Synopsis of the Thesis entitled

Synthesis and Characterization of LaX (X = O, S, F) Compounds and their Application in the field of Photoluminescence and Upconversion materials

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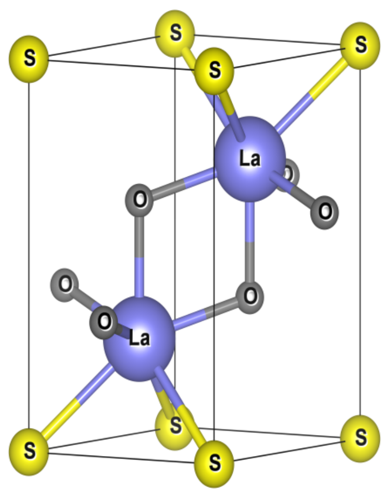
ABSTRACT

The rapid development of the optical technologies during the past years has notably increased the demand of luminescent materials for a large variety of applications. The advancement in the field of nanotechnology and material science has provides a thrust in exploration of various compounds and materials and has played an important role in optimizing the functionality of the materials. This advancement has worked as a catalyst especially in the area of luminescence which has significantly increased the demand of rare-earth-doped optical materials owing to their wide range of applicability. The study undertaken here majorly involves the synthesis of Lanthanum Oxysulfide (La_2O_2S), Lanthanum Oxide (La_2O_3) and Lanthanum Oxyfluoride (LaOF) which are versatile compounds having a wide range of utilities and their morphological and optical characterizations. The novelty of the work lies in employing the furnace combustion technique for the synthesis of Lanthanum Oxysulfide is an approach that limits the precursors there by minimizing the use of resources. The method dose not required to pass the H_2S, CS_2 or any hazardous gases during the reaction and also consume less time with giving maximum yield. The modified precipitation method has been employed for the synthesis of nanoparticles La_2O_3 and nanoparticles of LaOF. The extraction of Aloe Vera leaf called Aloe Vera Gel was used as surfactant for the synthesis of Nanoparticles of La_2O_3 and the extraction of Bilva leaf was used as surfactant for the synthesis of Nanoparticles of LaOF. For the study of down conversion photoluminescence, the five different types of rare earth elements were selected as dopant for each compound. They were Praseodymium, Terbium, Europium, Dysprosium and Thulium. For the study of Upconversion Photoluminescence, Six samples of various doping ratio of Ytterbium – Erbium, Ytterbium – Holmium and Ytterbium – Thulium were synthesized for each

compound. Upconversion nanoparticles are one of the most perspective materials due to their wide application range, the most important being in the bio-medicinal field where they can be used for labeling, sensing, treatment or drug delivery. The XRD and FESEM – EDAX techniques were used for morphological characterization and UV – Visible, Particle Size Analyzer and PL Testing were done for Optical Characterization of all compounds.



1. Introduction:

Rare earth material is beneficial in various commercial, industrial, medical, military and space applications. The synthesis of lanthanide – activated phosphors is pertinent to many emerging applications, ranging from high – resolution luminescence imaging to next generation volumetric full color display [1]. In the element periodic table, there is an extra bar out of the main table with atomic number between 57 to 71 are named lanthanides or rare earth elements. The elements are of f-block elements also called inner transition metals. Rare earth elements are a set of 17 chemical elements, the lanthanide along with the transition metals scandium and yttrium that are highly recognized for their versatile applications [2, 3]. Photoluminescence occurs when the material absorbs at least one photon and subsequently spontaneously emits another with a different energy, the process depending upon the structure of phosphor materials, surrounding environment and type of activators used. All rare-earth elements have similar chemical properties but differ in physical properties due to their electronic structure. There are seventeen rare earth elements, and all have unique optical properties, however, characteristic due to the same order of magnitude of Coulomb interactions and spin-orbit interaction (thus the intermediate coupling scheme applies) and the partially filled 4f orbital surrounded by completely filled 5s and 5p orbitals accounting for the radial wave function of 4f orbitals to be less extended then 5s and 5p orbitals [4]. The rare-earth compounds are intensively used in high-performance luminescence and display devices such as solid-state lighting, field emission diodes, in vivo fluorescence imaging, MRI imaging, UV-LED, Laser and especially in the biotechnological field because of their sharp inter-configurational transition lines between 4f levels [5]. The rare-earth hosts doped with another lanthanide ion are very efficient luminescent materials due to the high thermal stability, low phonon energy, and high rates of energy transfer.

