficient method for detecting SNPs.

Protein Detection

In vitro applications of protein detection by using fluorescent nano-particles in immune assays is very much helpful in various molecular biological needs as well as in diagnosis of various diseases. As advancement in ELISA test Lanthanide Chelates are used. This works on enamelling detection of fluorescence of Ur Chelates by UV rays for improving sensitivity towards fluorescence. For detection of single molecule in vivo or vitro applications for ultra-sensitivity or imaging nano-particles based methods needs to get developed.[38] This test showed the possibility of effective protein recognition on a substrate and could be utilized as a model for organically applicable issues utilizing counter acting agent covered nano-particles. The plausibility to utilize uncommon earth nano-particles in immunoassays rather than natural colours was exhibited by naming mouse IgG with $NaYF_4:Yb^{3+},Er^{3+}$ nanoparticles coupled to anti-mouse antibodies.

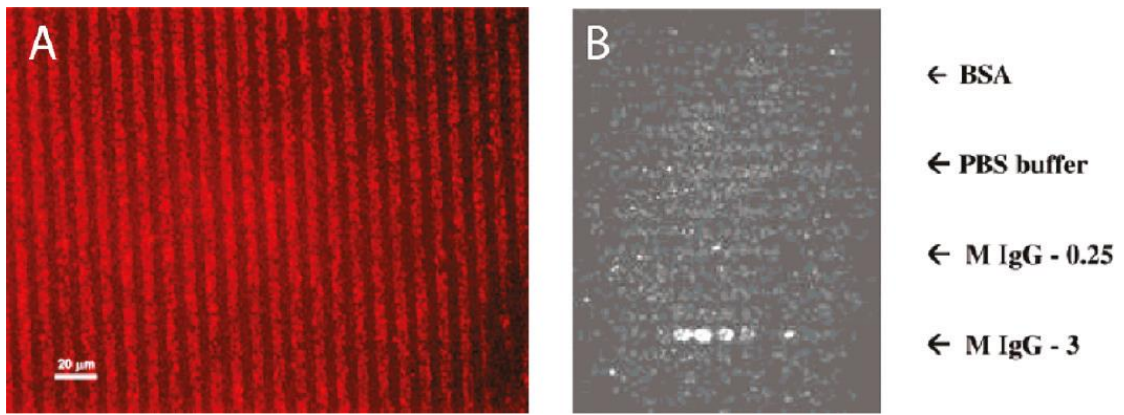


Figure 1.10: (A) Protein discovery on micro-patterns (B) Immunoassay: Presence of IgG revealed by emission of nanoparticles.

Cell Biology and in Vivo Applications

Non Specific Imaging

This is the most convenient method to use rare earth doped nanoparticles in living organisms when we use not a specified amount of injection of nanoparticles in cells.

