MORPHOLOGICAL STUDIES ON RARE EARTH ION DOPED KCeF$_4$ UPCONVERSION NANOPARTICLES

A DISSERTATION

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IN

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Submitted By

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I, **Astha Srivastava**, Roll No. **2K16/NST/03** of **M.Tech. Nanoscience and Technology**, hereby declare that the project Dissertation titled “**Morphological studies on Rare earth ion doped $KCeF_4$ Upconversion nanoparticles”** which is submitted by me to the Department of Applied Physics, Delhi Technological University, Delhi in partial fulfillment of the requirement for the award of the degree of Master of technology, is original and not copied from any source without proper citation. This work has not previously formed the basis for the award of any Degree, Diploma Associateship, Fellowship or other similar title or recognition.

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I hereby certify that the Project Dissertation titled "**Morphological studies on Rare earth ion doped $KCeF_4$ Upconversion nanoparticles**" by **Astha Srivastava**, Roll No. **2K16/NST/03**, Department of Applied Physics, Delhi in partial fulfillment of the requirement for the award of the degree of **Master of Technology**, is a record of the project work carried out by the student under my supervision. To the best of my knowledge this work has not been submitted or full for any Degree or Diploma to this University or elsewhere.

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ABSTRACT

Upconversion nanoparticles (UCNPs) are the fluorophores of new era. They comprise the unique property of converting near IR radiation (low energy) into visible radiation(high energy) through nonlinear optical process. Currently the Upconversion nanoparticles have gain importance as alternatives to traditional fluorophores, as they provide for a large scope in the field of imaging and bio detection assays in both – applications of in-vivo and in-vitro techniques.

Upconversion nanoparticles demonstrate extraordinary luminescent properties, including sharp emission band, low background signals, larger penetration depth in tissues, large stoke shifts and high protection from photo bleaching, hence making Upconversion nanoparticles elective hotspot for coming over current related constraints in conventional fluorescent probes. By and large for synthesizing Upconversion nanoparticles Rare Earth doped materials are utilized, due to their excellent properties like high chemical stability and low phonon energy.

Upconversion nanoparticles provide a great opportunity for enhancing solar cell efficiency. Photovoltaic cells convert sunlight into electricity, using photovoltaic effect. They help us in generating one of the cleanest and abundant energy to fulfill the energy requirements. But, the photovoltaics current's efficiency is hindered by the loss of photons of sub band gap during transmission. Photon upconversion provides us with the way to overcome the issue as the loss can be minimised by converting the transmitted photons of sub band gap into above band gap. Hence, by this technique the efficiency of solar cells could be increased.

In the project wet chemical route is used to synthesize undoped $KCeF_4$ and Rare earth doped $KCeF_4$ samples. The β-phase (hexagonal phase) of UCNPs is obtained.

The morphology, composition and structural properties of synthesized samples were observed and studied using X-Ray Diffraction, Fourier Transform infrared spectroscopy and Transmission electron microscopy. The obtained results confirm the formation of Upconversion nanoparticles.

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INTRODUCTION

Upconversion nanoparticles (1-100 nm) are those particles which exhibit the property of photon upconversion. In photon upconversion, at least two photons of moderately low energy levels are absorbed and converted into one or more transmitted photon with higher energy. For the most part, absorption happens in the infrared, while emission happens in the visible or UV regions of the electromagnetic range. Upconversion nanoparticles usually consist of lanthanide-or actinide-doped transition metals and are exceptionally compelling for their applications in bio-imaging and bio-detecting at the profound tissue level. They additionally have potential applications in photovoltaics and security, for example, infrared identification of perilous and hazardous materials.

Optical imaging is effortless approach to research tissue. For enhancing this optical labelling and imaging both the signal and additionally spatial determination, different optical tests have specifically been created in the past, to mark and investigate the correct area of recommended tissues. Particularly, the great classes of fluorescent probes, for example, fluorescent proteins, fluorescent dyes and QDs, have drawn an incredible consideration from both the researchers of science and science regions.

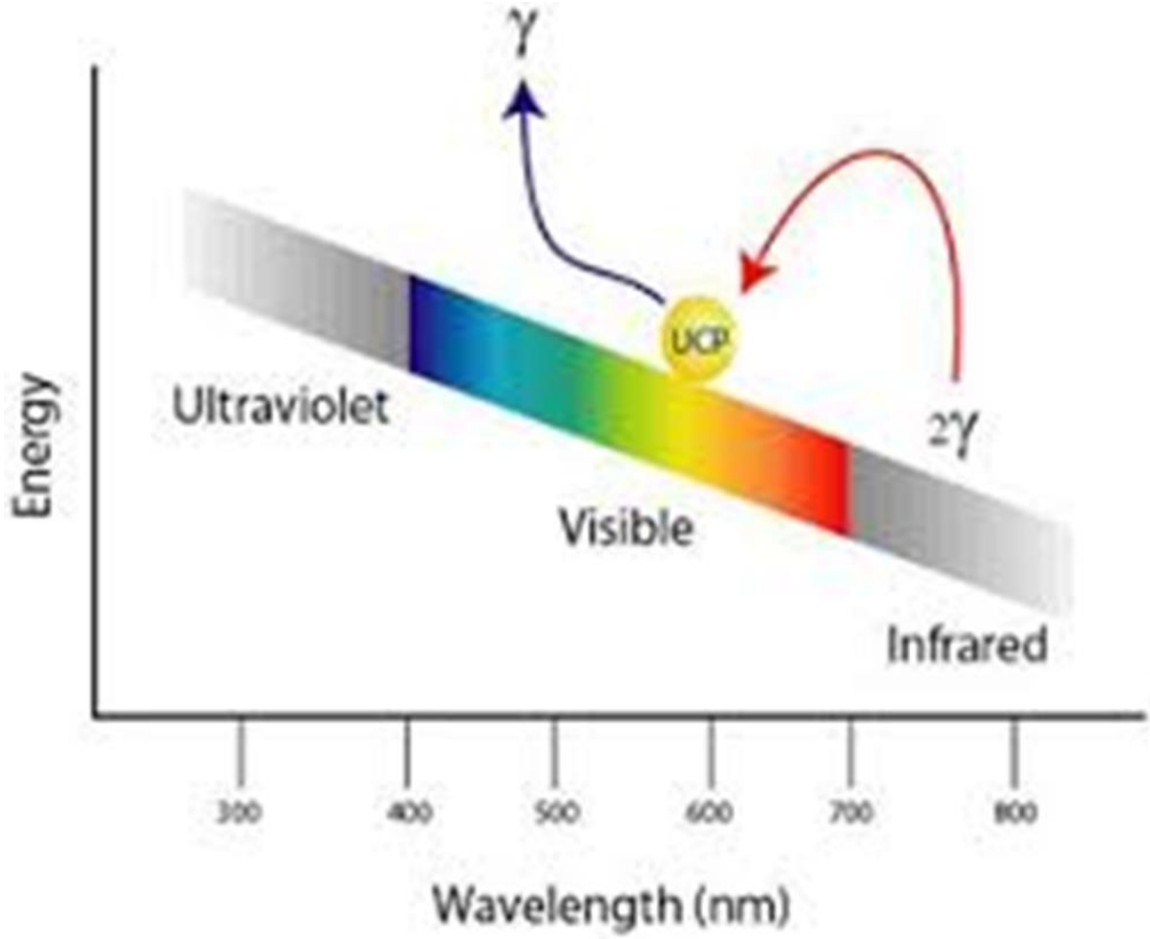


Figure 1.1. Energy Conversion using UCNPs

Because of these fluorescent tests, a few insider facts of living organisms from the single atomic degree and increasing till the invivo level of the tissue can be imagined and seen. Be that as it may, these settled fluorescent probes are encountering sure ineptitude while handling the riddles with consistently hoisting challenges and issues in life-science. For example, a solitary sub-atomic investigation is seriously constrained by the issues of deficient force and quick photo-bleaching of fluorescent probes, while in-vivo fluorescent optical imaging experiences a solid foundation of auto fluorescence and light disseminating and additionally a restricted imaging profundity. The requests for new fluorescent probes with greater brilliance, photo stability, and otherworldly noticeability for bio imaging is never-ending.

Upconversion NPs doped with Lanthanide series dopant are rising as another class of fluorescent probes, which hold extraordinary characteristics to defeat the natural deficiencies related with proteins, fluorescent dyes, and QDs. The outflow marvel from Upconversion NPs is, in its appearance, somewhat like multiphoton-energized fluorescence from regular biolabels, (for example, colors and QDs), since these two are created by changing over long wavelength excitation photons into short wavelength outflow photons. It is noticed that simultaneous excitation of multiple photons has been generally connected in fluorescent optical microscopy to demonstrate expanded determination, diminished example autofluorescence, and also expanded imaging profundity. Be that as it may, the lesser near IR absorption cross section of multiphoton marks mandates this procedure to subject to the utilization of high-peak power lase with very short pulses. Also, the photo bleaching as well as photo blinking issues are there for dyes or Q Dots in multiphoton microscopy, and the high peak power of the pulsed femto or pico laser utilized can deliver cause high photo damage in biological samples. It is different from synchronous multiphoton process in dyes and Q Dots, which includes the utilization of a indirect energy level, photon upconversion in Upconversion Nanoparticles depends on the successive absorbtion of photons of lower energy using stepping stool levels of energy of Lanthanide-doped particles. This quantum-mechanical distinction makes Upconversion Nanoparticles excitation magnitude much proficient than the multiphoton process, along these lines permitting excitation with a minimal cost laser diode with continuous wave at lower-energy luminescence; ordinarily lower limit is $\sim 10^{-1}$ W.cm^{-2}. Upconversion Nanoparticles likewise have other predominant points of interest for probe utilizes as a part of imaging. Firstly, the f– f intra electronic advances of Lanthanide-dopants create an arrangement of nuclear like peaks of line emission from Upconversion Nanoparticles. These emissions can decrease the possible outcomes of overlapping of spectra, and encourage the recieving of original signal during screening process of signal. Secondly, the transitions of f– f intra elecrons are shielded by the external complete shells of 5s and 5p electron, in this way providing resistance to oxidation-instigated photo-bleaching which is frequently observed for electronic transitions of natural dyes. Thirdly, the intra f– f electron transitions' parity-forbidden nature produces a long UC radiance decay (around 10 ms), giving much better scope to bio sensing, multiplexing and time-resolved imaging. Fourth, because of an collective emission of adequate number of dopants inside a single Upconversion Nanoparticle, radiance from a solitary Upconversion Nanoparticle does not demonstrate the squinting conduct, which is imperative for single-atom-imaging tests including a long-lasting perception. These interesting and unique properties of Upconversion Nanoparticles will offer practical methods to address the difficulties faced in single atom/ molecule-level, and additionally in deep tissue optical imaging level. It likewise rouses control of different photo-chemical responses in-vivo utilizing biocompatible and captivates near IR light along with the recurrence changing over capacity of Upconversion Nanoparticles.

1.1. Phosphors

Phosphors are when energized by an external appropriate source of energy, they radiate luminescence. Hence, they consist of the luminescence property. The energy source may vary from UV light to beam of electrons through electron gun. Phosphors absorb low wavelength energy photons, then they undergo excitation, high wavelength energy/ light, which could be termed as luminescence.

