Nanoparticle Doped Optical Fibers for High Energy Lasers

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NANOPARTICLE DOPED OPTICAL FIBERS FOR HIGH ENERGY LASERS

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Materials Science and Engineering

by
Amber L. Vargas
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Accepted by:
Dr. John Ballato, Committee
Chair Dr. Philip Brown
Dr. Stephen Foulger
ABSTRACT

Fabrication of rare earth (RE) doped optical fibers for use in fiber-based lasers and amplifiers is conventionally performed using a solution doping technique where RE salts (i.e., ErCl3) are dissolved in a solvent, introduced into the porous silica soot, dried and consolidated to form the active fiber core. This process does not allow for tailoring of the chemical environment about the RE. Alternatively, nanoparticle (NP) doping is more recent approach to incorporating rare earths into an optical fiber and have been shown to permit modification of the chemical environment around the RE in ways the enhance spectroscopic performance. This is due to the NP isolating the dopant from the host SiO2 glass by creating a protective “shell” surrounding the RE. The NP host should to have a lower phonon energy than the SiO2 (1100 cm\(^{-1}\)) matrix since the radiative and non-radiative processes influence lasing efficiencies. In this Thesis, lanthanum trifluoride (LaF3) was selected as the NP of choice since it possesses a low phonon energy (~350 cm\(^{-1}\)) and while the fluoride converts to an oxide during the fiber processing, a lower phonon energy environment still remains about the RE. More specifically, NP doping was performed for fabricating and studying erbium doped fibers, where Er\(^{3+}\)-doped lanthanum fluoride (Er:LaF3) NPs were synthesized and their properties investigated to determine advantages for NP doping to conventional soluble salt doping. In addition, for this Thesis, different rare earth NP suspensions were produced and studied along with the effects of different host materials in those suspensions. Slope efficiencies in excess of 70% were realized for Er\(^{3+}\) nanoparticle doping in a multimode fiber-based master oscillator power amplifier (MOPA). This Thesis will discuss the systematic study of NP and fiber properties. More specifically, NP doped
suspensions and fibers were characterized and discussed by their physical, chemical, and spectroscopic properties to develop an understanding as to how to tailor and HEL relevant performance parameters.
DEDICATION

This work is dedicated to my beloved family. Especially my parents, Mom and Dad, and for my older brother, Eric.
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Firstly, I would like to thank my professor Dr. John Ballato. I am forever grateful for the opportunity to work under his guidance. He has taught me an enormous amount and initiated life-long professional relationships.

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A special thanks to our “lab mom” Courtney Kucera who has helped me tremendously along my journey. I could not have done it without her never ending support. Thanks to my lab family and friends that helped me along the way. Especially my French boys, Maxime and Benoit who always kept the office lively and made me look forward to going to work. They have truly helped me grow as a scientist and I will be forever grateful.

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A very special thank you to my grandparents on both sides who have always supported me and pushed me to be successful. I would not be here today if it was not for my grandparents seeing the value in a good education and helping me stay focused along my journey.
Most importantly, my parents receive the greatest thanks for all the sacrifices they have made my entire life for my bother and myself to make sure we received the best education and could reach our greatest potential. My parents have always encouraged my interest in science and have helped me emotionally and financially over the years.
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CHAPTER ONE
INTRODUCTION

In 1917, Albert Einstein discovered one of the fundamental theories in physics, the quantum theory of radiation [1.1]. His quantum mechanical theory of stimulated emission is currently the root of the operation of fiber lasers. When a laser active ion is in an excited state, it may decay in one of two ways: 1) after some time (called the “lifetime”) the ion will spontaneously decay into a lower energy level releasing a photon and 2) photon emitted by incoming photons (stimulated emission) [1.1-1.3]. In this case, an incident photon causes the excited atomic electron to decay back to ground state emitting a stimulated photon whose properties are identical to those of the incident photon [1.1].

Einstein was just the first of many scientists to lay the groundwork for the current status of fiber lasers. In 1953, J.P. Gordon, H.J. Zeiger and Charles H. Townes built the first maser (microwave amplification by stimulated emission of radiation) that operated under the theory of stimulated emission. They published their work a year later [1.4,1.5]. Arthur Schawlow and Townes joined forces, postulating that the principle of the maser could extend to other areas of the electromagnetic spectrum, the infrared and visible light since microwaves are only one type of electromagnetic radiation [1.6-1.9]. Figure 1.1 depicts the electromagnetic spectrum. The visible region is from ~380 nm to ~700 nm and the infrared region is ~700 nm to 1 mm [1.10].
These wavelength regions allows for the creation of the laser (light amplification by stimulated emission of radiation) which operates at those shorter wavelengths. Schawlow came up with the idea of arranging mirrors at each end of the device’s cavity creating the laser beam. This research led to Townes and Schawlow patenting the laser [1.7]. In 1964 Charles Townes shared the Nobel Prize in Physics with Alexandr M. Prokhorov and Nikolai G. Basov for their fundamental work in laser theory [1.8]. In 1981, Arthur Schawlow shared a Nobel Prize with Nicolaas Bloembergen and Kai Siegbahn for their development of laser spectroscopy [1.8].

Schawlow and Townes set the groundwork for the laser by proposing the technique for generating monochromatic radiation in the infra-red optical region of the spectrum. In 1960, Theodore Maiman implemented their work and demonstrated the first laser in optical frequencies with a ruby [1.4,1.11]. Over the next 5+ years, Elias Snitzer and he colleagues took the lead for fiber laser research. In 1961, Elias Snitzer fabricated a single
mode fiber and demonstrating the first glass laser [1.4,1.12]. That same year he also demonstrated the first fiber-based laser/amplifier [1.4,1.13]. In 1964, Snitzer and colleagues created the first optical fiber amplifier [1.4,1.14]. Shortly after, in 1965, Snitzer developed the first co-doped erbium/ytterbium glass fiber laser [1.4,1.15].

In 1966, Charles Kao and George Hockham published a land-mark paper in which they identified glass impurities as the leading cause of optical loss and theorize glass optical fibers capable of transmission losses below 20 dB/km [1.4,1.16]. Kao presented a viable solution by using glass to transmit light over long distances provided impurities could be removed to bring the glass closer to its intrinsic loss. Paired with laser technology, he laid the groundwork for optical fiber communication [1.16]. This work lead to Kao earning the Nobel Prize in Physics in 2009 for “groundbreaking achievements concerning the transmission of light in fibers for optical communication” [1.4,1.17].

After Kao’s groundbreaking work, the global challenge to make low-loss optical fibers was accepted by many, though the most noteworthy were Keck, Maurer and Schultz at Corning, MacChesney at Bell Labs, and Izawa at ITT. These teams developed the fabrication processes employed to make the bulk preforms from which optical fibers are drawn. Only a few years after Kao’s work in 1970, Corning broke the record of 20 dB/km loss with Kapron, et al. achieving a loss of 7 dB/km [1.4,1.18-1.20]. In 1971 Rich, et al. were able to achieve less than 3 dB/m using a YAG: Nd laser [1.21]. In 1972 Keck, et al., were able to achieve total attenuation coefficient values of 20 dB/km or less in three different spectral regions (633 nm, ~800 nm, and 1060 nm) [1.19]. However, ten years after Kao, in 1979, the attenuation (loss) was reduced by four orders of magnitude to reach 0.2 dB/km [1.22]. One common source of loss, particularly in holmium doped fibers (between 700 nm and
1100nm), is the OH- absorption around 1.38 µm \[1.20\]. At longer wavelengths, the attenuation (loss) increases due to the excitation of vibrational modes of the glass network \[1.23, 1.24\].