Rare-earth materials have played an important role not only in optical technology but also in all high-tech industries such as petrochemical, ceramics, electronics, agricultures, lamps, laser, magnets, metallurgy, biological and pharmaceutical [6]. Due to the wide range of applications associated with the rare earth materials they were the preferred choice for this study. The main feature of upconversion materials is the absorption of low energy photons with the resulting emission of higher energy photons. Although the upconversion materials have many applications, e.g. by enhancing the solar cell efficiency [7], due to the fact that the excitation often lies within the biological transparency windows [8] they have found their way into multiple biological and medicinal usages, given that the particle size is adequately small to cause no unwanted disturbance to the living cells. The upconverting nanoparticles (UCNP) have received considerable attention in recent years, due to their broad range of potential applications: as nanothermometers [9, 10], for biological labeling and imaging, cancer treatment or drug delivery and therapy. The rare-earth oxysulfides are becoming more industrially relevant. They are an excellent laboratory system for the systematic investigation of rare-earth luminescence because virtually all rare-earth doped activators exhibit high luminescent efficiency and have the same crystallographic structure regardless of the ion size [11]. La2O3 possesses the prominent property of 4f orbital electronic configurations and exhibits a larger energy bandgap (Eg) compared to all other rare earth oxide groups. The magnetic behavior of lanthanum is diamagnetic in nature andit has a dielectric (e) constant of 27 PF/m, while it also contains the least energy in atomic lattice [12]. The Lanthanum Oxyfluoride has been drawn much attention due to their high chemical stability, low phonon energy and lasing characteristics hence has broad application in dielectric, optoelectronics, photonics and in luminescent materials for its unique electrical and optical properties [13, 14].

2. Objectives:

The aim of the work is to formulate the synthesis technique for each compound as it uses minimal amount of precursors, has no complexity in procedure, has maximum yield, to become ecofriendly with no Compromise in efficiency so it becomes an industrial friendly synthesis technique and to study their morphological properties and optical properties mainly down conversation photoluminescence & Upconversion photoluminescence.

- To formulate the industrial friendly synthesis technique for the production of rare earth doped Lanthanum Oxysulfide based phosphors and studies their morphological and optical properties.
- To formulate the industrial friendly synthesis technique for the production of Nanoparticles of Lanthanum Oxide and rare earth doped Lanthanum Oxide Nano phosphors and studies their morphological and optical properties.
- To study the potential application of Rare earth doped Lanthanum Oxide as UV emitting Phosphors.
- To formulate the industrial friendly synthesis technique for the production of Nanoparticles of Lanthanum Oxyfluoride and rare earth doped Lanthanum Oxyfluoride Nano phosphors and studies their morphological and optical properties.