In Inorganic Phosphors activator ions are doped in smaller quantities within host material. Host material may comprise of any oxide, halide, silicate, nitride or oxyhalide [1]. Activator ions may be Rare earth or transition metal ions. Activator ions act as centres of energy [2]. They have energy levels which could be formed directly through excitation, and indirectly through energy transfer[3].

Phosphor material should absorb incident energy and then emit it as soon as possible for Quantum Yield to be high enough. This is one of the basic points to take care about. Other important terms related to Phosphor are the Emission Spectrum, the Colour point, the Emission lifetime, the Lumen Equivalent, etc

In light of the luminescence property conventional phosphors are utilized as a part of different screens. Yet, the latest variant that is Upconversion Nanoparticles (UCNPs) have pulled in analyst's fascination due to their wide use in bio imaging and in Photo Dynamic Therapy. Conventional Phosphors deal with Stoke Emission mainly amd also, they act as down conversion particles as they absorb high energy photons and emanate low energy photon. This is the reason for which regular phosphors in bio imaging and labelling. are not utilized and further developed Upconversion nanoparticles are utilized.

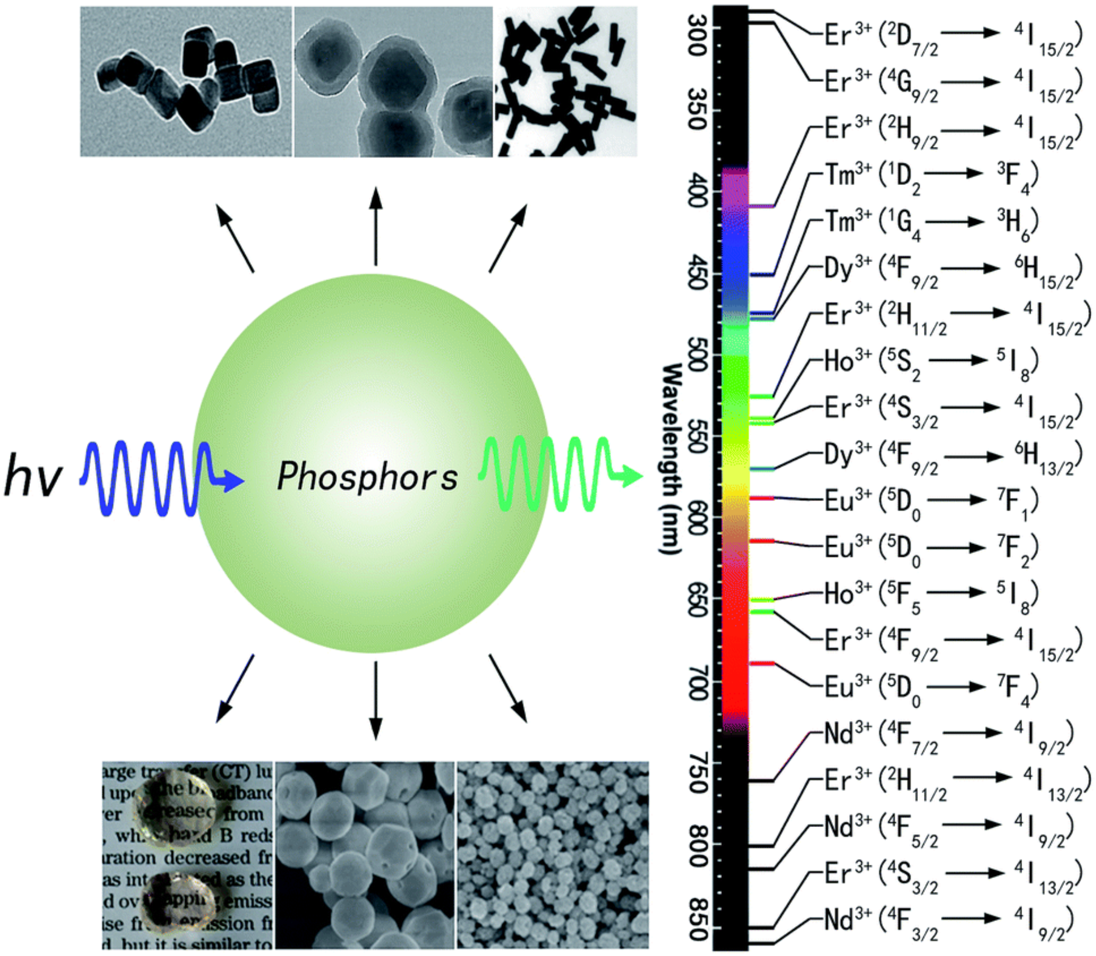


Figure 1.2. Radiatons of various wavelengths generated using Phosphors

In the region of semiconductor based technology with the development in technology and advanced researches and works very valuable and useful outcomes have been obtained from Quantum Dots (QD) and Upconversion Nanoparticles. They are generally helpful in light of their wide applications in imaging and bio marking.

1.2. Quantum Dots

Quantum Dots are of nano range and they consist of nano dimensions in all the three directions. They are from 2 to 10 nm in diameter. The emission of light through them is directly proportional to their size. The smaller the size of the particle, the emitted energy will be in blue light wavelength region and the bigger the size of particle, the emission of light will be in Red wavelength region. Quantum Dots are also known as the central particles of nanotechnology [4].

In the Quantum Dots the movement of holes occur in valance band, the electrons movement takes place in conduction band, the excitation of electrons and

holes take place in both, the conduction as well as valance bands and the binding of both the particles occur in all the three spatial directions and in both the bands.

There is a wide range of applications of Quantum Dots such as in gene therapy, tissue imaging by size in nano range, fine fluorescence and broad UV excitation. It could also be used for Fluorescence Resonance energy transfer (FRET) analysis and cell imaging and labelling.

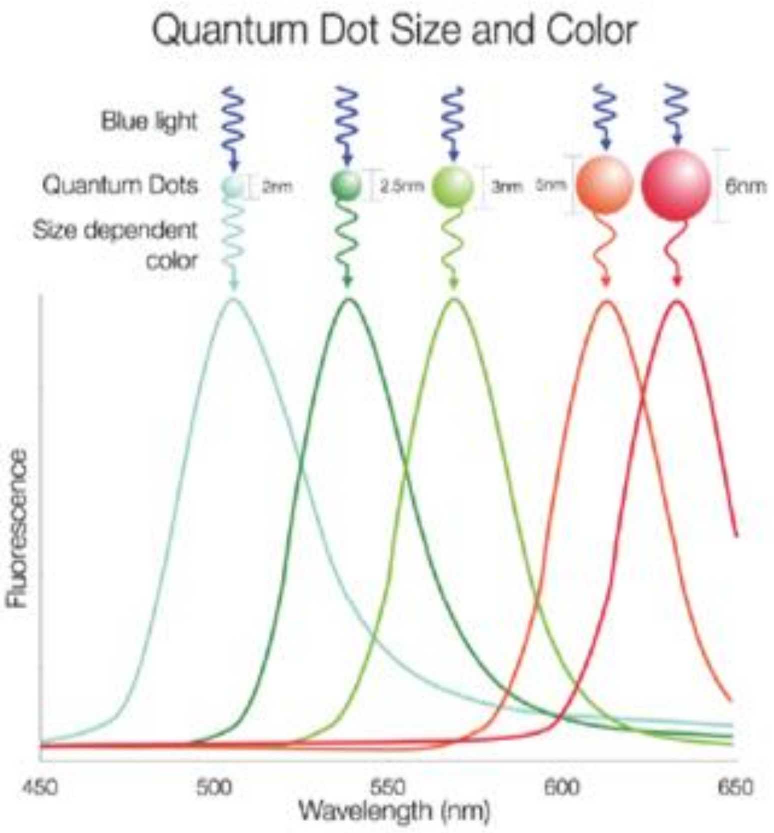


Figure 1.3. Wavelength of light depends on size of QD

There are very serious drawbacks of Quantum Dots like chemical instability and cyto-toxicity. These drawbacks and shortcomings put limitations on the use of Quantum Dots in bio imaging and related area.

So it became important to develop a new and more efficient particle to overcome the drawbacks of these Quantum Dots and improvement in the researches and results. So Upconversion nanoparticles (UCNPs) came into picture.

1.3. Upconversion Nanoparticles

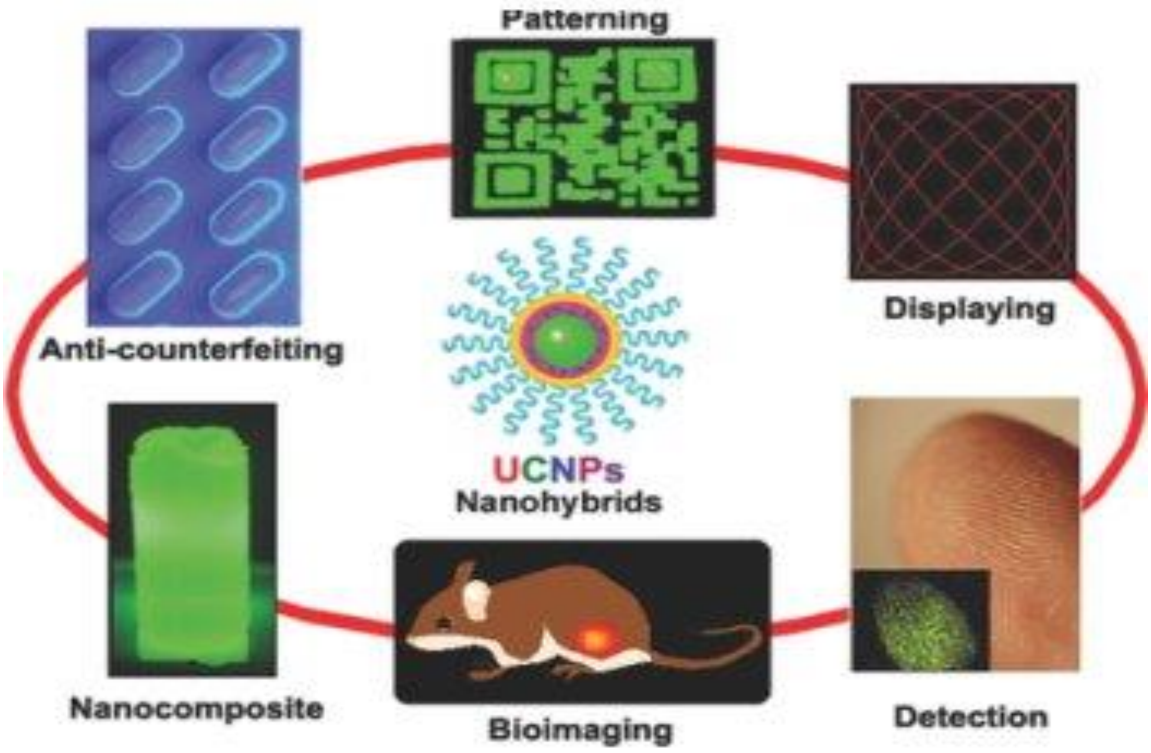


Figure 1.4. Applications of UCNPs

In the mid 1960s while using laser technology, Francois Auzel observed the Anti Stoke shift and it was given the name “Upconversion” [5].

Upconversion of photons is the phenomenon in which two or morephotons of low energy are incidental at the host lattice and after absorbing these incident photons particles jump to their excitation state and hence a high energy photon is emitted. The incident energy is generally lies in Infrared region while emitted energy lies in visible or ultraviolet region.