David Payne (Southampton, United Kingdom) \[1.6\] and Emmanuel Desurvire (Bell Labs) \[1.25\] were the next major contributors to the history of fiber lasers with their contributions to the development of the erbium doped fiber amplifier (EDFA) in 1986 \[1.4,1.6,1.25-1.28\]. Payne saw the need for a more efficient optical signal regeneration process. Traditionally, signal amplification happens through electronic repeaters which convert the optical signals into an electric current by a photodiode then the current is regenerated and converted back to optical light signals using a laser diode \[1.27\]. The drawbacks of this method are that the repeaters electronic speed is fixed and is very difficult to upgrade once installed (e.g., under the ocean), which limits the information rate, and wavelength multiplexing is difficult and expensive with electronic repeaters. Payne discovered that laser-diode-pumped erbium-doped fibers optical amplifiers are beneficial due to their gain around 1.55 µm, which overlaps the minimum loss spectral region for silica optical fibers used in long distance communications \[1.27\].

The global efforts that resulted in further developing the EDFA led ultimately to the development of high power fiber lasers, which are today used for a variety of manufacturing and defense applications. Rare earth (RE) doped high energy lasers (HELs) in particular, are useful for military defense applications. RE nanoparticle (NP) doped optical fibers have proven beneficial for controlling the spectroscopic properties of the glass fiber \[1.22,1.29 – 1.31\]. The following sections will discuss how optical fibers operate, how high energy lasers
work, and examples of lasers applications will be discussed. This chapter will discuss the significance of HEL for use at eye safer wavelengths and finally end with the purpose of this thesis work. This work was conducted in collaboration with the Naval Research Laboratory (NRL) in Washington, DC.

1.1 What are optical fibers?

![Schematic of an optical fiber and refractive index](image)

Figure 1.2 Schematic of an optical fiber and refractive index [1.23]

An optical fiber is a thin, typically cylindrical optical waveguide made of a centrally located core (refractive index $n_1$) surrounded by a cladding (refractive index $n_2$) as depicted above in Figure 1.2 [1.23]. This thesis will focus on optical fibers based of silica (SiO$_2$) glass specifically. Light is guided based on the principle of total internal reflection when $n_1 > n_2$. An increase in the refractive index can be obtained by doping the nominally SiO$_2$ fiber core with germania (GeO$_2$), phosphorous pentoxide (P$_2$O$_5$), and alumina (Al$_2$O$_3$). The cladding is typically surrounded by a polymer coating to protect the fiber from scratches and abrasions that would greatly reduce the fiber’s mechanical strength [1.23].
1.1.1 Benefits of Silica Glass

Some advantages for using silica glass as the principal optical fiber host are as follows: optically transparent so low loss over long distances, incredibly strong, thermal stability at temperatures greater than 1000°C, it is mechanically robust, can easily be mass produced (high yields), inexpensive, it is chemically inert, and relatively low nonlinearity [1.32-1.34]. Silica has a high thermal stability and can be drawn into fibers at temperatures of around 2000°C. Silica can be doped with various material with the purpose to raise or lower the refractive index (e.g. with GeO₂ or P₂O₅, or, with fluorine or B₂O₃ respectively) [1.35]. Nanoparticle doping silica preforms with rare earth ions is also possible for creating active fibers to be used in fiber amplifiers or fiber lasers.

1.2 Rare Earth Ions of Interest for High Energy Lasers

For this thesis, erbium (Er³⁺) and holmium (Ho³⁺) are attractive rare earth ions for doping into silica optical fibers for directed energy (DE) applications such as high energy lasers since they operate at wavelengths that are both safer to the eye and in a high atmospheric transmission window [1.24]. This allows for less scattering due to particles in the air. Most of the important atmospheric attenuators are H₂O, CO₂, clouds, fog, and aerosols in general. They exist in the atmosphere lower level, which is called the troposphere. For HELs on ships on the ocean, water is most important atmospheric attenuator through the troposphere [1.36].

Eye-safer is considered the region between ~1.5 µm and 2 µm [1.37]. Though technically not eye-safe due to the high powers employed, some degree of laser safety can be
gained by operating in this eye-safer region since the cornea, lens, vitreous- and aqueous-humor absorb the light and reduce the potential of retinal damage as shown in Figure 1.3 [1.24]. Eye damage from these wavelengths can be attributed to scattering of the laser beam due to aerosols, dust, targets, and other objects [1.38]. In addition, the high atmospheric transmission windows exist between ~1.5-1.75 µm and beyond 2 µm. Er has an emission in region near 1.5-1.6 µm while Ho has emission near 2 µm [1.24]. Holmium and erbium will be discussed later more in depth.

![Laser Damage of the Human Eye](image)

Figure 1.3 Laser damage to eye at different wavelengths [1.38]

1.3 Optical Fibers for High Energy Lasers (HELs)

In contrast to light bulbs that emit “white light”, or photons with a multitude of different wavelengths and phases in all directions, lasers produce narrow beams of single-wavelength light in a coherent beam. These narrow beams can precisely focus energy on a designated point. There are three primary types of HELs: chemical lasers; solid-state lasers;
and free electron lasers. These lasers are used for target tracking, laser pointing, thermal management, and beam control [1.39].

Fiber lasers are typically optical fibers doped with an active rare earth (RE) core as their gain media (e.g. erbium, holmium, thulium, etc…). Figure 1.4 depicts a straightforward schematic of how a fiber laser operates. The pump light is launched from a pump diode on the left through a mirror, the light is combined and sent into the active doped core fiber, and the generated laser light is extracted on the right [1.40].

![Figure 1.4 RE doped fiber laser schematic [1.40]](image)

Cladding pumping fiber lasers, shown below in Figure 1.5, have proven to be a powerful technique for power scaling fiber lasers. Instead of launching pump light into the active core, which typically is small in terms of size and numerical aperture (NA), high-power low-brightness pump light is launched into the larger (in size and NA) inner cladding. The brightness, $B$, (or radiance) of the beam is defined as

$$B = \frac{P}{A\Omega}$$

Where $P$ is the beam power per unit area ($A$) and unit solid angle ($\Omega$). For a circular cross-section $A=\pi r^2$ and $\Omega = \pi NA^2$, where $r$ is the radius [1.41]. The angle $\theta$, at which light is
accepted into the inner cladding is determined by the NA which is dependent upon the refractive indices for the fiber claddings, \( n_0 \) and \( n_1 \)

\[
NA = n_0 \sin \theta = \sqrt{n_0^2 - n_1^2} \ [1.42].
\]

As the pump light propagates down the fibers inner cladding, it interacts with the signal light and is gradually absorbed by the active RE core and converted into laser light. Light propagation occurs due to total internal reflection from the refractive index difference between the outer cladding and inner cladding [1.41]. The generated light is efficiently trapped inside the much smaller sized core area and lower NA core, resulting in laser light that is has low NA output yielding a high brightness, low divergence, single mode beam [1.42].