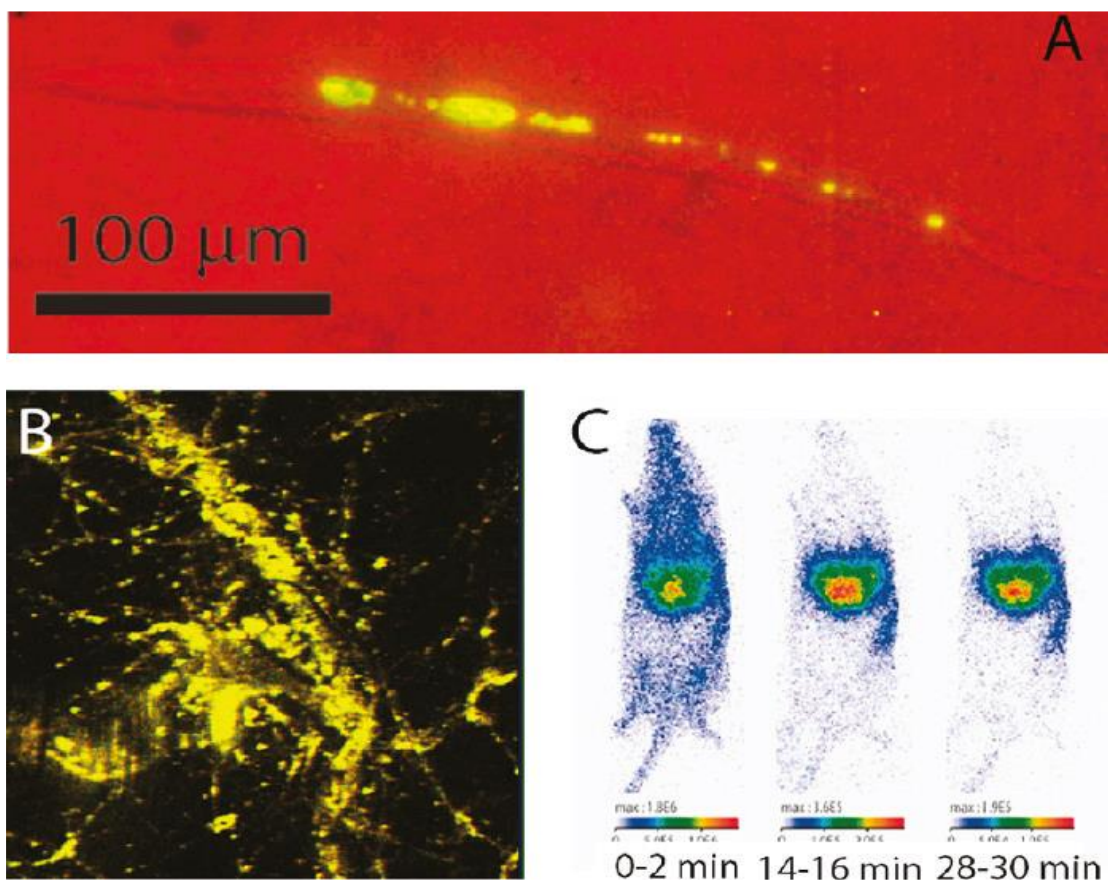


Figure 1.11: (A) Nonspecific imaging with upconversion nanoparticles. (B) Projection after injecting $\text{NaYF}_4:\text{Er},\text{Yb}$ in mouse (C) Images of carboxyl coated nanoparticles injected in a mouse.

Here with the help of experimental results it is being analyzed nanoparticles optical properties. It is also found that these particles does not exhibit toxic characteristics in cells. For this reason it becomes really helpful in protein imaging. These particles also does not show background fluorescent. In worms' imaging $Y_2O_3:Yb^{3+},Er^{3+}$ doped nanoparticles are used. In this process these nanoparticles gets mixed with the food of worm then the worm eat it so by this way there is no harm to the worm and then the fluorescent of these nanoparticles gets imagined with the help of infrared light for exciting these nanoparticles fluorescent property.

For better improved results in cell biology new combination of two techniques that nanoparticles and confocal microscopy gets mixed. Here rare earth doped nanoparticles $NaYF_4:Yb^{3+}, Er^{3+}$ are injected in Hela Cells. The variation in anti stoke shift is near to two nano meter which is very near to 2 photon microscopy results.

When the $MgSiO_3:Eu^{2+}, Dy^{3+}, M^{2+}$ particles inhaled by the small creatures, it is found that the passing organisms are clearly imagined which is first step in labelling of organisms by using upconversion nanoparticles.

Specific Protein Targetting

It is very important medium in cell biology to tag proteins with fluorescent materials. To get the details cell layout or structure in cell immune-chemistry field it is used in already noted cells. Although already existing methods for labelling by using dyes are also good but in living organisms' cell it is very much difficult to visualize because organic dyes are fast reacting and show the photobleaching effect which is not good in quality imaging of proteins. Because of the stability in excitation state rare-earth doped nanoparticles are very much helpful in cell biology because they are not toxic, their stability time is also high as well as the emitted energy is also in such a range which can not harm tissue cells.[39] For binding proteins with nanoparticles generally antibodies are used as functionalizing agent.

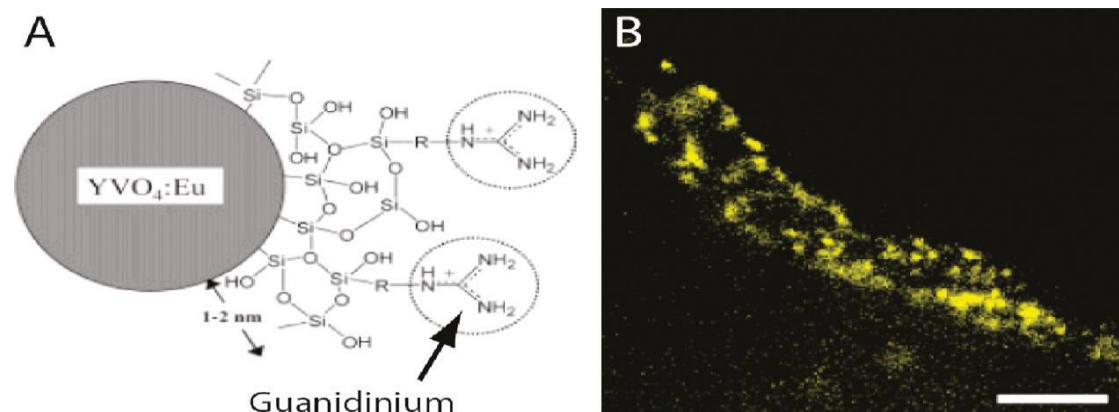


Figure1.12 (A) Marking of voltage-gated sodiumchannels utilizing $YVO_4:Eu$ nanoparticles.(B) Fluroescence image of living frog cardiomyocle.