Upconversion Nanoparticles are also depicted as UCNPs. UCNPs are those which show the property of Upconversion and are highly fine particles in the range of nano scales, mainly from 1 to 100 nm. UCNPs are basically the advanced version of conventional Phosphors. UCNPs have become a prime area of research in the domain of Photo Dynamic Therapy because of high and superfine use of UCNPs.

In upconvesion materials, for upconversion process to take place the mandatory condition is to have optically active excited state for longer time period [6]. For this to happen lanthanide ions are generally embedded into an insulated host lattice. This type of upconversion process is predominantly seen in d-block elements and in that too mainly for Rare Earth (RE) elements. Rare Earth (RE) elements generally have +3 oxidation state. For instance Lanthanide Series Ln^{3+} ions due to their $4f^n5d^{0-1}$ configuration exhibit f-f and f-d transitions [7].

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

These 3 components are required in a material for the of occurrence of upconversion phenomenon.

The Sensitizer is utilized for focusing the light on it and subsequently on gaining energy it goes to its excitation state and exchange the excitation energy with the activator particle. This activator particle carries on as the radiance focus. Sensitizer builds the luminescence proficiency.

Due to its simple energy level structure, the Yb^{3+} ion act as a sensitizer. And because of their ladder type of energy level structure Ho^{3+},Er^{3+} and Tm^{3+} ions act as Upconversion Activator ions [8]. The activator ions are mixed along with sensitizer ions in various different concentrations [9]. For Lanthanum doped $NaYF_4$ in Liu's group many researches and studies are being carried out which are basically related to surface modifications of these particles as well as their applications and utilization [9-12]. α phase of $NaYF_4$ could be transformed into β phase of $NaYF_4$. α phase of $NaYF_4$ is said more thermodynamically stable form as compared to β phase of $NaYF_4$ [13-14]. It is determined through experiments that the α $NaYF_4$ is more stable as compared to the β $NaYF_4$ mainly due to the fact that the transformation of α $NaYF_4$ to β $NaYF_4$ is very high due to free energy barrier, because of this it requires more transitional energy in cubic-to-hexagonal phase[15-17].

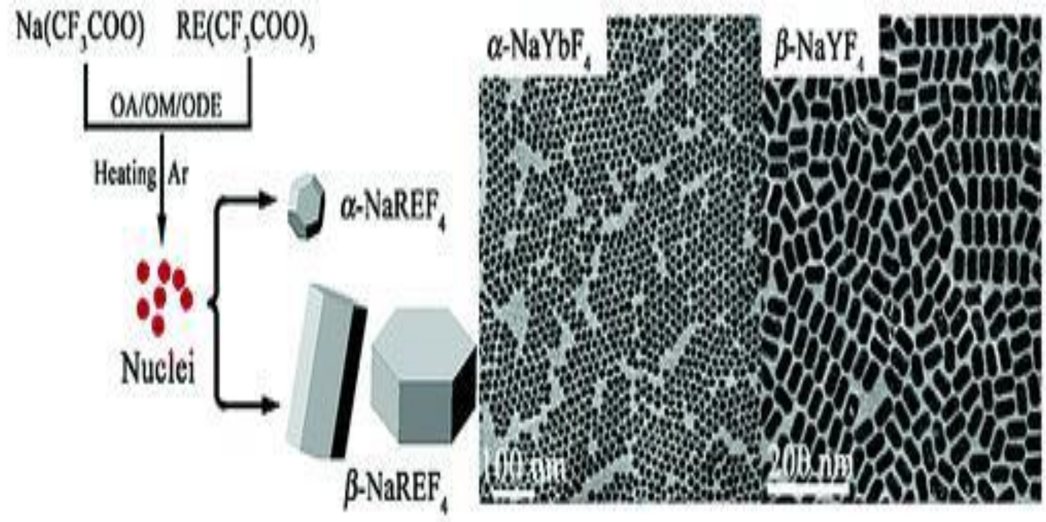


Figure1.5. Synthesis of α and β $NaREF_4$ nanocrystals[18]

The host matrix of $NaREF_4$ along with some doping is potent for the upconversion emission in RGB scale [19]. Due to its multisite characteristic and low photon energy this choice of $NaREF_4$ host matrix of upconversion particles is well suited [20]. Hence it could be determined and concluded that efficiency of Upconversion nanoparticles is influenced mainly by two parameters, firstly through the phonon dynamics and secondly due to the local crystal field [21-23].

There are three types of UCNP conversion mechanisms

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

Upconversion Nanoparticles are remarkable in light of their some exceptional optical properties like fast luminescence, the tissues could be deeply penetrated without harming cells, amazing factor for in vivo and in vitro applications and provide high protection from photo bleaching. That is the reason they have a decent extension in organic applications. They are biocompatible and can be coagulated in bio particles and can help in making different natural bio identifier tests and helpful modalities [24].

1.4. Difference between QDs and UCNPs

Quantum Dots and Upconversion Nanoparticles have a very fine difference in applications such as [25]:

Table 1.1: Comparison of Quantum Dots and Upconversion Nanoparticles [25]

Properties	**Quantum Dots**	**Upconversion NPs**
Size and Colour	The size decides the colour of the light emitted. If size is large the light emitted is in red region. If size is small, blue light is emitted.	The particle size does not matter.
Synthesis	Complicated as various steps are involved.	Easy processing and hence results in large production.
Time period	Prone to oxidation and hence more operating cost is requird.	Consist of oxides, hence no further oxidation takes place. So minimum defects during manufacturing take place.
UV Absorption	Broad region	In Narrow band
Solubility	Hydrophobic	Hydrophylic
Toxicity	Consist of elements like Pb, Cd, etc hence toxic	Not toxic

1.5. Anti Stoke Emission

Anti Stoke Emission is named after the name of famous physicist George G. Stokes [26]. In this process if an atom or a molecule absorbs a photon, it absorbs energy and jumps on the excited state. When energy of the emitted photon is more than that of energy of the incident photon, the energy difference is an Anti Stoke shift. In a crystal lattice, this energy is generated from dissipation of thermal photons, hence the crystal is cooled down during the process. This process of anti stoke emission plays a great role in upconversion nanoparticles related research. When a molecule emits a photon of a wavelength which is longer than that of absorbed photon of shorter wavelength, the process is known as Stoke fluorescence.

1.6. Upconversion Mechanism

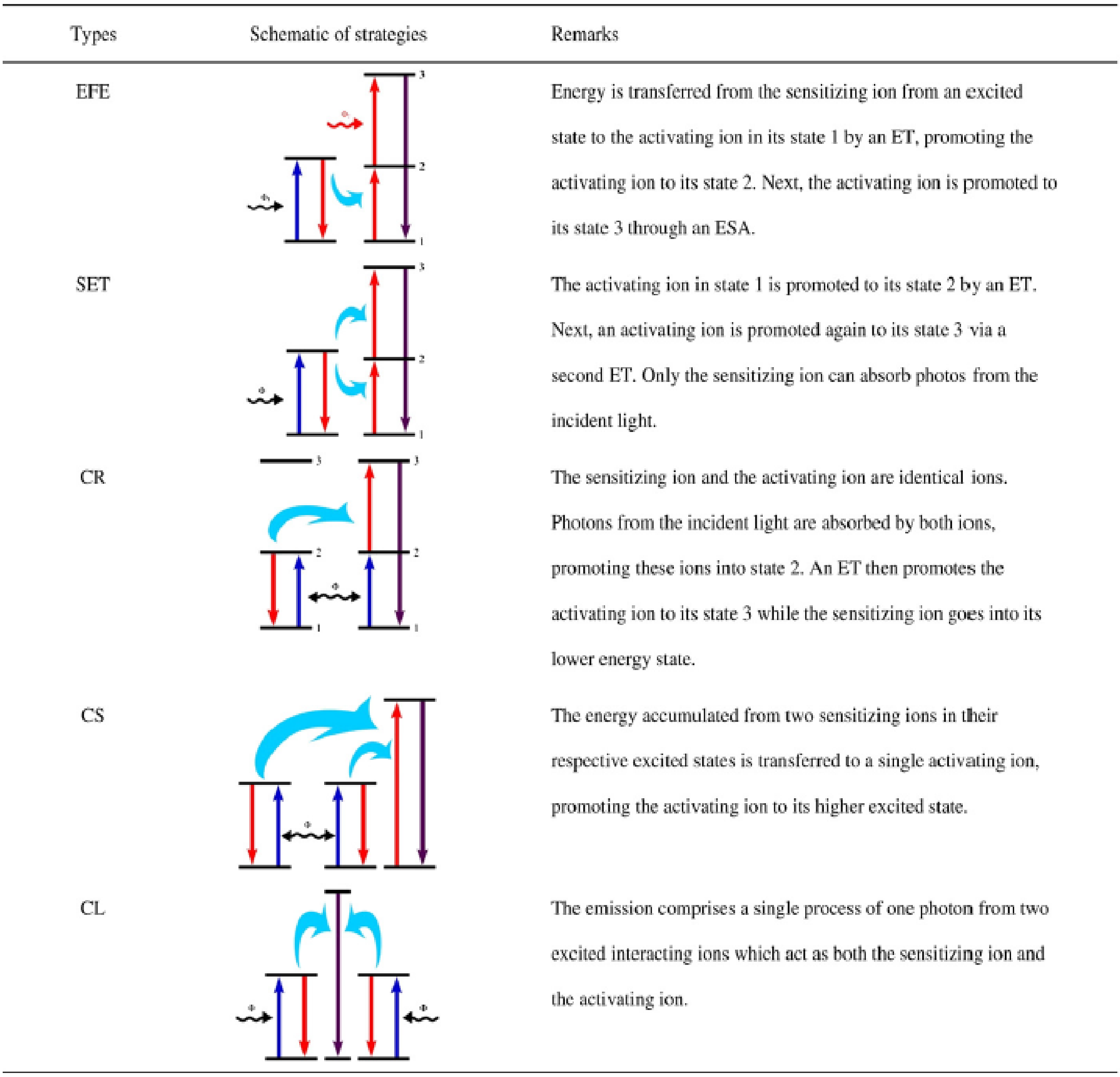
Upconversion mechanism may be classified using following mechanisms[27-29]:

1. Excited State Absorption

2. Energy Transfer Upconversion

3. Photon Avalanche

Upconversion nanoparticles may provide a great oppurtunity in the enhancement of efficiency of solar energy generation. They have the ability to convert low energy radiations into high energy radiations , through non-linear optical process. Various types of Energy Transfer mechanisms used for Upconversion are Excited State Absorbtion, Successive Energy Transfer, Cross Relaxation, Cooperative Succession, Cooperative Luminescence etc



Types	Schematic of strategies	Remarks
EFE		Energy is transferred from the sensitizing ion from an excited state to the activating ion in its state 1 by an ET, promoting the activating ion to its state 2. Next, the activating ion is promoted to its state 3 through an ESA.
SET		The activating ion in state 1 is promoted to its state 2 by an ET. Next, an activating ion is promoted again to its state 3 via a second ET. Only the sensitizing ion can absorb photos from the incident light.
CR		The sensitizing ion and the activating ion are identical ions. Photons from the incident light are absorbed by both ions, promoting these ions into state 2. An ET then promotes the activating ion to its state 3 while the sensitizing ion goes into its lower energy state.
CS		The energy accumulated from two sensitizing ions in their respective excited states is transferred to a single activating ion, promoting the activating ion to its higher excited state.
CL		The emission comprises a single process of one photon from two excited interacting ions which act as both the sensitizing ion and the activating ion.