![Figure 1.5 HEL schematic [1.41]](image)

### 1.4 Laser Applications

The below subsections will discuss examples of laser applications. These applications consist of welding, cutting, and manufacturing.
1.4.1 Automotive Applications

![Image of laser welding](image)

**Figure 1.6 Welding of car parts [1.43]**

The highly directional beam of a laser can be focused to a microscopic spot of high energy which is extremely beneficial in the automotive field where lasers are commonly used for welding and cutting parts. Modern high power lasers are key to efficient production engineering in the automotive industry. The automotive industry typically uses carbon dioxide (CO₂) lasers with high beam quality, easily scalable, stable welding and relatively low operational costs [1.44]. Figure 1.6 above, depicts a roof of a motor vehicle being welded to the vehicle body using a laser [1.43].

1.4.2 Biological Applications

![Image of LASIK eye surgery and stent fabrication](image)

**Figure 1.7 LASIK eye surgery [1.45] (left) and stent fabrication (right) [1.46]**
Due to their precise nature, lasers are commonly used in the bioscience field for LASIK surgery and stent fabrication depicted in Figure 1.7. LASIK is a medical procedure intended to reduce a person’s dependence for glasses by permanently changing the shape of the cornea using a laser to cut a flap in the cornea. A hinge is left at one end of this flap, then the flap is folded back revealing the middle section of the cornea, the stroma. Pulses from a computer-controlled NIDEK Excimer laser vaporize a portion of the stroma and the flap is replaced [1.46,1.47]. Another medical application is in the creation of stents which are commonly used for treating cardiovascular diseases. The process of manufacturing metal stents is challenging due to their geometric designs. Precise laser cutting is a crucial aspect of stent production in the medical field. The high beam quality of the fiber laser allows for a very small focus diameter and small cut widths making it an excellent tool for micro-cutting stents [1.48].

1.4.3 Energy Applications

Figure 1.8 Drilling for oil wells [1.49]
The use of lasers in the oil and gas industry has shown benefits for the fabrication of structures, welding and cutting pipelines, and drilling of the oil and gas wells. The high-power laser drill in Figure 1.8 operates by delivering the high-power laser beam to the rock surface and quickly heating it to very high temperatures. As one practical example, Foro Energy created this drill that combines laser power with a mechanical drilling bit. The thermal shock breaks the rock a couple of millimeters into the surface, then the mechanical drill clears it away [1.49].

1.5 Directed Energy (DE) Laser Applications

“Directed energy” is an umbrella term for technologies that produce a beam of concentrated electromagnetic energy. DE uses various wavelengths of the electromagnetic spectrum to travel at the speed of light so it is not impeded by gravity [1.50]. This is beneficial for military applications because it allows for precise targeting, instant effects, and provides the possibility of long-range usage. DE is extremely versatile allowing for incorporation into satellites, perimeter security systems, aircraft, and ground vehicles as directed energy weapons (DEWs). The U.S. Department of Defense defines DEWs as a “system using directed-energy, primarily as a direct means to damage or destroy enemy equipment, facilities, and personnel” [1.50].

High energy lasers (HELs) previously discussed in Section 1.3 also fall under this category of directed energy. Figure 1.9 below depicts applications of HELs in practical military use with the laser on the top of a Humvee and the Humvee body is the power source, fighter airplane, and a ship to shoot down targets at far distances. Since laser beams
travel at the speed of light, they provide immediate target detection information to the soldiers. The coherence of laser beams provide a highly focused energy which causes physical destruction to the structures. These weapons are able to engage multiple targets with few mechanical parts since they are constantly powered and reloaded by electrical and chemical power. Lasers weapons are also beneficial because they provide promising and cost-effective solutions for tactical missions [1.51].

![Figure 1.9 HEL examples [1.51]](image)

### 1.8 Purpose

In short, the purpose of this research is to create an efficient nanoparticle doped fiber that can be used as a high energy fiber laser or amplifier at eye safer wavelengths. Another focus of this research is to investigate the optimal conditions for synthesis of nanoparticles for doping optical fibers for fiber lasers. There are two common ways to
solution dope optical fibers: 1) traditional solution doping and 2) nanoparticle doping. Traditional solution doping tends to create agglomerates decreasing the efficiency of the fiber. This method also allows no mechanism for controlling the molecular environment about the RE$^{3+}$ ions when solution doped into the homogeneous glass [1.24]. However, in nanoparticle doping the nanoparticles can serve to isolate the dopant from the influence of the silica glass. The rare earth ions are “encapsulated” within the nanoparticle host [1.24]. NP doping can be used to tailor the environment around the RE and has proven the ability to enhance lifetimes, broaden emission spectra and enhance energy transfer [1.22,1.29,1.52].
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1.50 U.S. Joint Chiefs of Staff, Electronic Warfare, 106.
CHAPTER TWO
NANOPARTICLE SYNTHESIS AND CHARACTERIZATION

As mentioned previously, this research will employ a nanoparticle doping technique to fabricate rare earth (RE) doped optical fibers for high energy lasers. This chapter will discuss the synthesis process and characterization of the nanoparticle doped suspensions. This chapter begins with the selection of the nanoparticle host material, then discusses the fabrication of the nanoparticle (NP) and its suspension. The optimal pH when creating the nanoparticles in this research was determined through a stability study. The suspension characterization methods to be discussed include the following: dynamic light scattering (DLS), transmission electron microscopy (TEM), and X-ray diffraction (XRD).

2.1 Host Selection

Lanthanum fluoride (LaF₃) was chosen for the host material for this research since the synthesis of small nanoparticles (<10 nm) that exhibit the appropriate lanthanide emissions is well established within the Ballato Group [2.1, 2.2, 2.3]. The local environment, phonon energy, around the RE³⁺ can be tailored by incorporating it within a suitable nanoparticle that then is dispersed into the silica matrix. As long as the NPs are small and not-agglomerated, one can achieve the low loss and high strength associated with the silica host while also exhibiting the reduced phonon energy of the NP. In the case of LaF₃, the maximum phonon energy is ~350 cm⁻¹ [2.4]. It should be noted that the fluoride nanoparticles (LaF₃) are expected to convert to oxides at the elevated temperatures used to
process the subsequent silica preform. At temperatures above 2000°C where the preforms and fibers are processed, the fluoride will oxidize and the rare earth will be in an environment with heavier metal ions than that of the silica host. The La$_2$O$_3$ has a phonon energy of $\sim$400 cm$^{-1}$ which is still lower than silica (1100 cm$^{-1}$) [2.5].

2.2 Ligand Selection

In the field of chemistry, a ligand (or surfactant) is defined as a molecule made up of two regions: one part polar (a dipole or charged head) and the other non-polar (usually hydrocarbon chain) [2.6]. In this research the ligand employed was citric acid (C$_6$H$_8$O$_7$). Ligands are typically used to improve the ability of the NPs to suspend in the solvent, control growth/size of the particles, prevent clustering of NPs, and in some cases improve luminescence [2.7,2.8, 2.9]. This is accomplished by “encapsulating” the rare earth NPs with ligands which are typically composed of a polar organic “head” which attaches to the NP surface and a nonpolar alkyl hydrocarbon “tail” (Figure 2.1). Figure 2.1 depicts the ligand particle interaction mentioned previously. The chemical process behind this ideology will be discussed in the following section.
2.3 Nanoparticle (NP) Synthesis

The recipe for the suspensions employed in this Thesis originated from V. Sudarsan, et al., [2.10] and an example recipe can be found in the Appendix A. This section will discuss the recipe for one representative nanoparticle suspension (AV-47-41; Eu:LaF3; pH6). The relative amounts of La(NO3)3 and RE(NO3)3 will change depending on the doping concentration. To begin the suspension synthesis process, a triple neck flask was used to prepare a fluorinated ligand solution of 0.4444 g of ammonium fluoride (NH4F; Fisher Scientific), 2.3055 g of citric acid (C6H8O7; Alfa Aesar, anhydrous, 99.5%) and 160 mL of ultra-pure (UP) water (setup shown in Figure 2.2 below). Ultrapure water was obtained from a Barnstead Nanopure Diamond water purifier. UP water is purified water where microbial, inorganic, and organic contaminants are removed and the remaining water is “polished” to
remove remaining contaminants (ions). The water should have a resistivity approaching 18.2 MΩ-cm at 23°C [2.11].