For an experiment it is noted that when $\text{YVO}_4:\text{Eu}$ nanoparticles gets reacted with guanidinium group elements with the help of epoxy group members and as a result of reaction voltage- gated sodium gets excitation. After this process generated nanoparticles are used to bind the opening of sodium based channel which enables imaging by exciting the Eu^{3+} ions.[40] Because of long life span of nanoparticles two timely synchronized choppers gives a delay of $50\mu\text{s}$, which is the difference of acquisition and emission because of this delay cell fluorescent gets nullified and the problem of photobleaching gets resolved.

However the application of such kind of operations is limited in membranes. Because in membrane proteins the process needs an external injection of nanoparticles after doing extreme purification of proteins. So it is a big challenge against nanoparticles use in cell membrane based protein labelling.

Chapter 2

Literature Review

The most important and crucial part to lay the groundwork is its literature survey. All the important studies related with the chosen material, the issues and cavity within the work lay previously and new extent raised, forms the legwork of the new discovery. It pinpoints on the variety of scopes of the material, underlines the analysis that is then applied by current scenario, thereby saving a lot of time, funds and the potential of the people. It helps in unique creation of manuscripts around the globe and abstains from the recurrence of the work done previously.

2.1 Research Work Carried Out in the Field of UCNPs

MengWeng, Gopal Abbineni et al. have presented a paper on upconversion nanoparticles. In this paper they work on synthesis of rare-earth doped UCNPs using various methods like co-precipitation method, thermal decomposition method, hydrothermal method etc. and give comparisons of all these synthesis processes using different scenarios. Then they proposed modification of rare-earth doped NaYF_4 upconversion nanoparticles in which they modified the sample using inorganic shell layer and organic capping ligands. And in the end they give various biological applications of these RE-doped UCNPs based on FRET techniques for detection of diseases in rat. So this paper summarizes about the synthesis process of RE-doped NaYF_4 and their biological applications after surface modification.

Hao-Xin Mai, Ya-Wen Zhang et al. done a notable work on high qualitative Sodium RE Fluoride nanoparticles by using several products of NaYF_4 where RE can be Nd, Eu or Y under different synthesis conditions and give experimental analysis using XRD, FTIR, TEM techniques and presented optical properties of the sample.

Subrata Das, A. Amarnath Reddy, Shahzad Ahmad et al. done synthesis and optical characterization using $\text{KLaF}_4: \text{Eu}^{3+}$ nanoparticles. Here, it is proposed that the considering sample is strong red-emitter which is synthesized by using wet-chemical reaction route. In the result it is found that these are mono-phase nano-phosphors which exhibit very strong red colour and the emitting life span of energy is also longer when incident energy ray wavelength is less than 532 nm. These phosphors are comparable to other available high-rated phosphors like $\text{CaF}_2: \text{Eu}^{3+}$ and can be used for white light LEDs and other such displaying devices.

Shahzad Ahmad, G. Vijaya Prakash and R. Nagrajan have proposed work on hexagonal KLaF_4 in which they use phase-controlled synthesis procedure and studied the luminescence results of KLaF_4 nanoparticles. In the experimental work they noted that formation of KLaF_4 is affected by both the temperature of the reaction as well as ligands used with Lanthanum precursor. $\text{La}(\text{O}^i\text{Pr})_3$ and $\text{La}(\text{acac})_3$ gives hexagonal

nano particle when it is heated for a day under 65 degree centigrade temperature. Here, it is found that cubic to hexagonal transformation in structure of KLaF_4 can be happened due to interface nucleation mechanism. This method does not need calcinations. Emitted photon's energy is also calculated and which is lesser than NaYF_4 . A new optically transparent thick film of PMMA which has $\text{KLaF}_4:\text{Er}^{3+}$ was formed at lab for opening a new window of research of the hexagonal KLaF_4 for various applications which replaces NaYF_4 with better results.

Shhzad Ahmad, Subrata Das et al. have a presented a paper on optical properties of KLaF_4 with Tb^{3+} in both the cubic and hexagonal nanoparticles which is synthesized by solution method which emitted energy in green light region which varies as per the concentration of Tb^{3+} ion. Their magnetic and optical properties get analysed. These phosphors are used in displaying applications.

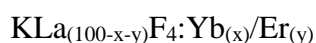
Cedric Bouzigues, ThiemyGaccoin, and AntigoniAlexandrou presented a notable work on biological applications of nanoparticles which are rare-earth based particles. In this paper various vitro and vivo applications of nano phosphors is highlighted. Their uses in bio imaging of tissues in cell biology which help in detecting early stage diseases so that they can get cured in time.

Chapter 3

Experimental Work

3.1 Synthesis Procedure Wet Chemical Route

For the experiments, $\text{La}(\text{acac})_3 \cdot x\text{H}_2\text{O}$ [Tokyo Chemical Industries] and KF [Fisher Scientific] were used. For doping, YbCl_3 and ErCl_3 [Sigma Aldrich, 99.99%] were used. The reactants were dissolved in methanol [Sisco Research Laboratories]. The lanthanum solution subsequently followed by the RE ion solution was added dropwise to the KF solution at 65°C under magnetic stirring for three and a half hours. The resulting solution was centrifuged at 13000rpm and washed with methanol thrice to obtain the yield. After 24hours in vacuum oven it heated at 40 degree Celsius then we will get all samples in powdered form.