Figure 1.6. Energy Transfer process types [28]

1.7. Mechanisms for Syntesis of RE doped Upconversion Nanoparticles

Different types of mechanisms for UCNPs are -

1.Thermal Decomposition method

2. Co precipitation Method

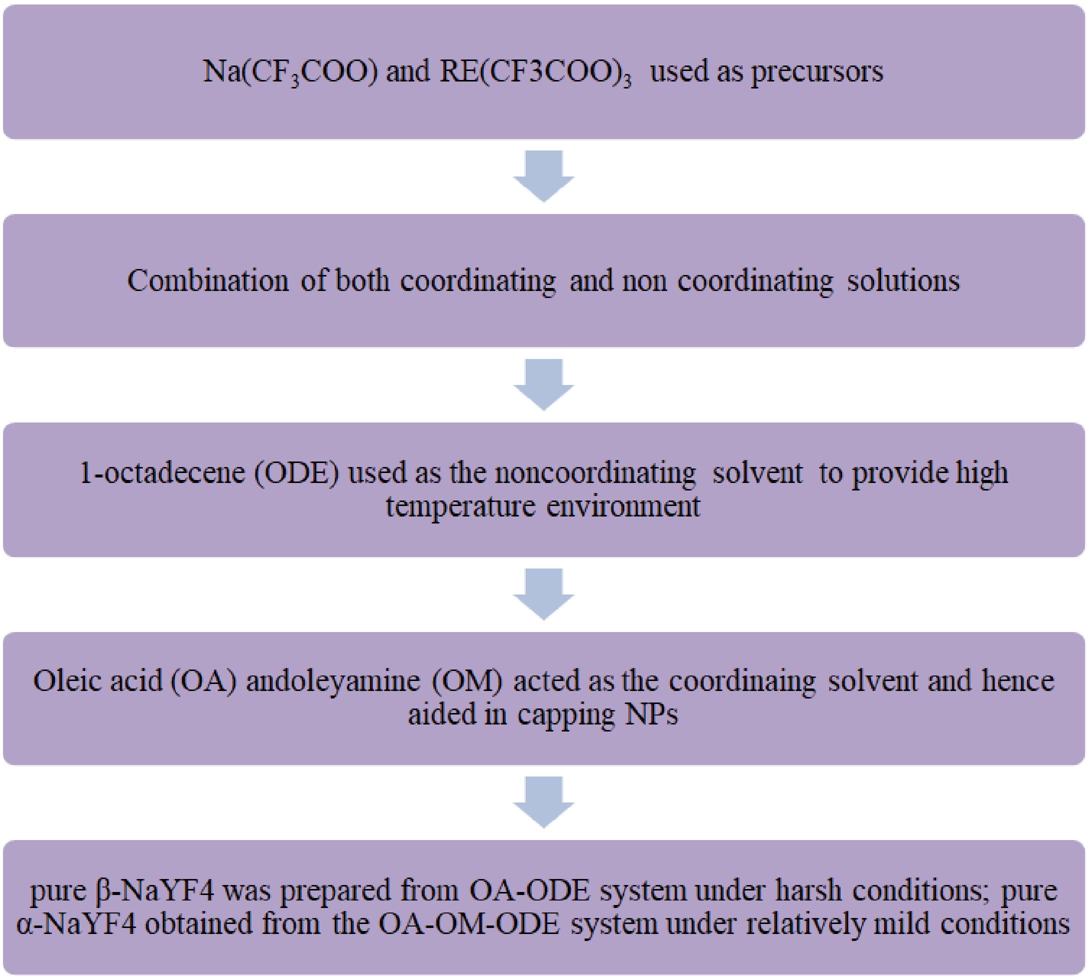
3. Hydrothermal / Solvothermal Method

4. Combustion Synthesis

1.7.1. THERMAL DECOMPOSITION METHOD

It is one of the easiest methods for synthesizing KYF_4 UCNPs due to presence of metallic tri-fluroroacetates. Metallic tri-fluroroacetates show the unique property of Thermal Decomposition.

Mai et al. [30] has given a procedure to synthesize high quality $NaReF_4$ nanoparticles. The pure β-Sodium Yttrium Fluoride was prepared from OA-ODE system under harsh conditions, and pure α-Sodium yttrium fluoride were obtained from the OA-OM-ODE system under relatvely mild conditions



$Na(CF_3COO)$ and $RE(CF3COO)_3$ used as precursors

Combination of both coordinating and non coordinating solutions

1-octadecene (ODE) used as the noncoordinating solvent to provide high temperature environment

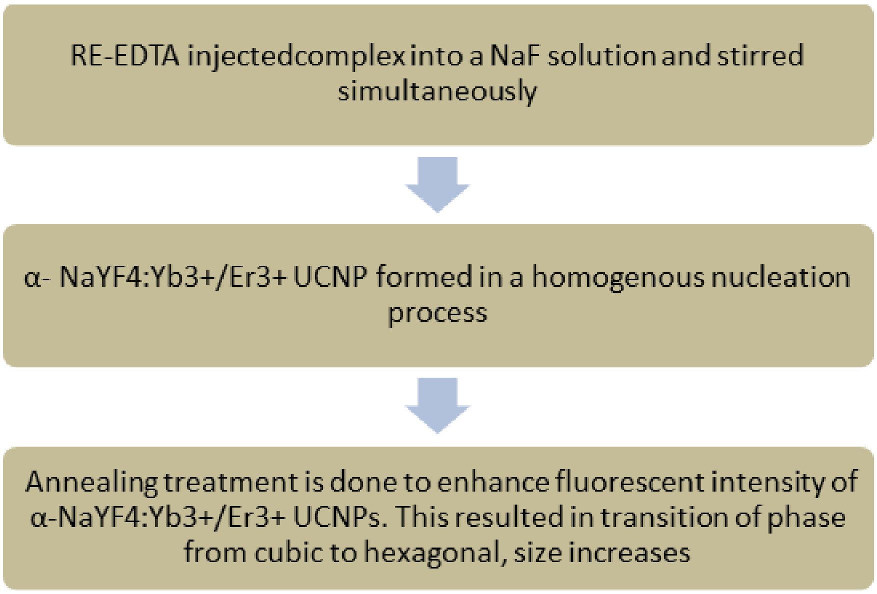
Oleic acid (OA) andoleyamine (OM) acted as the coordinaing solvent and hence aided in capping NPs

pure β-NaYF4 was prepared from OA-ODE system under harsh conditions; pure α-NaYF4 obtained from the OA-OM-ODE system under relatively mild conditions

1.7.2. COPRECIPITATION METHOD

Due to the mild reaction conditions, low costs for required equipment, simple protocols and short reaction times, the coprecipitation method is an easy and convenient approach to synthesize RE-doped Sodium Yttrium Fluoride Upconversion NPs[29]

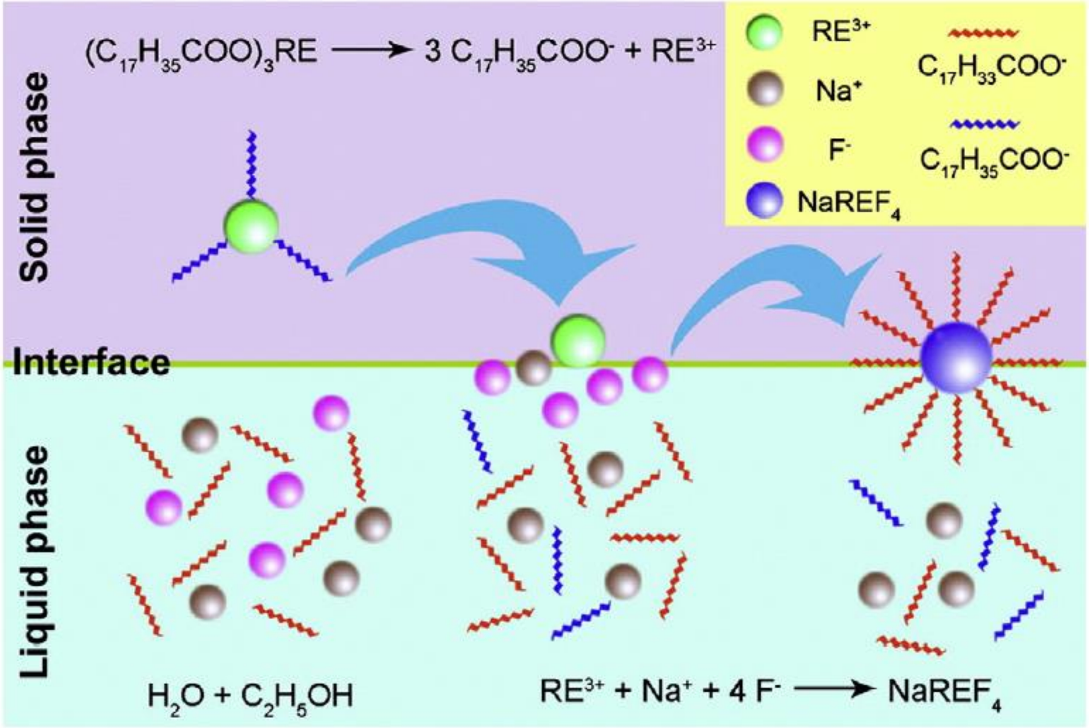
Yi et al.[29] first gave the method for the coprecipitation to synthesize $NaYF_4$:Yb,Er Upconversion NPs with the aid of EDTA.



Wei et al [30] gave a method similar to the above one for synthesizing $NaYF_4$:Yb,Tm Upconversion NPs in the presence of EDTA to facilitate their use and application at higher temperature conditions also as it prevents the agglomeration by controlling the pH.

1.7.3. HYDROTHERMAL / SOLVOTHERMAL METHOD

This Decomposition technique requires a condition of higher pressure and temperature, generally above the solvent’s critical point. Generally specialized reaction-vessels such as autoclaves are used for providing a closed condition to the reaction[31-33].



. Mechanism for the synthesis of NaREF4 UCNPs by solvothermal method

Figure 1.7. Mechanism

1.8. Potential Applications of Upconversion Nanoparticles

Upconversion nanoparticles elective hotspot for overcoming current constraints in conventional fluorescent probes. By and large for synthesizing Upconversion nanoparticles Rare Earth doped materials are utilized, due to their excellent properties like high chemical stability and low phonon energy. Upconversion nanoparticles provide a great opportunity for enhancing solar cell efficiency. Photovoltaic cells convert sunlight into electricity, using photovoltaic effect. They help us in generating one of the cleanest and abundant energy to fulfill the energy requirements. But, the photovoltaics current’s efficiency is hindered by the loss of photons of sub band gap during transmission. Photon upconversion provides us with the way to overcome the issue as the loss can be minimised by converting the transmitted photons of sub band gap into above band gap. Hence, by this technique the efficiency of solar cells could be increased.