Figure 2.2 Schematic of suspension in triple neck flask on hotplate

The fluorinated ligand solution was placed in a hot water bath at 70°C inside of a glass dish ¾ full of water and condenser balls to prevent the water from evaporating. A stir bar was placed in the triple neck flask to continuously stir the suspension, around 500 rpm, until the suspension appeared clear. The rare earth suspension was comprised of 0.5353 g of europium (III) nitrate hexahydrate (Eu(NO₃)₃•6H₂O; Alfa Aesar, 99.9%), 1.2124 g of lanthanum (III) nitrate hexahydrate (La(NO₃)₃•6H₂O; Alfa Aesar, 99.99%) as the host for the rare earth solution (RE solution), and 4 mL of UP water. The RE solution of host material nitrate, rare earth dopant nitrate, and UP water was made in a centrifuge tube while the fluorinated ligand solution was being stirred and reaching the appropriate temperature. The centrifuge tube was sonicated until the nitrates were completely dissolved. Before testing the pH of the fluorinated ligand solution, the pH reader was calibrated using buffer solutions of 4.01, 7.00, and 10.01. Then the pH of the fluorinated ligand solution,
which was originally around 2.90, was adjusted dropwise to 5.15 using ammonium hydroxide (NH₄OH; British Drug Houses) to control particle size and to create space for ligand to join. Once the pH is adjusted the first time, the rare earth solution was added dropwise close to the center of the vortex. The suspension typically appears to have a cloudy haze when dropping in the RE solution; this is due to the formation of the nanoparticles. The pH is measured again once all of the rare earth solution had been added and is readjusted to a pH of 5.15. The combined suspension then stirs for 1.5 hours at 70°C and is cooled to room temperature.

2.4 Results and Discussion

This section will discuss the analysis of RE doped NPs in suspension form starting with phase identification using XRD to confirm the presence of the LaF₃, followed by stability studies to find optimal suspension synthesis conditions, and ending with TEM to confirm NP size and DLS results.

2.4.1 X-ray Diffraction (XRD)

Figure 2.3 Schematic of XRD [2.12]
XRD was performed using a Rigaku MiniFlex 6G x-ray diffractometer to determine a specimen’s crystal structure by comparing the specimen’s diffraction spectrum with International Center for Diffraction Data (ICDD) database containing over 60,000 diffraction spectra. XRD can also help identify the chemical compounds present. As depicted in Figure 2.3, x-ray radiation from x-ray tube passes through the Soller slits which are made from a set of closely spaced tin metal plates that align the x-ray beam. The divergent x-ray beam passing through slits strikes the specimen and x-rays are diffracted to form a convergent beam at the receiving slits before passing through a monochromatic filter and then the detector [2.12].

Bragg’s law is the condition for diffraction that is used to determine the angle of light diffraction off a specimen:

\[ n\lambda = 2d_{hkl}\sin\theta \]

Where \( n \) (an integer) is the order of reflection, \( \lambda \) is the characteristic x-ray wavelength, \( h, k, l \) are Miller indices related to the particular sample, \( d_{hkl} \) is the interplanar spacing between the planes of atoms (A and B in Figure 2.4), and \( \theta \) is the angle of scattering relative to the planes A and B. If Bragg’s law is not satisfied, the diffracted beam will be very low-intensity due to the deconstructive interference [2.13].
The XRD conditions for this research are as follows: CuK\(_\alpha\) radiation source (Cu K\(_\alpha\) radiation (\(\lambda=1.54059\ \text{Å}\)), from 5-65 °2\(\theta\), and steps at 0.02 °2\(\theta\). Figure 2.5 shows the XRD pattern for the LaF\(_3\) nanoparticles. The pattern exhibits the prominent characteristic peaks of the LaF\(_3\) hexagonal structure (top image) found in the ICDD database. The broad diffraction pattern of the sample peaks is typical of very small crystals [2.14]. The XRD results verifies the successful formation of LaF\(_3\). (002) and (110) planes overlap to make the first AV-47-83 peak, 1. AV-47-83 peak 2 matches arises from the (111) reflection. Peak 3 is the combined low intensity index (112). (300) and (113) planes are combined to make peak 4 in the sample. The (004), (302), (220), and (221) planes combined to make the broad peak 5. (311), (114), and (222) planes combine to make the low intensity broad peak 6. Peak 7 shows the characteristic peak of the (223) plane. Sample peak 8 displays the characteristic peaks of (311), (114), and (222) indices. All of the sample peaks combine suggest the successful incorporation of LaF\(_3\) when compared to the PDF card from the ICDD database.
Figure 2.5 X-Ray diffraction pattern from ICDD database (top) compared to sample pattern (bottom)
2.4.2 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) was used to determine the particle size in the nanoparticle doped suspensions. Figure 2.6 depicts a simple schematic of a TEM which has the following components along its optical path: light source, condenser lens, specimen stage, objective lens and projector lens [2.15]. For this research, TEM was preformed using a Hitachi H7600 with 120 kW acceleration velocity. Sample preparation included placing a single drop of the nanoparticle suspension on a 200 mesh copper grid from Ted Pella. Representative TEM images of doped LaF$_3$ are depicted in Figure 2.7 below. The average NP size was approximately 11 nm, confirming they are indeed “nanoparticles”.

Figure 2.6 Schematic of transmission electron microscope and optical path [2.15]
2.4.3 Dynamic Light Scattering (DLS)

Dynamic light scattering (DLS) is a technique commonly used to determine particle size in a suspension. Particles suspended in a liquid solvent typically undergo random Brownian motion (particles random movement in a fluid) causing light to be scattered [2.16]. The magnitude of the scattering vector q is expressed as
where $\theta$ is the scattering angle of light, $\lambda$ is the wavelength of light in the medium, and $n$ is the refractive index in the solution [2.16, 2.17]. The particle size is determined using the Stokes-Einstein equation

$$D_H = \frac{kT}{3\pi\eta D}$$

where $D_H$ is the hydrodynamic diameter, $k$ is Boltzmann’s constant, $T$ is temperature, $\eta$ is the viscosity, and $D$ is the translational diffusion coefficient [2.18]. Although DLS determines the particle size, it is not the genuine particle size but rather the correlation of the particle and the movement within liquid. The hydrodynamic diameter depicted in Figure 2.8 is the particle diameter + the electrical double layer. The electric double layer is a two-layer representation of the ion distribution at the surface between the solid (negative charge) and the solvent in suspension. The first layer, the Stern layer, consists of a dense layer of ions of the opposite charge around the NP [2.19]. In this research, the tail of the ligand (citric acid) forms the Stern layer. The second layer is the diffuse layer which is the charged atmosphere of ions of the opposite charge to the NP. The high concentration of counter ions within the diffuse layer gradually decreases with increasing distance from the nanoparticle until equilibrium is reached [2.19].
Figure 2.8 Hydrodynamic diameter [2.19]

A Malvern Zetasizer DLS was used for a suspension stability studies at different pH levels to determine the optimal pH for doped colloidal stability. Doped lanthanum fluoride was initially used in this study then the host material was changed (different host material study in Appendix B). DLS was also used to estimate the particle size based on the hydrodynamic diameter. For this study, samples were dispersed in ultra-pure water (n=1.330) inside of a disposable cuvette. Measurement specifications are as follows: T= 25.0 °C, viscosity= 0.8872 cP, light scattering angle= 173°. 70 measurement scans were taken, once every 10 minutes, for a total measurement duration of about 12 hours.