$y=3\%$ of MW of ErCl_3

$x=15\%$ of MW of YbCl_3

$\text{La}=82\%$ of MW of $\text{La}(\text{acac})_3$

each quantity normalized for 10 ml methanol solution.

KF: Potassium Fluoride

$\text{La}(\text{acac})_3$: Lanthanum acetylacetonate

$\text{YbCl}_3 \cdot x\text{H}_2\text{O}$: Ytterbium Chloride hexahydrate

$\text{ErCl}_3 \cdot x\text{H}_2\text{O}$: Erbium Chloride Hexa Hydrate

All the analyzing tools that help in analyzing the sample with respect to its phase, its surfacemorphology, its internal structure, and tell about the functional group inside it, are called characterization techniques. These techniques tell us about all the properties of the sample, its features and its tolerance to the outer environment.

3.2 X-Ray Diffraction (XRD)

X-Ray Diffraction popularly known as XRD is an analytical technique which uses the dual nature of X-Rays as wave and particle for gaining details about the internal structure of crystalline materials. This is done on the basis of diffraction patterns of different materials.

The fundamental principal is based on constructive interference of matter and x-Rays. According to Bragg's law that is $n\lambda = 2d\sin\theta$. When in cathode ray tube monochromatic x-rays are generated at high voltage, these rays are targeted on material. After indicating these rays have both types of constructive and destructive interference. Then these diffracted rays are processed collected and counted.

In XRD after doing structural analysis we could get following details:

1) Lattice Parameters:By indexing constant parameter “a” and “w” which leads to know further indices like miller indices like h, l, k are identified. Which further help in getting lattice constant by using Bragg’s law.

2) Phase Identity:With the help of phase calculation presence and absence of a particular element can determined. If all the peaks are high it means matter is pure. And it also tells single as well as compound structure of material.

By applying different angles and different values all possible information of material can get. By using XRD technique unknown materials are identified. This technique is useful in determination of unit cell dimensions. And can measure purity and fines of any crystalline material.

To know about the crystal quality, and the composition of synthesized materials, XRD is done. All the information regarding the miller planes, and the crystalline size is obtained by X-Ray diffraction. X-Rays can also distinguish the amorphous from the crystalline material. A variety of information is obtained from the diffraction performed. Information regarding the lattice parameters, crystal plane and the cell structure is obtained. For a specific material, the formation mechanism used and information regarding all the crystal phases that exist in prepared material is stated. It also states the ratio of amorphous to crystalline in synthesized material. Average size of crystal, can be obtained from the peak width, and the size of particle is inversely proportional to peak width. Lastly it tells about the structural distortion that can be calculated from the inter-planer distance.



Fig 3.1: XRD Apparatus at DTU campus

This technique is very much efficient and quick for determination. These are easily available tools and the results are easy to comprehend.

But it has some limitations too like for using this technique homogeneous mixture is ideal and it needs a reference data for understanding results. And if it goes on high angles then can exhibit reflections instead of refraction.

3.3 Transmission Electron Microscopy (TEM)

For getting features of crystal structure and to study about semiconductors fabrication, TEM tool is very powerful tool. Transmission Electron Microscopy works on the principal of microscopy but it utilizes energetic electrons for giving information of sample like monographic, compositional and crystallographic properties of sample.

TEM was first introduced by Ernst Ruska. It consists of nine components like an electron source, Thermionic Gun, Electron Beam, Electromagnetic Lenses, Vacuum Chamber, 2 Condensers, Sample Stage, Phosphor or Fluorescent screen and a Computer to process the data.