3. Summary of Research Work:

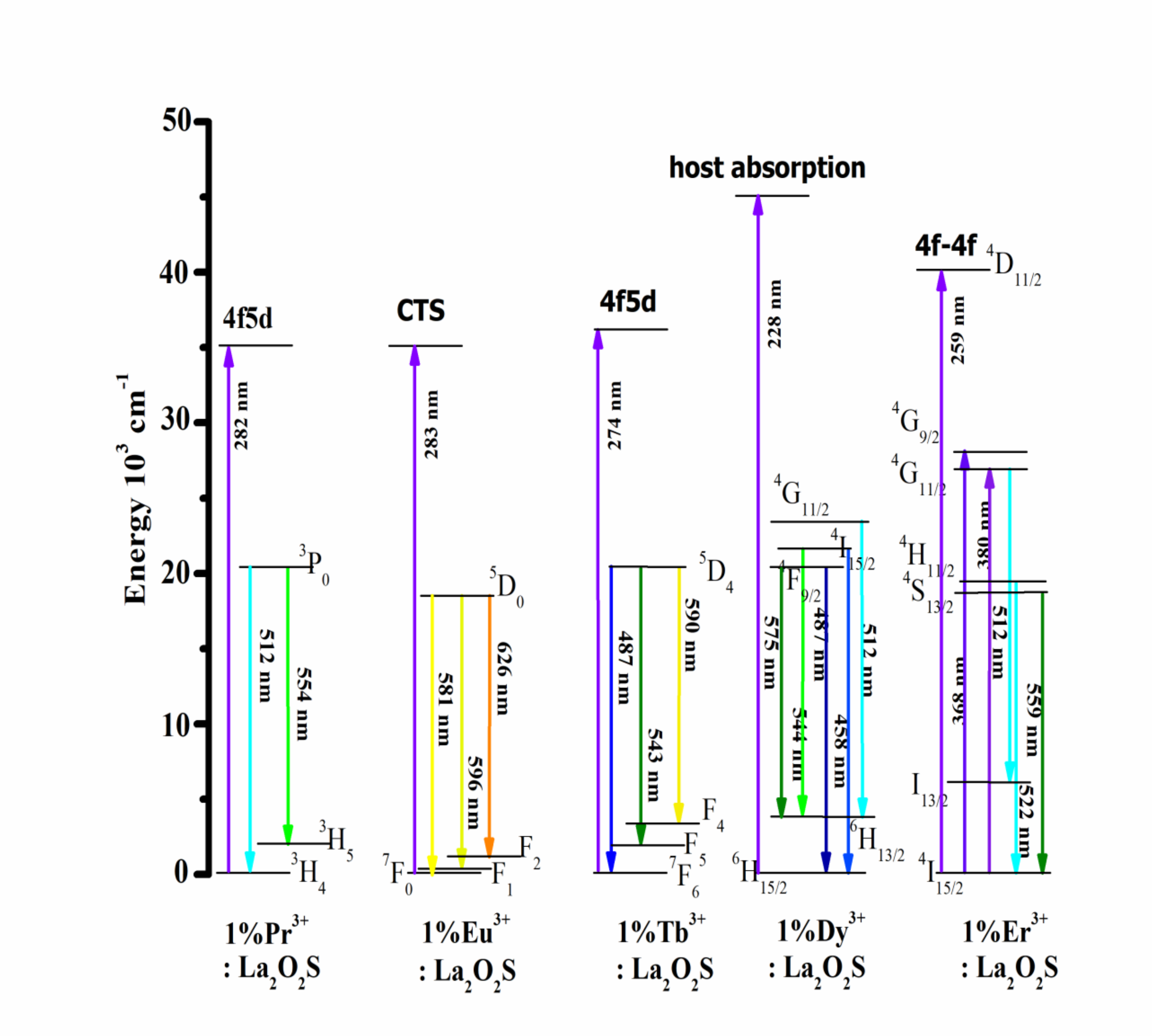
The work has been presented in five chapters as summarized below:

Chapter 1: Introduction of Luminescence properties of Rare earth elements

It contains the basic theory that why rare earth elements has play an important role in lighting technologies and display device industry. The various levels of absorption and emission in rare earth elements like 4f – 4f transition, 4f – 5d transition, CTS and energy transition from host lattice to dopant are describe in details in this chapter. There are brief details about the types of Luminescence and detail explanation about Photoluminescence and Upconversion Photoluminescence.