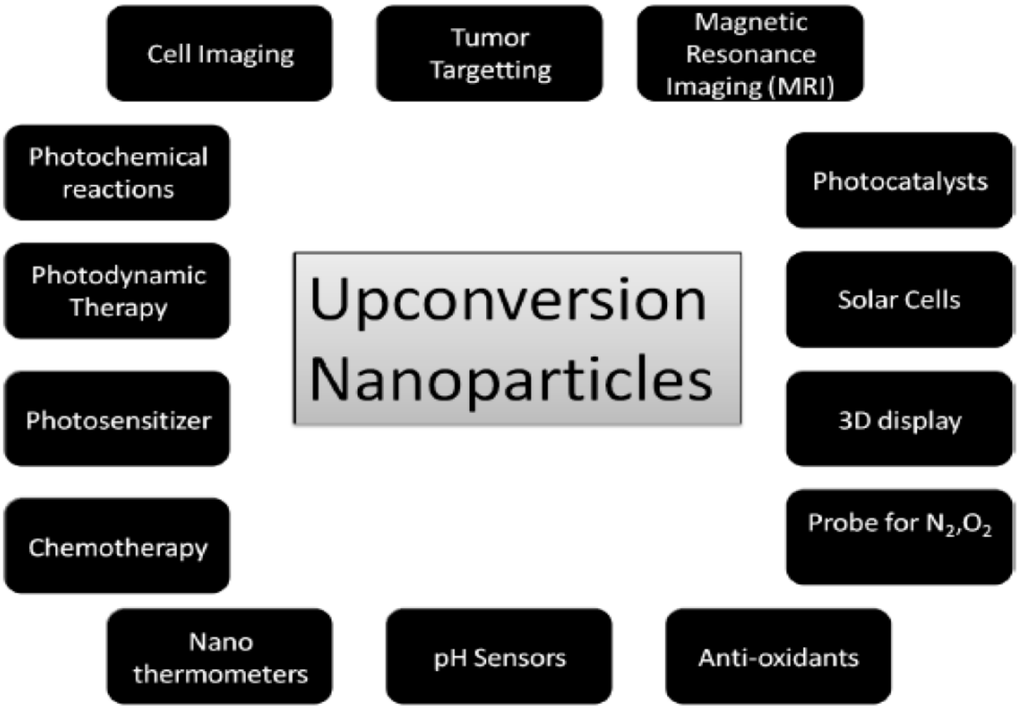


Figure **1.8.** Various Applications of Upconversion Nanoparticles

2

LITERATURE REVIEW

Meng Wang, Gopal Abbineni, April Clevenger et al. have presented a paper on Synthesization, Surface-Modification and Biological applications of Upconversion NPs. It tells about different types of Upconversion Processes and Energy Transfers such as ESA, SET, CR, CS,CL, etc In the paper they have described about various methods for synthesis of Upconversion Nanoparticles their merits and utilization. The methods used for the formation of RE-doped $NaYF_4$ Upconversion Nanoparticles are Coprecipitation method, Hydrothermal/ Solvothermal Method, Thermal-decomposition Method and other various methods. They also gave methods for surface modification of RE-doped Sodium Yttrium Flouride Upconversion Nanoparticles through inorganic shell layers using amorphous silica as well as organic capping ligands using HEDP. It also mentions various biological applications of RE-doped Sodium Yttrium Flouride Upconversion Nanoparticles such as in-vitro cellular-imaging and in-vivo tissue-imaging**,** in-vitro cell-labeling and imaging.

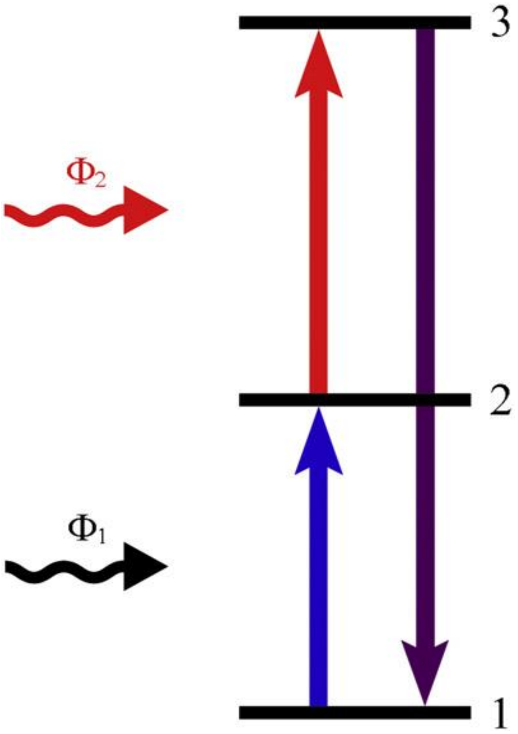


Figure 2.1. Energy Transfer scheme related to ESA

Hao-Xin Mai et al. have conducted a very noteworthy experiment on Sodium RE Fluoride Upconversion Nanoparticles. They worked with several variants of $NaYF_4$ using various RE dopants like Nd, Eu or Y at different synthesizing conditions and performed experimental analysis using FTIR, XRD, TEM, etc. This paper also describes about various optical properties of the given sample.

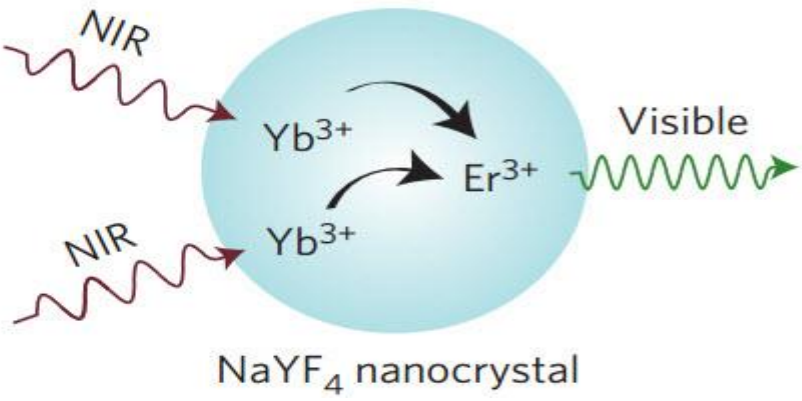


Figure 2.2. Upconversion through $NaYF_4$ nanocrystal

A Sarakovskis, J Grube et al. has worked on $NaLaF_4$:Er^{3+} upconversion processes at different doping concentrations. The Upconversion process efficiency basically depends on the rate of radiation less transitions within RE ion and therefore on the phonon energy of the medium i.e. for lower phonon energy the efficiency of Upconversion is higher. The optical properties of the sample is determined and studied and its possible application in Upconversion phosphors is being estimated.

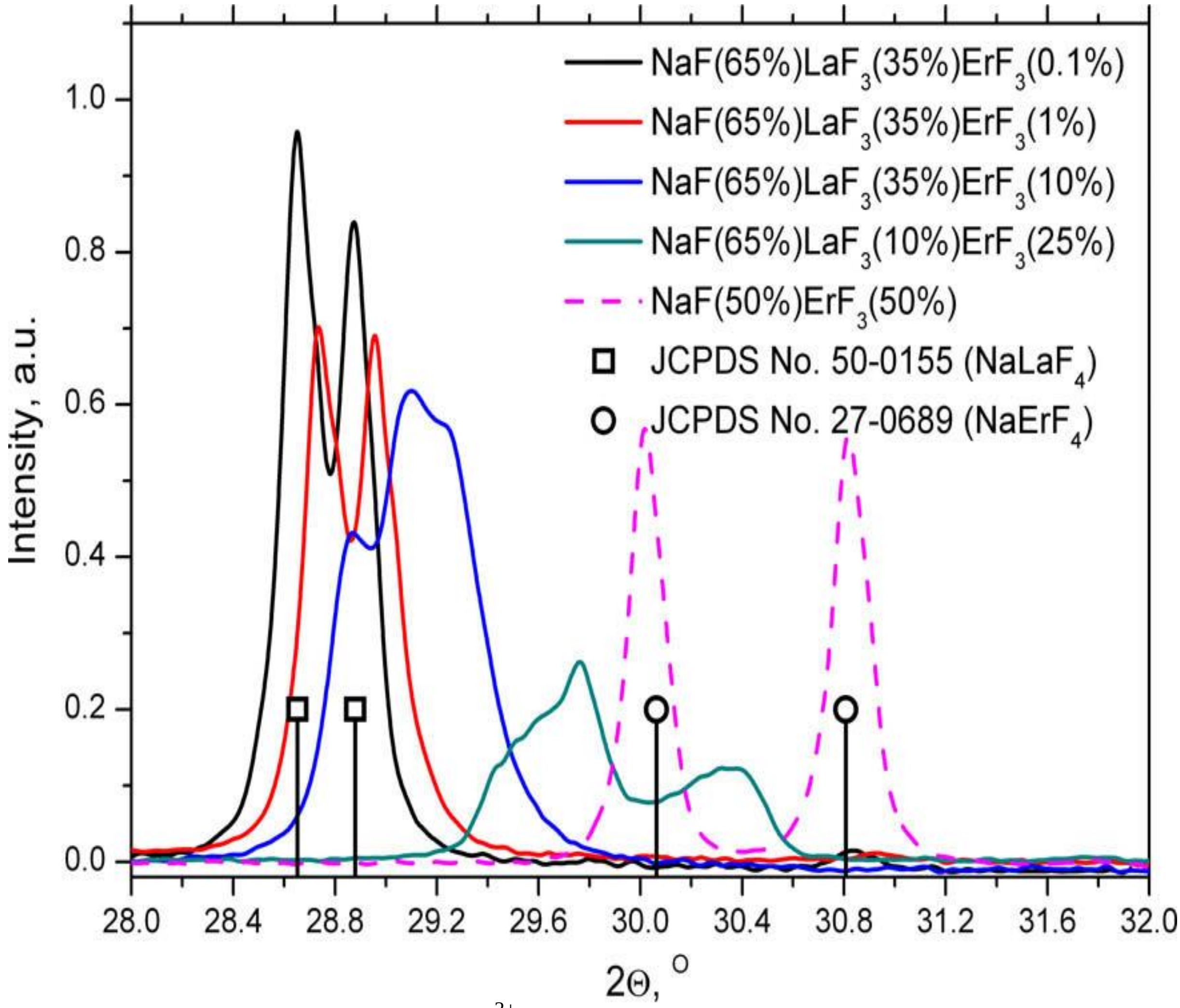


Figure 2.3. XRD Pattern of $NaLaF_4$:Er^{3+} samples at different concentrations of LaF_3 and ErF_3

Subrata Das, A Amarnath Reddy et al. have prepared monophasic KLaF4 with cubical symmetry doped with different Eu3+ concentrations. It was synthesized using wet chemical method. The nanophosphors of 5 nm size were obtained. The optical characterization of the sample was done and in results it was found that the sample exhibits very strong red colour, and longer lifetimes when excited at different wavelengths lower than 532 nm. It may be used in white LEDs and other displaying devices.