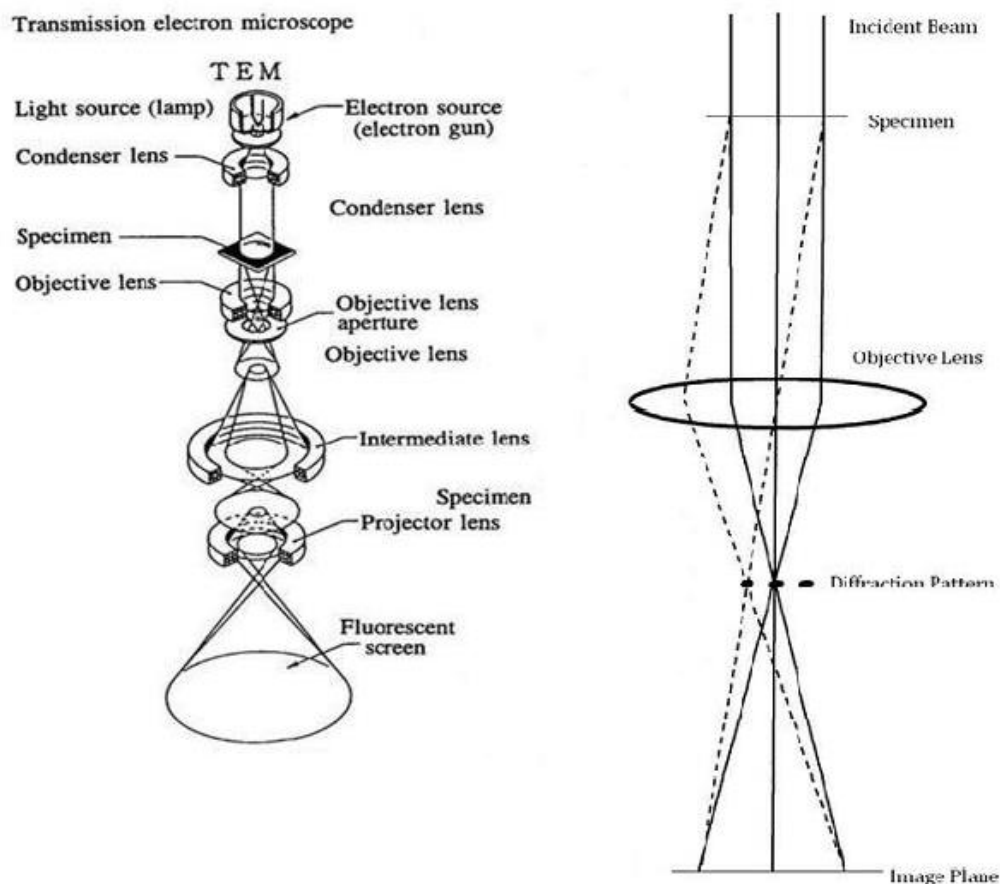


Figure 3.2: TEM Tool and Ray Diagram of Diffraction Mechanism.

The process in TEM imaging involves firstly in vacuum chamber where interaction happen between high energy electrons and sample. The electron beam is passed through various electromagnetic lenses and then the electron beam passed through

solenoids where after contacting the screen it gets changed to light wave and gave an image.

The resolution of the image can be manipulated by adjusting the voltage of gun to limit the speed of the electron beam. Then the solenoid coils project this image on photographic plate.

The present TEM Studies were carried out at the Indian Institute of Technology, Delhi

3.4 Fourier Transform Infrared Spectroscopy (FTIR)

It is analytical technique, which is used to identify the organic groups that are present in the sample. When IR light falls on the material, it absorbs certain wavelengths and rejects other. FTIR measures this absorption by the material of interest. Previously IR instruments use prism or monochromator. This was dispersive type spectrometer (Ferraro & Basile, 1975). Firstly interferogram of sample signal is collected with interferometer, which measures a complete range of infrared frequencies. Spectrum is obtained at the output, with several intermediate steps. The spectrometer digitizes and reads the interferogram, then FT function is performed and then the spectrum is obtained (Smith, 2009). It is a technique that plots infrared intensity with wavelength (wave number).

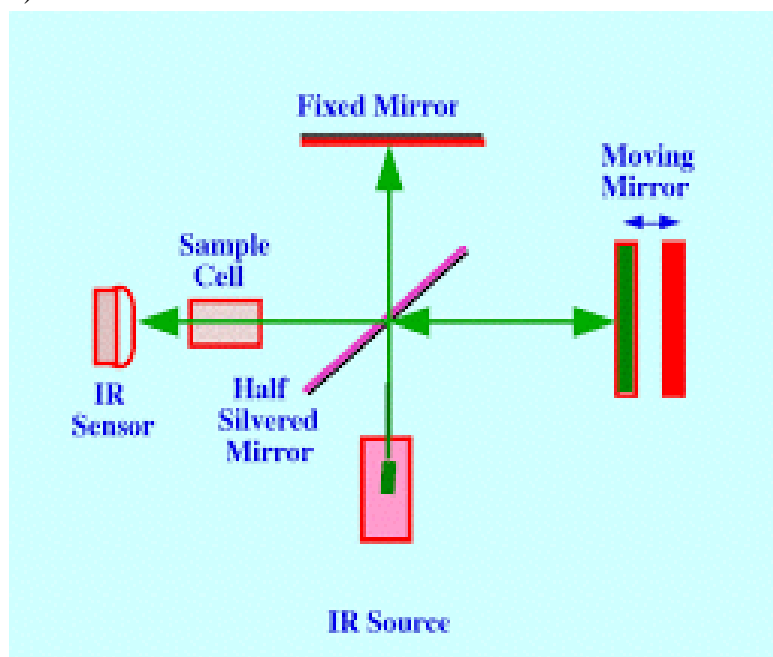


Figure 3.3 FTIR Spectrometer components

With reference to wave number, IR can be categorized into far infrared, mid infrared and nearinfrared with wavenumber in range $4-400\text{cm}^{-1}$, $400-4000\text{cm}^{-1}$, and $4000-14000\text{cm}^{-1}$ respectively. This spectroscopy analyses vibration characteristics chemical functional groups in the material (Siesler, Ozaki, Kawata, & Heise, 2008). As the IR

interacts with matter, there is a stretch, or a bend in the chemical bonds, that are present in the sample. With this, the chemical functional group, irrespective of the structure of the molecule, tends to absorb a specific wave number IR rays.