Graphs of the DLS pH stability study data over a 12 hour period can be seen in Figures 2.9-2.11. The 12 hour time period allows for the sample to settle and aggregate over time, increasing the hydrodynamic diameter size. Aggregation occurs in these samples due to the increasing population of larger particles. The rare earth nanoparticle suspensions used for this analysis were the aforementioned doped lanthanum fluoride with different pH levels.
of 4, 6, 9, which were arbitrarily chosen to have a high, medium, and low pH. A hydrodynamic diameter of $<50$ d.nm (Z-average of diameter in nanometers) is desired to form nanoparticles around 10 nm as was confirmed with the TEM results in section 2.4.2. Figure 2.9 (pH 4) shows an average hydrodynamic diameter particle size of about 500 d.nm which is larger than desired. Figure 2.10 shows the pH 6 suspension with an average hydrodynamic diameter around 45 d.nm which is close to the desired. Figure 2.11 (pH 9) shows a very unstable suspension, with particle sizes varying greatly over time. A pH value of 6 was determined to be the optimal pH for the formation of a “stable” solution since it demonstrates the desired particle size and most uniform particle distribution under 100nm over the 12 hour time study. pH values of 4 and 9 visibly appear white/cloudy and precipitate out of suspension. pH 6 suspension typically stay clear and in suspension.

![DLS Stability Run pH 4 in Water Eu:LaF₃](image)

**Figure 2.9 DLS of RE NP pH 4 suspension diluted in water**
Figure 2.10 DLS of RE NP pH 6 suspension diluted in water

Figure 2.11 DLS of RE NP pH 9 suspension diluted in water
2.5 Conclusion

In conclusion, XRD confirms the successful formation of the host material (LaF₃) by comparing sample XRD spectrum results to the ICDD database powder diffraction files. TEM results confirmed the expected nanoparticle size with an average around 10 nm. DLS data showed that pH 6 is optimal for LaF₃ nanoparticle synthesis with the best particle stability. Due to the results from the TEM, XRD, and DLS data, the LaF₃ nanoparticle suspension with a citric acid ligand will be solution doped and studied further.
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CHAPTER THREE
ERBIUM NANOPARTICLE DOPED FIBER FABRICATION AND CHARACTERIZATION

The research conducted as part of this Thesis employs a nanoparticle doping technique to fabricate rare earth (RE) doped optical fibers for high energy lasers. This chapter begins by discussing the difference between traditional solution doping and nanoparticle solution doping techniques. Fiber fabrication will follow with how the preforms were produced using the modified chemical vapor deposition (MCVD) method, how the nanoparticles were doped into the preform using the in-situ solution doping method and, finally, the fiber draw process. This chapter will finish with fiber characterization. The characterization techniques used in this research include the following: scanning electron microscopy (SEM) with energy dispersive x-ray (EDX), preform and fiber refractive index profiling (RIP), fiber absorption, and fiber amplification efficiency using a master oscillator power amplifier (MOPA). This chapter will specifically discuss erbium (Er$^{3+}$) results.

In an attempt to optimize the spectroscopic properties of the rare earth ions, solution precipitation chemistry was employed to create the desired suspensions. Multiple fibers and suspensions were produced and used for testing. Since specific concentration details are proprietary to the Naval Research Laboratory (NRL, Washington DC), while many preforms were fabricated, NRL samples will be specified based on the data they made available for use.
3.1 Solution doping vs. Nanoparticle (NP) doping

 Particularly as relates to power-scaling fiber lasers to output powers > 100W, the concentration of laser active RE\(^{3+}\) ions in the fiber should be increased, both to minimize the active fiber length in order to reduce nonlinear processes and to enable clad pumping. This is a great concern for RE\(^{3+}\) ions that have complex energy level structures (erbium, specifically, for this chapter) [3.1]. The energy levels for the trivalent RE ions can found below in Figure 3.1.

![Energy level diagram for rare earth ions](image)

Figure 3.1 Energy level diagram for rare earth ions [3.2]
For dopants with more complex electronic energy level structures, increased RE\textsuperscript{3+} concentrations can facilitate the unwanted excited state energy transfer processes and can lead to concentration quenching since the RE\textsuperscript{3+} ions are, on average, closer to each other in the host when doped at higher concentrations. However, in nanoparticle doping of silica fibers, the rare earth ions are encapsulated within the nanoparticle host, which ideally separate them from one another [3.1]. This section will discuss the differences of traditional solution doping versus nanoparticle doping of optical fibers. Going forward, RE nanoparticle doping will be the doping technique used in this research.

3.1.1 Traditional Solution Doping

Fabrication of rare earth (RE\textsuperscript{3+})-doped optical fibers typically is performed using the traditional solution doping technique where the appropriate salts, such as erbium chloride (ErCl\textsubscript{3}) and aluminum chloride (AlCl\textsubscript{3}), are added to reduce RE clustering in the resultant oxide glass [3.1-3.6]. These rare earth salts are dissolved in a solvent, typically water, and introduced into a layer of porous silica soot (porous SiO\textsubscript{2}) on the inside of the (MCVD) preform. The Al\textsubscript{2}O\textsubscript{3} (from the oxidation of the AlCl\textsubscript{3}) in the resultant glass acts to reduce Er\textsubscript{2}O\textsubscript{3} (from the ErCl\textsubscript{3}) concentration quenching in one of two ways: (1) rare earth cluster dispersion with enhanced solubility, creating a more homogeneous distribution of the rare earth in the glass or (2) rare earth dopants partition into alumina-rich microscopic regions in the glass yielding a preferred local modification to the rare earth environment [3.5]. While solution doping works well and is the method-of-choice for a very wide variety of active fibers, ranging from the ubiquitous erbium doped fiber amplifier (EDFA) to the high power...
Yb fiber laser, it provides no mechanism for controlling the molecular environment around the RE$^{3+}$ ions in the glass [3.1,3.6]. As the neighboring ion-ion distance decreases, the probability of ion-ion interaction increases, which results in excited state energy transfer processes, such as upconversion and quenching, greatly reducing laser efficiency [3.1].

3.1.2 Nanoparticle (NP) Doping

The introduction of rare earth ions into the glass matrix also can be realized through the use of nanoparticle (NP) doping, where the RE ion is incorporated into the NP, and the NP is then doped into the silica glass soot of the nascent preform [3.7]. Nanoparticle doping is used to provide an added level of influence over the local chemical environment about the RE, which permits tailoring of energy transfer and radiative and non-radiative spectroscopic dynamics [3.8]. As mentioned previously, in nanoparticle doping, the NP is “isolated” within the glass host (core of the optical fiber), which allows for the RE ions to be separated in the host to reduce ion-ion interactions that can lead to quenching. This is also beneficial because the silica lattice will not influence the REs behavior since the NPs serve to “isolate” the dopant from the SiO$_2$ glass. While the use of NPs offers a means to reduce the effects of concentration quenching of the RE ions, they also offer a means to tailor the local environment of the rare earth ion [3.7]. Previous NP doping using LaF$_3$ hosts done by Kucera, et al., [3.9] demonstrated tailored emission spectra, indicating effective isolation of RE$^{3+}$ ions. NP doping provides a means to introduce heavy metal species into the glass host for the effective reduction of phonon energy (near the active ion) [3.10], but in a relatively small quantity still enabling a relatively low fiber numerical aperture (NA) [3.11].
3.2 Fiber Fabrication Process

The following subsections will discuss the preform solution doping process and fiber draw process. The solution doping step will be broken into two parts to discuss the NRL in-situ method compared to Clemson University’s conventional method for solution doping preforms.