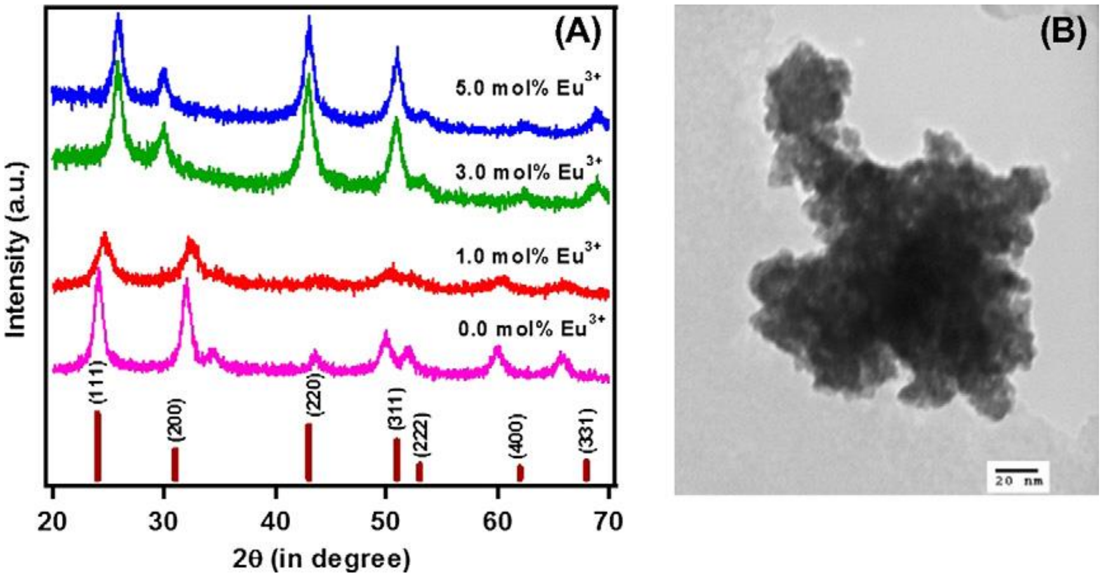


Figure 2.4. Room temperature (A) X-ray diffraction pattern of x mol% (x = 0, 1, 3, 5) Eu3+-doped KLaF4 nanophosphor.
(B) TEM image of 5 mol% Eu3+-doped KLaF4 nanophosphor

Cedric Bouzigues, ThiemyGaccoin, and AntigoniAlexandrou have done a great work over applications of RE based upconversion nano particles.
This paper highlights a lot of in-vitro and in-vivo applications of nano phosphors. Their usein cell biology, especially in bio imaging of tissues will help in early stage detection of diseases and hence curing them in time.

Shhzad Ahmad, Subrata Das et al. have depicted in detail optical properties of $KLaF_4$ doped by Tb^{3+}. It was synthesized as the cubic as well as the hexagonal structure nanoparticles. It is being synthesized by solution method. It emitted energy in the region of green light and the intensity of light varies according to the concentration of Tb^{3+} dopant. Their optical and magnetic properties were thoroughly analysed. The main application of these phosphors is for displaying purposes.

Shahzad Ahmad, G. Vijaya Prakash and R. Nagrajan have proposed work on

KLaF4 with hexagonal structure. In this paper they have done phase controlled synthesis and by optical characterization studied the luminescence results of KLaF4nanoparticles. In the experimental work it was noted that both the ligands used with Lanthanum precursor and the temperature of the reaction affected the formation of $KLaF_4$. $La(acac)_3$ as well as $La(OiPr)_3$ both form hexagonal nano particle structure if heated under 65 degree centigrade temperature for a day.

Here, it is being observed that conversion of $KLaF_4$ from cubic to hexagonal structure has taken place due to interface nucleation mechanism.The energy of emitted photon is also calculated and it is observed that it is less than

$NaYF_4$. With the help of $KLaF_4:Er^{3+}$ a new optically transparent and thick film of PMMA was formed at lab. It can be useful for opening a new path and helping in research of the hexagonal $KLaF_4$. It may be utilized for various applications which could result in replacement of $NaYF_4$ and we could get better results.

As an upconverter, Ln-doped Sodium Yttrium Fluoride has been added to the photoanodes for Q dot sensitized solar cells. Compared with the solar cells containing pure Titanium-di-oxide, the upconverter based solar cells show a 17.5% increase in the photocurrent and an increase of 20% in the efficiency of power conversion.

Upconversion mechanisms in rare-earth doped glasses to enhance the efficiency of silicon solar cells - using energy transfer between Ho^{3+} and Yb^{3+} ions. Analysis of various nanostructures for efficient photon upconversion resulting in high efficiency in photovoltaics.

Upconversion nanoparticles may provide a great oppurtunity in the enhancement of efficiency of solar energy generation. They have the ability to convert low energy radiations into high energy radiations , through non-linear optical process. Various types of Energy-Transfer mechanisms used for Upconversion are ESA, SET, CR, CS, CL etc

Rare Earth doped materials may be used effectively to enhance the efficiency of silicon solar cell. Energy transfer in these materials produce an upconversion emission with a spectral range just above the Si band gap. When these glasses are placed at the rear of a bifacial Si solar cell, the upconverted radiation can be absorbed by Si and generate electron–hole pairs that contribute to enhance the cell efficiency.

Integration of Lanthanide-doped Sodium Yttrium Fluoride with the photoanodes for Q-dot sensitized solar cells results in higher photocurrent and hence increase in efficiency. $NaYF_4$ is regarded as the best upconversion matrix due to its unique characterstics like low phonon energy, good chemical stability and superior refractive index.

Organic-inorganic lead halide based perovskite solar cells have received broad interest due to their merits of low fabrication cost, a low temperature solution process, and high energy conversion efficiencies. Rare-earth (RE) ion doped nanomaterials can be used in perovskite solar cells to expand the range of absorption spectra and improve the stability due to its upconversion and downconversion effect.

We can use these materials effectively to enhance the efficiency of solar cells by doing some modifications in the layers .

3

EXPERIMENTAL PROCEDURE

3.1. Synthesis Through Wet Chemical Route

Undoped $KCeF_4$

The Undoped $KCeF_4$ nanoparticles have been prepared through Wet Chemical Route method using Cerium-acetyl-acetonate / $Ce(acac)_3.xH_2O$ and Potassium fluoride/ KF.

Ce(III)2,4-pentanedionate hydrate was mixed in methanol. The resultant Ce solution was kept on magnetic stearer for 45 minutes.

KF was dissolved in methanol in another beaker and the Ce solution was added drop by drop in KF solution using pipette. The resultant solution was placed on a magnetic stearer at 65°C for three and a half hours. Then it was centrifuged at 14000 rpm at 60°C for 10 minutes. Supernated liquid was removed to obtain the precipitate. The precipitate was washed thrice with methanol to obtain the yield. After keeping it for 24 hours in vacuum oven at 40°C it was dried up. Then using mortar and pestle it was converted in powdered form.

Doped $KCeF_4$

$KCeF_4$ was doped with Europium and Ytterbium.

The Doped $KCeF_4$ nanoparticles have been prepared through Wet Chemical Route method using Cerium-acetyl-acetonate / $Ce(acac)_3.xH_2O$, Potassium fluoride/ KF, Europium chloride hexahydrate/ $EuCl_3.6H_20$, Ytterbium chloride hexahydrate/$YbCl_3.6H_20$. The reactants were mixed in methanol. The Ce solution, Eu solution, Yb solution were added drop wise to the KF solution. The resultant solution was kept at magnetic stearer at 65°C for three and a half hours. Then it was centrifuged at 14000 rpm at 60°C for 10 minutes. Supernated liquid was removed to obtain the precipitate. The precipitate was washed thrice with methanol to obtain the yield. After keeping it for 24 hours in vacuum oven at 40°C it was dried up. Then using molten pastel it was converted in powdered form. Two variatns were made with composition-

$KCe_{(100-x-y)}F4:Yb_{(x)}/Eu_{(y)}$

In one of the solutions

y=3% of MW of $EuCl_3.6H_2O$

x=20% of MW of $YbCl_3.6H_2O$

Ce=77% of MW of $La(acac)_3$

Each quantity normalized for 10 ml methanol solution.

In other solution

y=3% of MW of $EuCl_3.6H_2O$

x=5% of MW of $YbCl_3.6H_2O$

Ce=92% of MW of $La(acac)_3$

each quantity normalized for 10 ml methanol solution.

$KCe_{(100-x-y)}F4:Yb_{(x)}/Eu_{(y)}$			
	Undoped	Doped Sample 1	Doped Sample 2

Ce	100%	77%	92%
X	0	20%	5%
Y	0	3%	3%

Table 3.1. Concentration of Dopants in Samples

The structure and composition of the samples were checked with the help of X-ray diffraction/XRD. Fourier Transform Spectroscopy was conducted for identifying and conforming chemicals present in the samples.

3.2. X-Ray Diffraction (XRD)

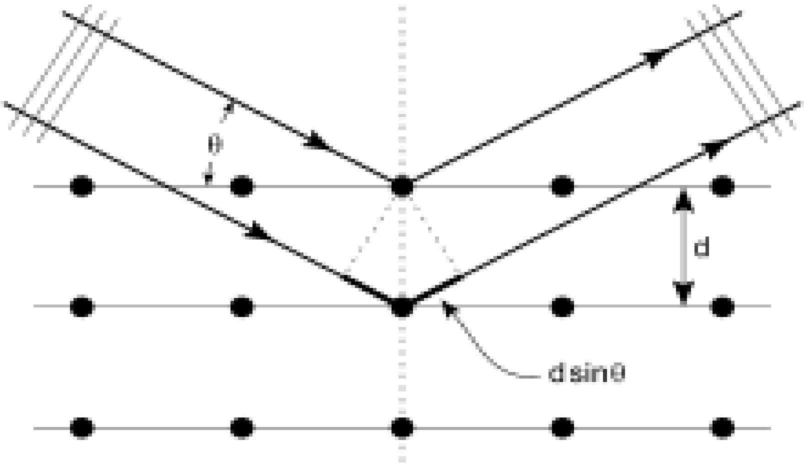


Figure 3.1. Diffraction through lattice during XRD

XRD is an analytical technique used to determine structure, composition, phase and other physical properties of any given sample. It uses dual nature of X-rays i.e. both wave nature and particle nature for obtaining details about internal structure of crystalline materials.

The basic principle of XRD is based upon constructive interference between x-Rays and matter.

As per Bragg's Law n n $\lambda = 2d\sin\theta$. When x-rays incident on a crystal surface, they are scattered from the lattice of the crystal, The peaks obtained from the X-ray diffraction plot satisfty following conditions:

1. The angle of incidence = angle of scattering.

2. The path length difference is equal to an integer number of wavelengths.

The maximum intensity condition given in Bragg's law help us in calculating details about the crystal structure.

When monochromatic X-Rays are generated in a Cathode Ray Tube (CRT) at a very high voltage and are targeted on a material. After interacting with the material, these rays form constructive as well as destructive interference. These rays are processed, collected and then counted.

By structural analysis we may determine the following parameters:

1. Lattice Parameter: In a crystal lattice it refers to the physical dimension of unit cells. We generally have 3 lattice constants a, b and c.
2. Phase Identity: By calculating phase we can confirm the presence of a particular element in the sample. It can be used to tell the level of purity/impurity in a sample. It can be used for simple and compound, both types of materials.

   Hence this technique can be used to determine dimensions of a unit cell. It can be used to confirm the presence of any element as well as to identify the unknown materials.

   XRD could also be used to determine composition of synthesized materials, and crystal quality, purity. It can also be used to distinguish between amorphous and crystalline materials and hence determine the properties. Information related to cell structure, lattice parameters, crystalline size and various other details of a material could be obtained using XRD. For any synthesized material ratio of amorphous part to crystalline part could be calculated and stated. From the width of the peak obtained the average size of a crystal could be obtained as the size of the particle is inversely proportional to the width of the peak. Structural distortion could also be calculated from inter planar distance obtained using XRD.

Figure 3.2. XRD Apparatus at DTU Campus

Through this technique, parameters may be determined quickly and very efficiently using easily available tools. The results are easy to comprehend.