3.5 Upconversion Studies

Upconversion studies were carried out using Maya 2000 Pro-NIR spectrometer using a variable power 980nm laser source at the Indian Institute of Technology Delhi.

Chapter 4

Results and Discussion

4.1 XRD Analysis

The X-ray diffraction pattern of the as prepared $\text{KLaF}_4:\text{Yb}^{3+}\text{Er}^{3+}$ is presented in Fig. 2 and the obtained pattern is identified as cubic phase of KLaF_4 having spacegroup $Fm\bar{3}m$. It is known that KLaF_4 is mainly found in two phases, namely, α -phase (cubic) and β -phase (hexagonal), depending on the synthesis methods. The α -phase is Meta stable at high temperature while the β -phase form is thermodynamically stable. The cubic KLaF_4 is isomorphic with that of CaF_2 , in which the K^+ and La^{3+} ions are randomly coordinated and each cation is coordinated by F^- ion again. The obtained peaks were only corresponding to the α -phase of KLaF_4 .

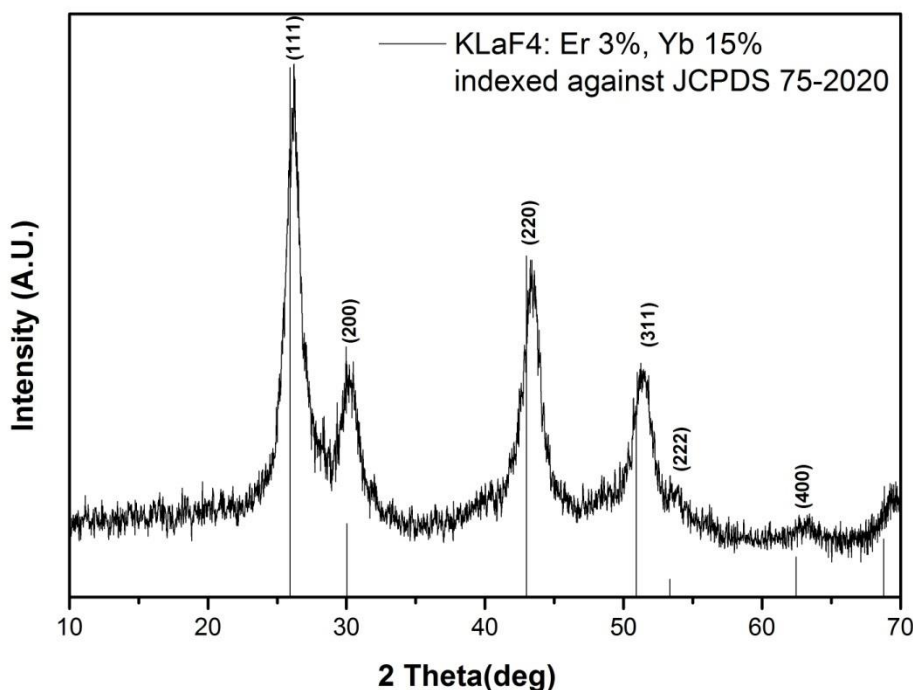


Figure 4.1: XRD of UCNPS $\text{KLaF}_4 : \text{Er}^{3+}\text{Yb}$

The crystalline nature of material was demonstrated by X-Ray diffraction. XRD perform in range of 10° to 70° . This diffraction pattern matched with that of standard JCPDS 75-2020 of KLaF_4 having a cubic phase.

First peak is observed at 26.22° corresponding to plane of (111). By using Scherrer equation, particle size was calculated to be around 6.11 nm. The interplane distance was found to be 3.395\AA . For the cubic structure Lattice parameters are equal i.e.

$a=b=c$. So lattice parameters obtained via above values of Miller Indices and interplanar distance are $a=b=c=5.88\text{\AA}$.

4.2 TEM Analysis

As it can be seen from Fig. 4.2, the transmission electron microscopy (TEM) revealed the presence of agglomeration in the sample. The average size of the spherical particles was obtained to be nearly 6nm which is close to the results obtained from XRD.