3.2.1 Silica Soot Formation

The global challenge to produce low-loss optical fibers was accepted by many, though the most successful were those by Corning (Corning, NY), Bell Labs (Murray Hill, NJ), and ITT (Tokyo, Japan). These teams developed the fabrication processes to make bulk preforms from which optical fibers are drawn. The main processes can be categorized as being chemical vapor deposition (CVD) methods with Corning developing the outside vapor deposition (OVD) method, Bell Labs developing the modified chemical vapor deposition (MCVD) method, which is used in this research, and ITT developing the vapor axial
deposition (VAD) method. Each CVD method uses the same basic chemistry, involving the thermochemical oxidation of a volatile halide [3.13]. For this research, an SC Control Ltd. MCVD lathe was used.

Figure 3.3 Porous silica soot imaged using an SEM [3.14]

The MCVD process is described in this section and the following three subsections, beginning with the formation of the silica soot and its deposit. Before the doping process can begin, the glass substrate tube (Heraeus Quarzglas 19 mm inner diameter x 25 mm outer diameter x ~500 mm long fused silica tube) is attached to the exhaust tube on the tail-stock side of the lathe and the input tube (gas flow tube) on the head-stock side of the lathe. After this glasswork setup, the preform substrate tube is cleaned by a traversing hydrogen-oxygen carriage flame down the outside length of the preform while sulfur hexafluoride (SF$_6$) flows through the inner surface. The gas flow set up for this process are shown in Figure 3.2. Once the substrate tube is cleaned, a porous silica soot is deposited. Figure 3.3 depicts the
porous silica soot that is deposited on the inside of the glass tube due to the following chemical reactions of the gasses:

\[ \text{SiCl}_4 \text{ (g)} + \text{O}_2 \text{ (g)} \rightarrow \text{SiO}_2 \text{ (s)} + 2\text{Cl}_2 \text{ (g)}. \]

During this process a mixture of oxygen gas (O₂), silicon tetrachloride gas (SiCl₄) and occasionally other high purity gases (e.g. germanium tetrachloride (GeCl₄) and phosphorus oxychloride (POCl₃) to increase the refractive index and fluorine (F) and boron trichloride(BCl₃) to decrease the refractive index [3.12]) are passed through a rotating silica glass tube, which is heated with a traversing oxygen-hydrogen flame to a temperature of at least 1350 °C. This process may be repeated depending on the number of layers needed for a given fiber design. Once the silica soot is cooled, the preform is ready for solution doping. Although beyond the scope of this Thesis, the interested reader is referred to the following seminal review articles of the MCVD process and its history [3.15-3.18]. The following two subsections will discuss the two different nanoparticle doping techniques used in this research.

3.2.2 NRL In-situ Solution Doping Process

Figure 3.4 NRL NP in-situ doping [3.14]
Once the silica soot is cooled, the preform is ready for in-situ solution doping where the lathe is set up to an angle of about 30˚ (as seen in Figure 3.4) and the NP suspension was pumped into the preform at a rate of about 10 mm/min. Then the tube was set to rotate slowly (0.5 RPM) for 75 minutes to soak the porous soot layer with the NP suspension. Once this soaking stage was complete, the suspension is drained from the preform and the computer program associated with the deposition recipe is continued to dry the preform.

### 3.2.3 Clemson Solution Doping Process

![Figure 3.5 Clemson NP doping](image)

Once the silica soot core layers are deposited, the preform was ready for solution doping. The preform was carefully removed from the lathe and placed vertically in a holder as shown in Figure 3.5. About 200 mL of the nanoparticle suspension was pumped into the preform at a rate of ~20 mL/min and left to soak for 60 minutes. Once the soot was
soaked, the preform was drained, and the preform was reattached to the lathe for the fabrication process to continue.

3.2.4 Preform Fabrication

After the preform’s doped core is dried, the process can continue to consolidate, or sinter [3.12], the soot and collapse the porous core into a solid glass. The consolidation, sintering to form a solid glass rod (comprising both the doped core and the pure silica cladding), occurs at a temperature in excess of 1700°C. During the collapse step, the oxyhydrogen torch traverses the rotating glass tube creating a local hot zone where the glass softens to promote viscous flow of the tube walls [3.19]. This causes the core to collapse and for a solid glass rod called the preform. The preform is collapsed within several passes from a 25 mm outer diameter to a 12 mm diameter at a temperature in excess of about 2000°C. Once the preform is cooled to room temperature it is carefully detached from the lathe. The presence of nanoparticle in the preform core has been verified using SEM and a representative image is shown in Figure 3.6.

Figure 3.6 SEM of a nanoparticle doped core [5.20]
3.2.5 Fiber Draw

Optical fiber was drawn following the schematic provided in Figure 3.7. First the glass preform was lowered into the furnace where the temperatures were controlled, ranging from about 1900°C to 2100°C for a silica-based preform. At these temperatures, the preform tip is sufficiently above its glass transition temperature to viscously deform allowing a small piece of glass to fall from the tip of the preform. This creates a neck-down region, which stretches the preform rod from around 12 mm diameter into a thin strand, the optical fiber, with an outer diameter around 125 µm. Then the operator threaded this strand of fiber through the coating dye, which ultimately applies a polymer coating to the glass in order to protect the fiber during subsequent use, then the coating is cured using an
ultraviolet lamp. The fiber was pulled by a tractor belt (capstan) situated at the bottom of the draw tower and then wound onto a fiber spool [3.21]. The diameter monitors were used to monitor the diameter of the fiber and maintain a diameter of about 125 µm. For the preforms fabricated as part of this Thesis, the outer glass diameters of the fibers typically yield a core diameter of about 12 µm.

### 3.3 Results and Discussion

This section will discuss the analysis of RE doped fibers starting with elemental analysis using energy-dispersive x-ray spectroscopy (EDX) on a scanning electron microscope (SEM). Then preform refractive index profile, fiber refractive index profile, fiber rare earth absorption, and finally testing fiber performance, amplifier efficiency, with a master oscillator power amplifier (MOPA) will all be discussed, and results will be given. The fibers to be discussed in both this chapter and elsewhere in this Thesis are listed in Table 3.1.