But this technique has a few limitations also. For characterization homogeneous mixture is required, a reference data is needed for understanding the outcomes. If incidence is at higher angles then it may result in reflection instead of refraction.

3.3. Transmission Electron Microscopy (TEM)

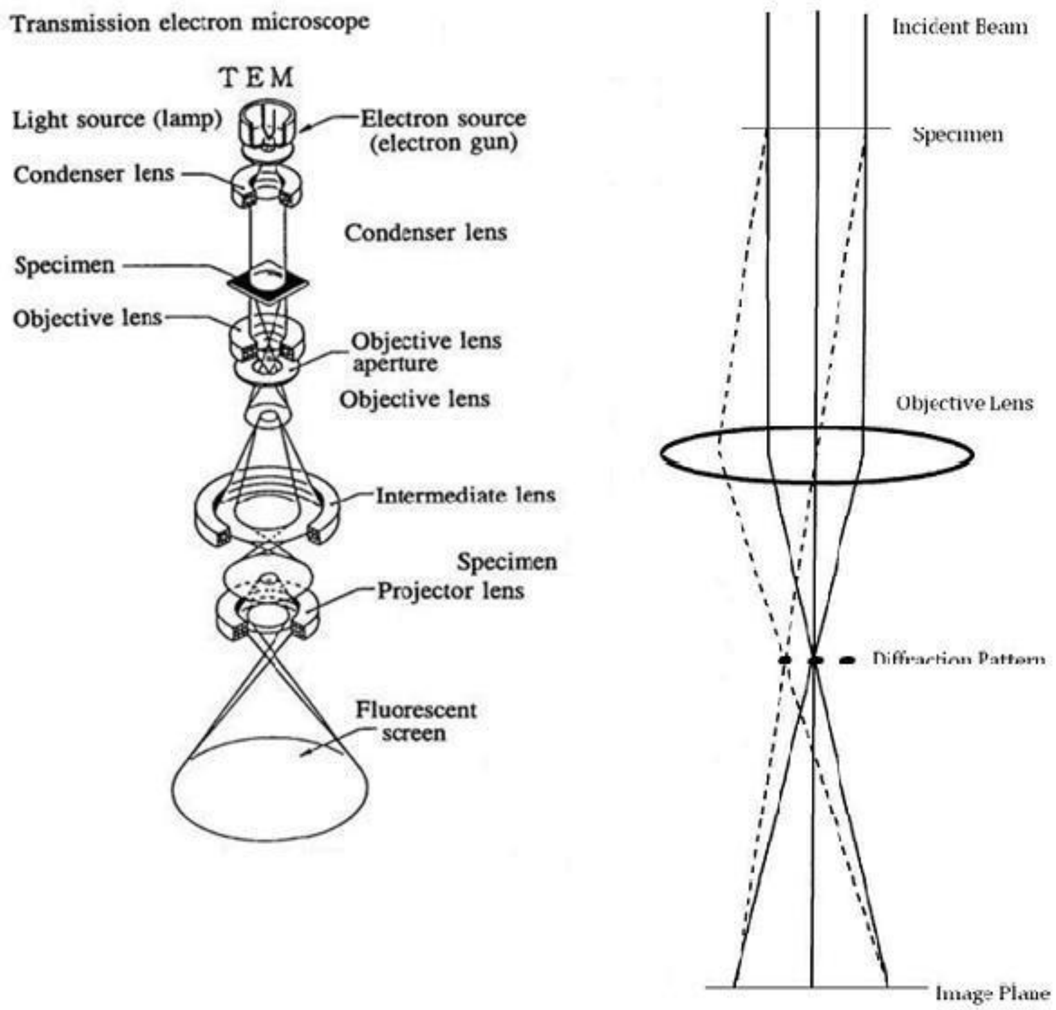


Figure 3.3. TEM Tool and Ray Diagram for Diffraction Mechanism

For TEM a vacuum chamber is required. In this chamber interaction takes place between high energy electrons and the matter.The beam passes through electromagnetic lenses and then through solenoids, where it gets changed to light wave when comes in contact with screen. Hence, an image is obtained.

By adjusting the voltage of gun to limit the speed of the electron beam the resolution of the image can be manipulated. Then the solenoid coils project this image on photographic plate.The TEM Studies of this sample were carried out at the Indian Institute of Technology, Delhi.

3.4. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is generally used for identifying inorganic and organic groups present in the sample. It can be used to quantitate components of unknown mixture and to analyse solids, liquids and gases. In this technique the data is collected and converted from an interference pattern to a meaningful spectrum. It could be used for identifying the types of molecular bonds present in the sample molecule through an infrared absorption spectrum.

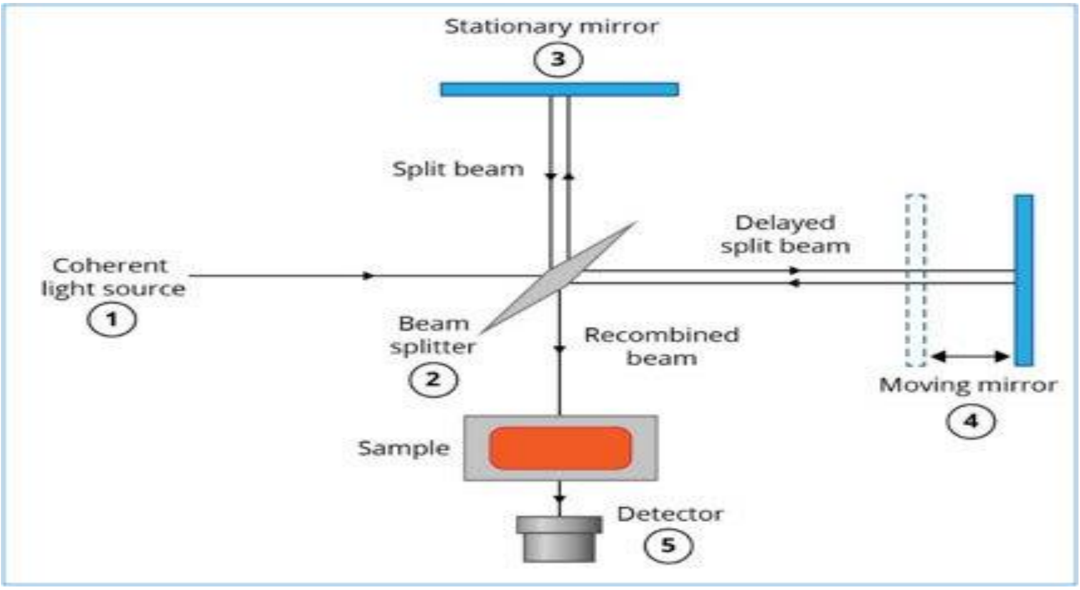


Figure 3.4. FTIR Spectrometer

The basic principle used is the vibration of molecular bonds at various frequencies. Molecular bonds vibrate at different frequencies which depend on the elements and the type of bonds. For any particular bond, there are various specific frequencies at which it can vibrate. According to wave number, IR can be categorized into far infrared, mid infrared and near infrared with wavenumber in range 4-400cm^{-1} , 400-4000cm^{-1} , and 4000-14000cm^{-1} respectively.

As per quantum mechanics, these frequencies correspond to the ground state (lowest frequency) and several excited states (higher frequencies). One way to increase the frequency of a molecular vibration is to excite the bond light energy absorption . For a given transition between two states the light energy (determined by the wavelength) must be exactly equal to the difference in the energy between the ground state and the first excited state. As the IR interacts with matter, there is a stretch,or a bend in the chemical bonds, that are present in the sample. The advantages of FTIR are its high sensitivity performance with the permanently aligned, high cube corner interferometer, hyperspectral imaging, customizable workspaces, easy measurement mode and high throughput screening devices.

4

RESULTS AND DISCUSSION

4.1. XRD ANALYSIS

The XRD patterns of undoped and doped $KCeF_4$ samples are shown in Figure 4.1. The obtained patterns resemble with and are recognized to be of Hexagonal Crystal Structure of $(KCeF_4)_{1.5}$ having space group of P-62m (JCPDS File No. 75-2020). Through the X Ray Diffraction the crystalline nature of the samples was confirmed. The XRD was performed in the range of 20 degrees to 80 degrees.

The diffraction peaks are shifted by 1-2 degrees on the higher side because of Eu^{3+} doping. Therefore these shifts in the XRD peaks are attributed to the substitution of the Ce^{3+} ions having larger ionic radius (115 pm) with Eu^{3+} ions which comparatively have smaller ionic radius (108 pm) in the host lattice [34-36]. As Eu^{3+} ions have selectively replaced the sites of much larger ionic radius sites of Ce^{3+} ions, with the increase in concentration of Eu^{3+} doping the decrease in lattice parameters of the sample is reasonable.

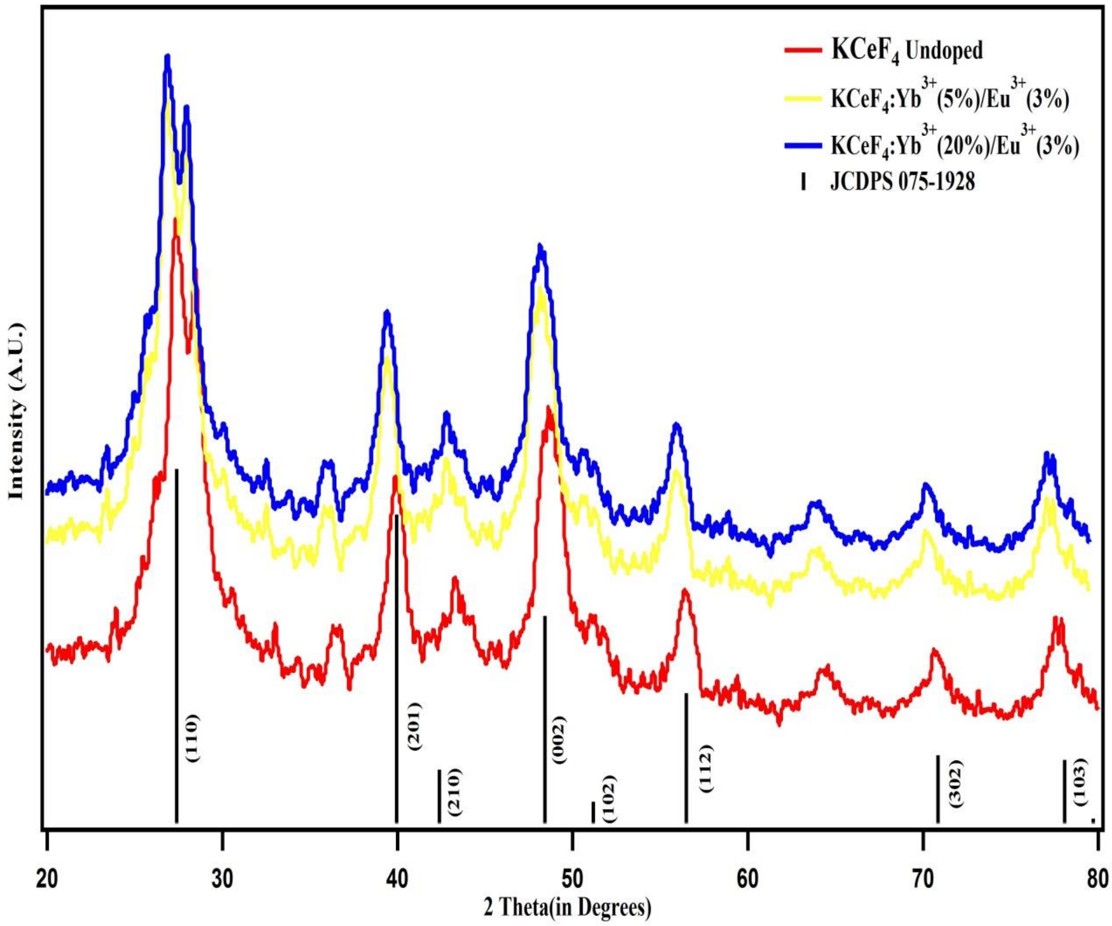


Figure 4.1. XRD of $KCeF_4 : Yb^{3+}/ Eu^{3+}$ UCNPs

Through the XRD plot, the mean size of the nanoparticles in sample is calculated using Scherrer formula.