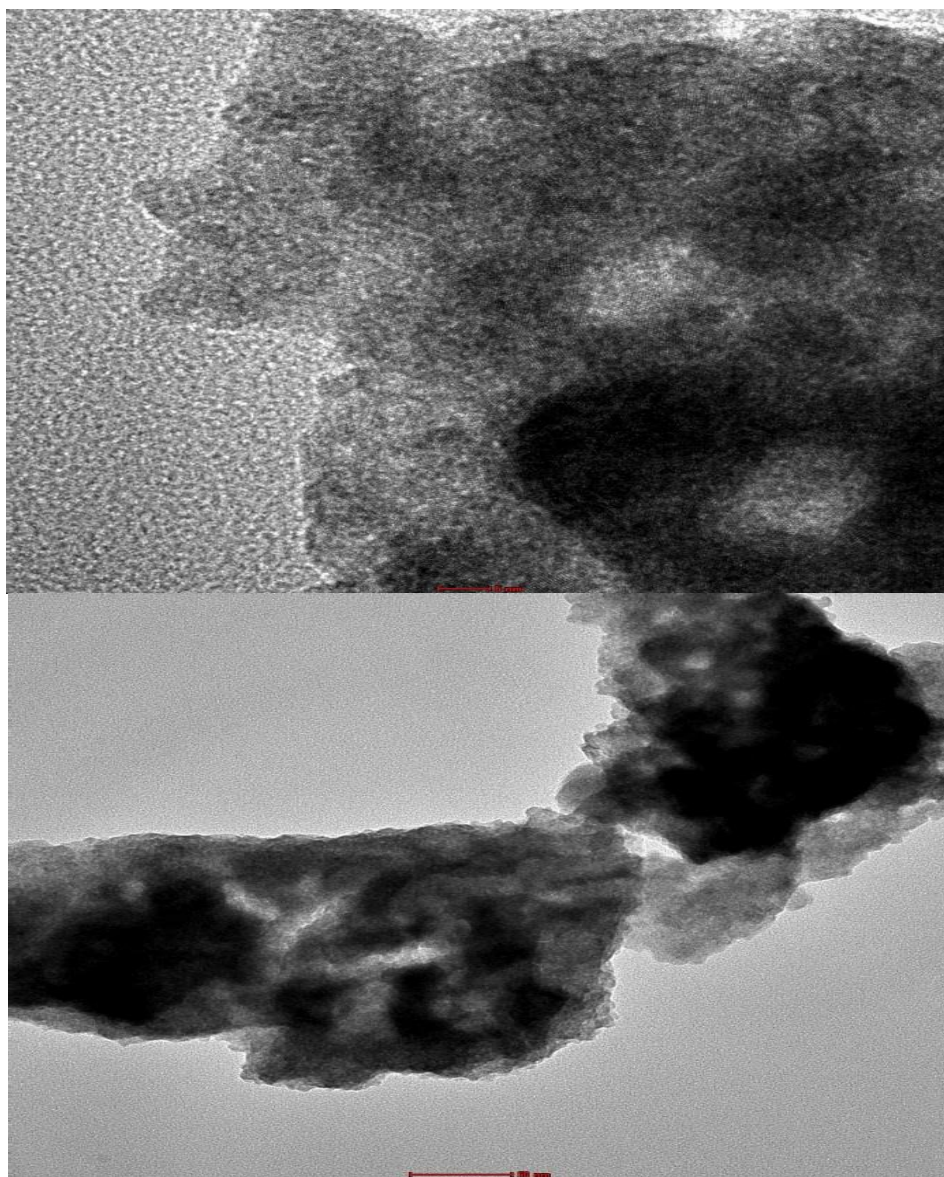


Figure 4.2 TEM images of synthesized particles.