<table>
<thead>
<tr>
<th>Fiber Name</th>
<th>Fiber Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>DB17616 (Clemson)</td>
<td>Er:LaF$_3$</td>
</tr>
<tr>
<td>(Preform LA17416)</td>
<td>NP Doping</td>
</tr>
<tr>
<td>NRL 171107</td>
<td>Er/La</td>
</tr>
<tr>
<td></td>
<td>NP Doping</td>
</tr>
<tr>
<td>NRL 170901</td>
<td>Er/Yb</td>
</tr>
<tr>
<td></td>
<td>Soln Doping</td>
</tr>
</tbody>
</table>

**Table 3.1 Fiber Composition**
3.3.1 Scanning Electron Microscopy (SEM)/ Energy-dispersive X-ray spectroscopy (EDX)

![Figure 3.8 SEM configuration [3.22]](image)

To analyze the composition of the preform and fiber, energy-dispersive x-ray spectroscopy (EDX) along with a scanning electron microscope (SEM) was used. The schematic in Figure 3.8 shows the main components of the SEM. The SEM works by scanning an electron beam across a surface to create an image with a finely converged electron beam that detects the signals produced from the sample to create and image [3.22]. Low-energy secondary electrons excited on the sample’s surface are the most common signal detected. High-energy backscattered electrons and X-rays are emitted from below the specimen surface with elemental specific information [3.23]. EDX spectra are analyzed using Inca software from Oxford.
For this research the Hitachi SU6600 SEM was used. The SEM operated at an acceleration voltage of 15 kV with a 10 mm working distance under variable pressure because the samples were not conductive. The Clemson erbium doped lanthanum fluoride (Er:LaF$_3$) nanoparticle fiber listed in Table 3.1 was created and analyzed using EDX with SEM for this research. Figure 3.9 shows the line scan of the preform sample with 11 data points. The data points correlate to graph points in Figure 3.10. Figure 3.11 is the line scan of the Er:LaF$_3$ fiber (DB17616) with 11 data points across the core of the fiber. These points relate to the points on the compositional analysis graph (Figure 3.12). The EDX graphs confirmed the successful incorporation of the RE (erbium) and host (lanthanum) into the preform and the fiber. A line scan was performed across the core of both and the elemental concentration was determined at each spot along the line scan. Figures 3.10 and 3.12 have a dip in the graph due to the germania vaporizing [3.24].

![Figure 3.9 Preform LA17416 SEM image](image-url)
Figure 3.10 Preform LA17416 EDX analysis. Note that SiO$_2$ is not shown to more clearly focus on the core dopant concentrations.

Figure 3.11 Fiber DB17616 SEM image
Figure 3.12 Fiber DB17616 EDX results. Note that SiO₂ is not shown to more clearly focus on the core dopant concentrations.

3.3.3 Preform Refractive Index Profile (RIP)

Figure 3.13 Preform refractive index profiler
In a conventional optical fiber, the transmission of light through a waveguide is achieved with a core of higher refractive index surrounded by a cladding. This can be achieved by doping the core with elements that increase the refractive index or by doping the cladding with elements that decrease the refractive index. Refractive index profiling systems are used to give dimensional information such as core diameter and maximum index difference, which is related to the numerical aperture (NA) [3.25].

The normalized frequency (V, also called the V-number) for a waveguide can be derived from the refractive index profile, defined by:

\[
NA = \sqrt{(n_1^2 - n_2^2)}
\]

\[
V = \frac{2\pi}{\lambda} a NA
\]

where \(n_1\) is the refractive index of the core, \(n_2\) is the refractive index of the cladding, \(a\) is the core radius, and \(\lambda\) is the wavelength of light [3.26]. The numerical aperture (NA) is the measure of light that can be collected by an optical fiber (or lens) [3.27]. The V-number determines the number of modes the fiber will support [3.26].

For this research the Photon Kinetics system P104, Figure 3.13, preform analyzer was used to determine preform refractive index profile at a wavelength of 633 nm and refractive index fluid cell (n=1.458). This preform analyzer uses a (633 nm) laser scanning across the width of the preform in a cell full of a known refractive index oil to make its measurements. The laser beam passes at an angle deflected due to the preforms refractive index profile. The preform refractive index profile is used to determine the quality, characteristics, and draw specifications for the optical fiber. It is used to predict the light transmission characteristics of the fiber that is ultimately drawn from the preform and
provide dimensional information that is necessary to guide the final preform manufacturing processes.

Figure 3.14 is the refractive index profile of an erbium nanoparticle doped preform (NRL 171107). This preform has a fiber core of 0.945 mm and a cladding diameter of 12.09 mm with a clad/core ratio of 12.79. This preform was drawn into a fiber. Table 3.2 lists the preform and fiber specifications.

![Refractive index profile of NRL 171107](image-url)

**Figure 3.14 Refractive index profile of NRL 171107**
<table>
<thead>
<tr>
<th>Preform</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Core diameter</td>
<td>Clad diameter</td>
</tr>
<tr>
<td>0.945 mm</td>
<td>12.09 mm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fiber</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Core radius</td>
<td>Cutoff wavelength</td>
</tr>
<tr>
<td>3.28 µm</td>
<td>1.35</td>
</tr>
<tr>
<td>Core diameter</td>
<td>OD</td>
</tr>
<tr>
<td>6.6 µm</td>
<td>83.9 µm</td>
</tr>
</tbody>
</table>

Table 3.2 NRL 171107 Preform and fiber specifications

3.3.4 Fiber Refractive Index Profile (RIP)

The fiber refractive index profile was obtained by comparing the fiber to an oil of known refractive index (n=1.460 at 589 nm) using the instrument depicted in Figure 3.15, an
Interfiber Analysis IFA100 Optical Fiber Analyzer. There are several options for measuring the profile and calculating the MFD etc... but for this research, the fiber profile was measured at 950 nm. The system calculated the mode field diameter (MFD) and the effective area \( A_{\text{eff}} \) at 1534 nm, as is shown in Fig. 3.18.

The MFD is a measure of the transverse extent of the light mode’s intensity guided in a fiber. MFD can be determined using the Petermann II method, which uses the actual intensity distribution over the range of far field angles [3.28, 3.29]. MFD defines the light edges as they reach a value of \( \frac{1}{e} \) their initial intensity since it partially propagates into the cladding [3.29]. If the core has a high refractive index, a large index difference, then the MFD is smaller than the core diameter and vice versa. MFD and \( A_{\text{eff}} \) are both wavelength dependent [3.30]. \( A_{\text{eff}} \) calculates the cross-sectional area of the near-field intensity distribution across the fiber [3.28].

Figures 3.16 – 3.18 are the fiber refractive index profile information for NRL NP-doped fiber 171107. Figure 3.16 is the 2-D refractive index profile of the fiber, while Figure 3.17 is the 1-D cross-section that was selected and fed into the mode solver software. This fiber has a core radius of 3.28 \( \mu \text{m} \), a core diameter of 6.6 \( \mu \text{m} \), and an outer diameter of 83.9 \( \mu \text{m} \). This fiber has a \( n_{\text{core}} = 1.470764 \) and \( n_{\text{clad}} = 1.446772 \) at a \( \lambda = 1.534 \mu \text{m} \). As seen in Figure 3.18, the MFD calculated is 7.6 \( \mu \text{m} \) and the \( A_{\text{eff}} = 43.4 \mu \text{m}^2 \). Based on the equation above, the NA for this fiber was 0.26456 yielding a V value for this fiber is 3.55. Since this value exceeds V = 2.405, which is the cut-off condition for a cylindrical waveguide to be single mode, then this particular fiber is multimoded. Though the fiber’s modality is not critical for the purposes of the exploratory research of this Thesis, this calculation was given as an
example of how the fiber fabrication and characterization methods described above come together to define the light-guiding characteristics of the fibers fabricated.