Scherrer formula –

$$d_c = \frac{k\lambda}{\beta \cos\theta}$$

where, d_c = mean size (in nm)

k = shape factor (dimensionless) (~0.9)

λ = X-ray wavelength (~0.154 nm)

β = line broadening at half the maximum intensity (FWHM) (in radians)

θ = Bragg angle

The mean size of the nanoparticles is approximately **3.4 nm.**

Now with the help of Bragg's law, lattice spacing 'd' could be calculated.

Bragg's law –

$$n \lambda = 2 d \sin \theta$$

where, n = order of excited state

λ = X-ray wavelength (~0.154 nm)

θ = Bragg angle

d = lattice spacing

The lattice spacing 'd' is calculated to be approximately of **0.335 nm**

4.2. TEM ANALYSIS

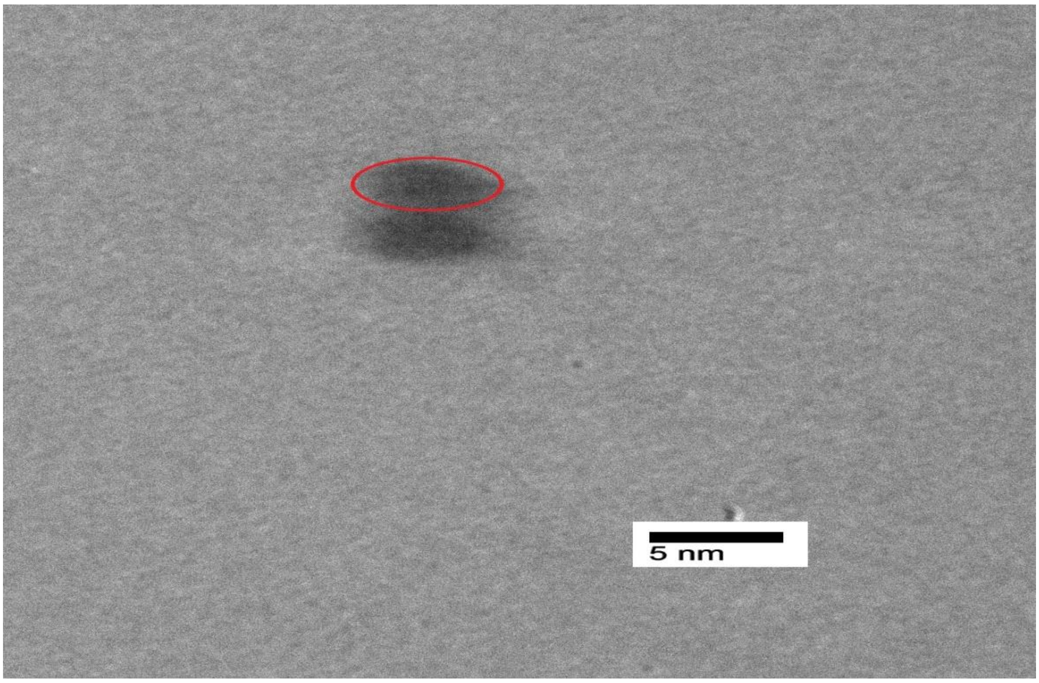


Figure 4.2. Size of particle observed using TEM

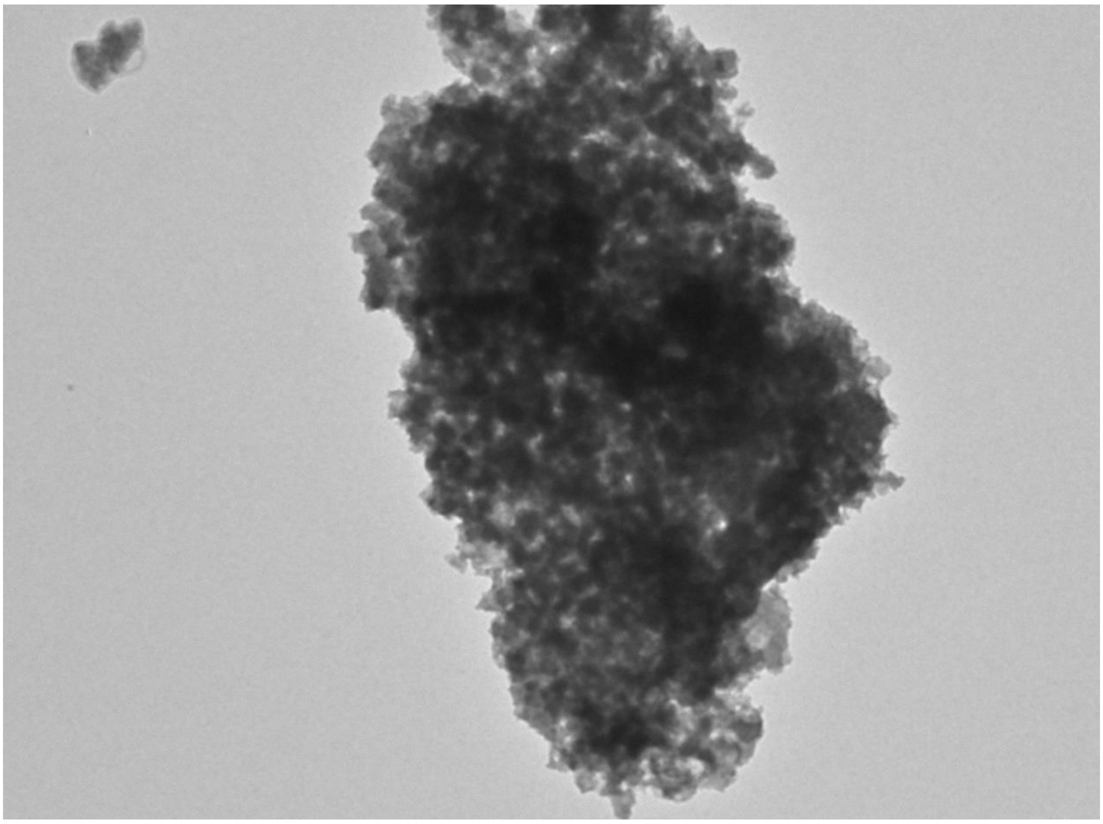


Figure 4.3. Images obtained using TEM

From Transmission Electron Microscopy (TEM) the average size of the particles of the sample is obtained to be nearly 3.5 nm which is approximately equal to the size calculated through XRD analysis, hence, verifying the experimental results and calculations done.

4.3. FTIR ANALYSIS

FTIR studies were performed for the samples of undoped and doped $KCeF_4$. Relevant data has been provided in Fig. 4.4. In this the FTIR spectrum of an un-doped $KCeF_4$ sample is compared with $KCeF_4$:Yb^{3+}(20%)/Eu^{3+}(3%) sample. The broadband observed at 3328 cm^{-1} can be attributed to O-H stretching vibration. The bands observed at 1390 cm^{-1} and 1533 cm^{-1}can be assigned to the symmetric and antisymmetric stretching vibration of the hydroxyl (-OH) group respectively. [37]

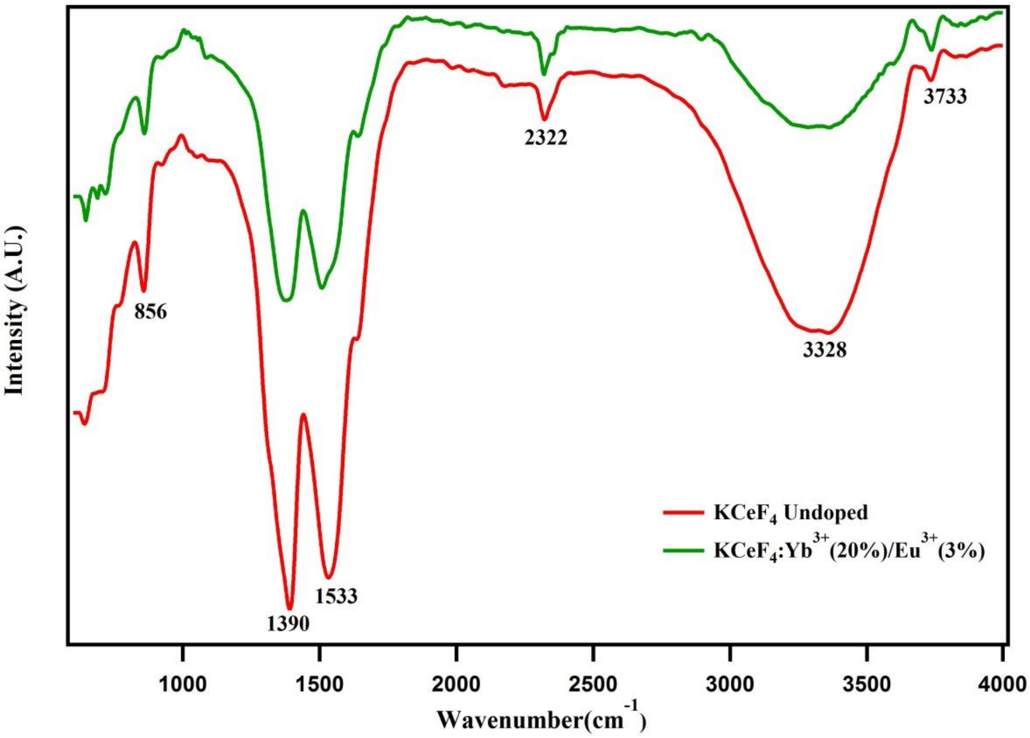


Figure 4.4. FTIR Analysis

5

CONCLUSION

The undoped and rare earth ion doped $KCeF_4$ upconversion particles have been successfully synthesized using wet chemical route. Various experiments have been carried out like XRD, FTIR, TEM for morphological studies of the samples. Undoped and doped samples both are compared through these analysis.

These studies confirm the successful synthesis of desired $KCeF_4$ rare earth (Eu^{3+} and Yb^{3+}) doped and undoped $KCeF_4$ nanoparticles.

The results obtained by XRD confirm the presence of $KCeF_4$ rare earth (Eu^{3+} and Yb^{3+}) doped and undoped upconversion nanoparticles with hexagonal phase (β - phase) . The calculated particle size is in nanometers range. Therefore confirming the formation of nanostructure of $KCeF_4Yb^{+3}$ Eu^{+3} . The particle size is verified by TEM analysis. Through FTIR analysis the presence of OH ions in the sample is observed which proves that the given samples favour the enhancement of intensity of red luminescence.

6

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