4.3 FTIR Analysis

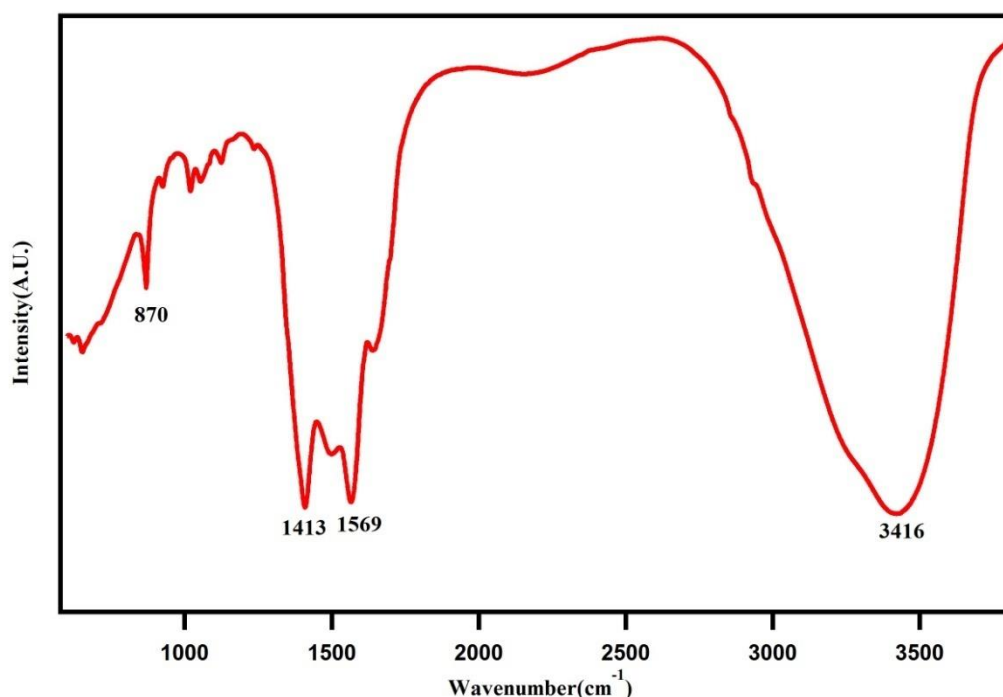


Figure 4.3: FTIR Analysis

In the FTIR spectra of Er^{3+} doped hexagonal KLaF_4 , presence of bands at 3416 cm^{-1} and 1569 cm^{-1} gives the information of absorbed no of OH^- ions in the sample. So by doing FTIR analysis it is easy to detect OH^- ions for favourable multi-phonon relaxation of $^2\text{H}_{11/2}$ state which in turn enhanced the intensity of the red luminescence. The difference in energy in $^4\text{F}_{9/2}$ and next level of $^4\text{F}_{9/2}$ is same as of the $^2\text{H}_{11/2}$ and $^4\text{F}_{9/2}$ levels and that is 3416 cm^{-1} . So the possibility for the multi-phonon relaxation of $^4\text{F}_{9/2}$ level can be compared to $^2\text{H}_{11/2}$ level. The medium peaks at 1413 cm^{-1} and 870 cm^{-1} can be attributed to C-H bending vibrations [19].

4.4 Photoluminescence Analysis

The upconversion luminescence (UCL) of $\text{KLaF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ was obtained at room temperature under excitation with a CW (continuous waveform) diode laser at 980 nm in the range of 500-700 nm. As shown in Fig.1, upon CW excitation at 980 nm, UCNP's show characteristic UCL emission from Er^{3+} with green emission bands at 525 and 544 nm and a red emission band at 655 nm. These peaks are assigned to the $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transitions of Er^{3+} , respectively.

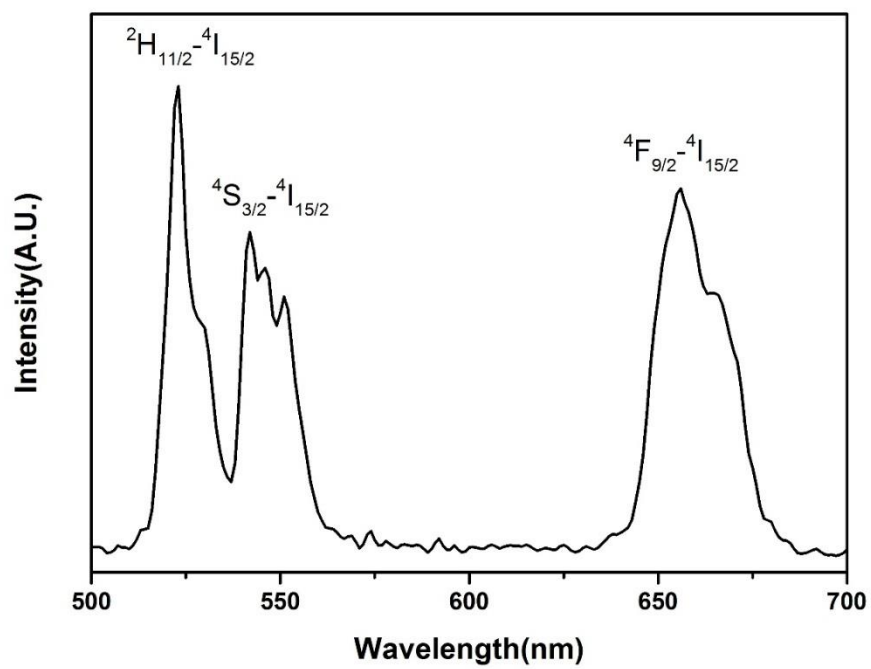


Fig.4: Upconversion luminescence spectra

Chapter 5

Conclusion

The present work was carried out to investigate the synthesis and characterisation of highly luminescent upconversion nanoparticles. We have successfully synthesized upconversion nanoparticles of $\text{KLaF}_4\text{Yb}(15\%)\text{Er}(3\%)$ using weight chemical route. Because this method is simple and low cost comparative to other routes. The crystallographic and morphological studies shows the successful synthesis of desired $\text{KLaF}_4\text{Yb}^{+3}\text{Er}^{+3}$ upconversion nanoparticles.

The result obtained from XRD shows that I got cubic phase (α -phase) $\text{KLaF}_4\text{Yb}^{+3}\text{Er}^{+3}$ upconversion nanoparticles and the calculated particle size is in nanometers range. There by the confirming of formation of nanostructure of $\text{KLaF}_4\text{Yb}^{+3}\text{Er}^{+3}$. The particle size is verified by TEM analysis. FTIR analysis show the presence of OH ions in the sample which favour the enhancement of intensity of red luminescence. The upconversion spectra confirms the green and red emission band.

The combined study concludes the work done can be used in several area such as bio imaging, photodynamic therapy, nano sensors, solar cells, drug deliveries to the list few.

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