Chapter 2: Synthesis, Morphological, Optical, Photoluminescence and Upconversion Photoluminescence Characterization of Rare earth doped La_2O_2S Phosphor

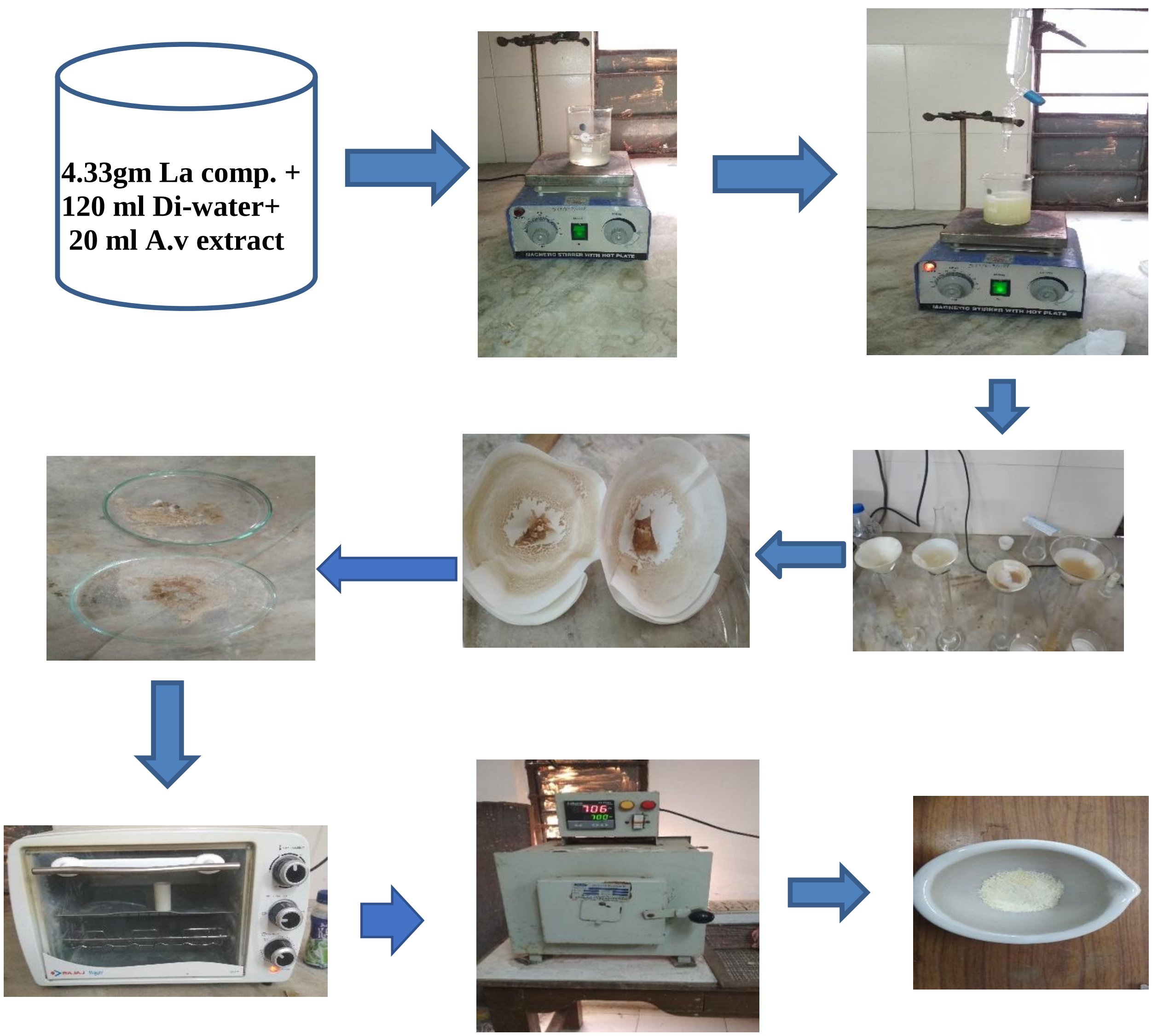
It contains the introductory part of Lanthanum Oxysulfide, different synthesis routes for La_2O_2S and results & analysis of synthesized samples. The chapter has covered three studies. In first, there was a comparative study of structural data from the XRD spectrum of three different synthesis techniques, A Solid State Technique, hydrothermal Technique & Furnace Combustion technique for approaching the novel method for the synthesis of Lanthanum Oxysulfide Crystal. The comparative study of structural parameters from XRD revealed that the furnace combustion technique without any added flux was the best technique among the solid-state and hydrothermal method for the synthesis of La_2O_2S as the product had perfect hexagonal lattice with space group 164: $p\bar{3}m1$ and had a crystallite size of 31.9 nm. The optical energy band gap of lanthanum oxysulfide synthesized by the furnace combustion technique was around 4.5 eV, calculated from the UV – Visible spectrum. The furnace combustion technique had several advantages that will make it an industrial friendly technique like it acquired less time for preparation, used minimum precursor, no needed any pre, or after the process, an outstanding amount of yield and product had perfect hexagonal lattice and had Nano crystallite size. In the second study, the five samples of 1% Ln^{3+} (Ln = Pr, Eu, Tb, Dy, Er) doped Nano crystallite La_2O_2S were synthesized by furnace combustion technique, and their structural, morphological, optical & photoluminescence properties were investigated. The XRD and EDAX technique used for structural & morphological analysis, The UV – Visible spectroscopy was used for optical study, and PL spectroscopy used for photoluminescence. From the XRD, all five samples had similar peaks, and all peaks were matched with JCPDS files of hexagonal lattice and had Nano crystallite size. EDAX spectra confirmed the incorporation of Ln^{3+} ions in host La_2O_2S. The study of UV – Visible spectra had revealed information about band gap, refractive index, absorption wavelength, and molar extinction coefficient. From the PL excitation spectra, there were four types of absorption observed, 4f -5d type absorption recorded in 1% Pr^{3+}: La_2O_2S and in 1% Tb^{3+}: La_2O_2S, CTS was seen in 1% Eu^{3+}: La_2O_2S, host absorption in 1% Dy^{3+}: La_2O_2S and 4f – 4f type of absorption recorded in 1% Er^{3+}: La_2O_2S. The PL emission spectra for 1% Pr^{3+}: La_2O_2S had the highest peak at a wavelength of 512 nm due to the energy transition from ${}^3P_0 \rightarrow {}^3H_4$, for 1% Eu^{3+}: La_2O_2S was at 616 due to the ${}^5D_0 \rightarrow {}^7F_2$, for 1% Tb^{3+}: La_2O_2S was at 543 nm as ${}^5D_4 \rightarrow {}^7F_{4,}$ for 1% Dy^{3+}: La_2O_2S was at 575 nm due to ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ and PL emission spectra of 1% Er^{3+}: La_2O_2S was first time recorded in a visible region with the highest peak at 550 nm due to energy transition from ${}^4S_{13/2} \rightarrow {}^4I_{15/2.}$ The six samples of different composition of Yb – Er, Yb – Tm and Yb – Ho were synthesized as upconversion materials and study their morphological and upconversion Photoluminescence.



Chapter 3: Synthesis, Morphological, Optical, Photoluminescence and Upconversion Photoluminescence Characterization of Rare earth doped La_2O_3 Nano Phosphor

The Chapter contains detail study of two different types of synthesis routes for synthesis of Nanoparticles of Lanthanum Oxide (La_2O_3) and also contains the detail study of morphological and optical characterization of rare earth based La_2O_3 phosphors. The first technique was Self Emulsion Polymerization. This technique was though had a potency but the complexity was very high so a different was selected for the synthesis of Nanoparticles of Lanthanum Oxide.

The second route was modified precipitation techniques with using Aloe Vera Gel as bio -surfactant for synthesis of Nanoparticles of Lanthanum Oxide. This technique has capability to become the industrial friendly. This technique was employed to synthesized downconversion and upconversion rare earth doped La_2O_3 Nano phosphors. The morphological and optical characterizations of synthesized samples are discussed in this chapter.



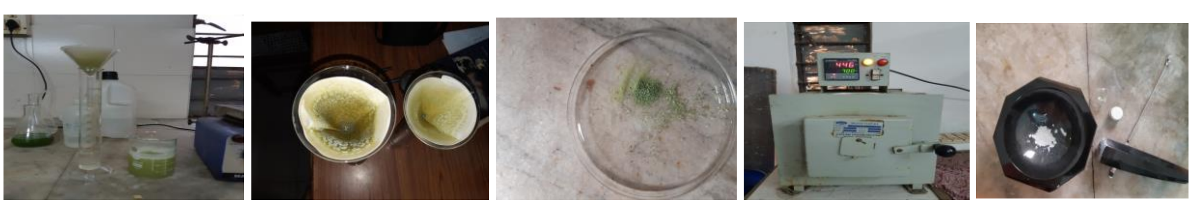
Synthesis route for the Nanoparticles of Lanthanum Oxide

Chapter 4: UV emission and energy transfer process in XCe^{3+} - YGd^{3+}: $La_{2-(X+Y)}O_3$ phosphors & XPr^{3+} - YGd^{3+}: $La_{2-(X+Y)}O_3$ phosphors

It describe one of the potential application of rare earth doped Lanthanum Oxide as UV emission phosphors. The Chapter has also contains the study of energy transfer process that enhancing the photoluminescence characteristics between Ce - Gd and Pr to Gd in La_2O_3 crystal. The UV radiation spectrum is divided into three categories, UVC (200 – 280 nm), UVB (280 – 315 nm) and UVA (315 – 400 nm). Here the emissions are of UVB and UVA types. They are used in many applications such as photocopying, phototherapy and in producing a long lasting tan.

Chapter 5: Aegle marmelos gel assisted precipitation method for the synthesis of rare earth doped Nanoparticles of LaOF phosphors and their Morphological, Optical, Photoluminescence and Upconversion Photoluminescence Characterization

It contains the introductory part of Lanthanum Oxyfluoride, synthesis routes for rare earth doped LaOF and results & analysis of synthesized samples. The aegle marmelos gel is used as bio – surfactant in the precipitation route for synthesis of rare earth doped Nanoparticles of LaOF phosphors.



Synthesis route for the Nanoparticles of Lanthanum Oxide

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List of Publications:

1) Shah, K., Ćirić, A., Murthy, K.V.R., Chakrabarty, B.S., Investigation of a new way of synthesis for Nano crystallites of La_2O_2S & 1%Ln^{3+} (Ln = Pr, Eu, Tb, Dy, Er) doped La_2O_2S and study their structural and optical properties**,** Journal of Alloys and Compounds, 2021, 851, 156725

2) Hirani, D., Shah, K., Chakrabarty, B.S.**,** Synthesis and optical properties of zirconia (Zro_2)-polyacrylicacid (PAA) nanocomposites**,** International Journal of Scientific and Technology Research, 2019, 8(12), pp. 4001–4004

3) Kolte, K.R., Shah, K., Chakrabarty, B.S.**,** Exploring lanthanum sulphide characteristics for its physical properties**,** International Journal of Scientific and Technology Research, 2019, 8(12), pp. 957–961

List of Papers under publication process:

1) Aleksandar Ćirić[a*], Kevil Shah[b], Milica Sekulić[a], B. S. Chakrabarty[b], Miroslav D. Dramićanin[a], Upconversion photoluminescence of $La_2O_2S:Yb^{3+}/Er^{3+}$ nanoparticles created by a novel Furnace Combustion Technique without Flux

Submitted in Luminescence the journal of biological and chemical luminescence, Wiley

2) Aleksandar Ćirić[a*], Milica Sekulić[a], Kevil Shah[b], Bishwajit. S. Chakrabarty[b], Miroslav D. Dramićanin[a], Upconversion photoluminescence of Lanthanum Oxysulfide nanoparticles co-doped with Yb^{3+}/Ho^{3+} and Yb^{3+}/Tm^{3+} synthesized by optimized combustion technique

Submitted in Optical Materials journal, Elsevier