Figure 3.16 NRL 171107 2-D refractive index profile

Figure 3.17 1-D refractive index cross-section
3.3.5 Fiber Absorption Measurement

![Figure 3.18 Mode solver software calculations](image)

![Figure 3.19 Optical spectrum analyzer](image)
The absorption associated with the erbium-doped core was measured using the cutback method with an Agilent 83437A EELED source and an Ando 6315 optical spectrum analyzer (OSA) shown in Figure 3.19 above. The absorption of \( \text{Er}^{3+} \) in the core serves as a good measure of the erbium concentration in the fiber [3.31]. The absorption spectrum is created by plotting the attenuation (dB/m) versus wavelength (nm). The initial fiber length for attenuation measurements is selected by the approximated RE concentration in fiber. The cutback method measures the optical power transmitted through a long piece of fiber compared to the power through a short piece [3.32]. For this research, the initial fiber length was 1 m and the cutback length was 0.5 m so the absorption is measured per meter at a precisely determined length.

NRL 171107, shown in Figure 3.21, has a relatively high erbium core absorption of 35.7 dB/m at 1530 nm.

Figure 3.20 Erbium core absorption spectrum for NRL 171107 Er /La NP co-doped fiber
3.3.6 Master Oscillator Power Amplifier (MOPA)

A master oscillator power amplifier (MOPA) is a fiber amplifier set-up that allows us to measure several aspects of amplifier performance, one of which is the slope efficiency of active optical fibers (amplifier performance). The MOPA depicted in Figure 3.21 is an erbium amplifier where ground state electrons of the RE dopant are excited (“pumped”) to a metastable electronic energy level by an incident photon. A signal photon is introduced to de-excite the ions at the signal wavelength, creating stimulated emission. A signal photon is introduced to de-excite the ions at the signal wavelength, creating a stimulated emission. If there is sufficient stimulated emission to overcome the fiber loss, then gain is achieved. For this particular erbium doped system, the pump wavelength is 980 nm (out of band) or 1475 nm (in-band) and the signal wavelength is 1560 nm. Pumping at 980 nm, which excites electrons from the Er $^4I_{15/2}$ ground state into the Er $^4I_{11/2}$ excited level, results in low absorption of the Er$^{3+}$ ion (energy level diagram in Figure 3.1) [3.33]. Pumping directly into the Er $^4I_{13/2}$ level results in resonant pumping [3.31,3.33]. A HEL requirement is to have high
output powers, so sufficient pump power must be absorbed by the active fiber over a short length to generate the high signal output power. In-band pumping or resonant-pumping is preferred for high energy lasers due to their high output power and slope efficiency. To improve the conversion efficiency an in-band pump approach can be employed, theoretically enabling quantum defects of about 5% for erbium [3.33].

For this research, the MOPA setup uses a pump wavelength of 1476 nm and a 1560 nm signal. As shown in Figure 3.21, the pump and signal were combined in a wavelength division multiplexer (WDM) and the output from the WDM was spliced to the test NP doped fiber. A filter on the output was used to separate the amplified signal from the unabsorbed pump. The slope efficiency was determined by linearly fitting the output power signal versus absorbed pump power measured at each length as the fiber was cut back. The launched power was measured by cleaving the Er-doped laser fiber shortly after the splice with the SMF [3.1]. The fiber being tested must be cleaved with an angle to obtain good amplification. The small cleave angle minimizes the end reflection so the fiber does not act as a laser by reflecting the light back down it [3.34,3.35]. The slope efficiency was measured at each fiber length as the fiber was cut back. The initial pump and signal powers were measured by cleaving the Er-doped fiber very close to the splice with the single mode fiber [3.31].

Erbium in-band pumping is more beneficial for high power lasers due to that fact that the output has a higher possible efficiency. The theoretical maximum efficiency for 1475 nm (in-band) pumping an erbium doped fiber is about 95% using the MOPA setup in Figure 3.22, although in reality only about 80+% (quantum efficiency) is achievable. The theoretical maximum efficiency of the 980 nm pump (out of band) is about 62% which is relatively low
compared to 1475 nm pumping. Fluorescence quantum yield (Quantum efficiency), \( \eta \), is defined as

\[
\eta = \frac{\tau_{\text{rad}}}{\tau_{\text{nonrad}}} \quad [3.36].
\]

95% will never be achievable because there will always be internal losses in addition to non-radiative relaxations. The fluorescence quantum yield is system dependent based on the radiative and non-radiative decay of electrons [3.36].

NRL 170901 was an erbium/ytterbium solution co-doped fiber that was pumped at 1475 nm using the MOPA to optimize the fiber’s efficiency. RE co-doping is an alternative way to reduce erbium ion clustering, it allows the co-dopant to act as “spacers”. For these nanoparticle doped fibers, the La and Yb remain optically inactive when lasing for resonant pumping of Er [3.26]. Figure 3.22 is the slope efficiency of cutbacks along this fiber at different lengths starting with a fiber length of 3.81 m and cutting back until 1.81 m. The highest slope efficiency of 56.58% was at a distance of 3.31 m (Table 3.1). Figure 3.23 is a more in-depth confirmation that the highest slope efficiency is at a fiber length of 3.31 m. Figure 3.24 depicts the slope efficiency of the erbium/lanthanum NP co-doped NRL 171107 fiber along serval cutback lengths. It has the highest slope efficiency of \(~70.70\%\) at a distance of 3.16 m (Figure 3.25). NRL 170901 and NRL 171107 are different in many ways but they afford an opportunity for general comparison of solution doping versus NP doping for amplifier efficiency.
Figure 3.22 MOPA slope efficiency of erbium solution doped NRL 170901 fiber

<table>
<thead>
<tr>
<th>Length (m)</th>
<th>Slope Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.81</td>
<td>56.35</td>
</tr>
<tr>
<td>3.31</td>
<td>56.58</td>
</tr>
<tr>
<td>2.81</td>
<td>56.22</td>
</tr>
<tr>
<td>2.31</td>
<td>54.95</td>
</tr>
<tr>
<td>1.81</td>
<td>51.99</td>
</tr>
</tbody>
</table>

Table 3.3 Slope efficiency of erbium co-doped NRL 170901 fiber at different lengths
Figure 3.23 Slope efficiency of erbium co-doped NRL 170901

Figure 3.24 Slope efficiency of an erbium/lanthanum NP co-doped NRL 171107 fiber with cutbacks along fiber
Figure 3.25 Slope efficiency of an erbium/lanthanum NP co-doped NRL 171107 fiber

3.4 Conclusion

The goal of the research was to study nanoparticle doping of optical fibers and develop the first Er:LaF$_3$ doped fibers lasing at eye-safer wavelengths; this being an initial stepping-stone to the development of efficient RE nanoparticle doped high energy fiber lasers. EDX with SEM confirmed the successful incorporation of the RE (Er$_2$O$_3$) and the host (La$_2$O$_3$) in the preform and the fiber. The preform RIP showed NRL 171107 has a core diameter of 0.945 mm and a cladding diameter of 12.09 mm. The fiber RIP showed a core diameter of 6.60 µm and the outer diameter is 83.9 µm. Calculations in the Thesis found this to be a multimode fiber. Absorption was measured at erbium’s wavelength of about 1530
nm. A high erbium absorption is desired in the core over the length of the fiber for these laser applications. NRL171107 has an absorption of 35.7 dB/m which is relatively high for these applications. Length is also important in MOPA results. The pump will be absorbed (absorption = function of length) then signal is supposed to be amplified, but light emission can be reabsorbed. The fiber needs to be long enough to be fully absorbed the light but not long enough to emit and continue the amplification process. NRL 171107 had a high slope efficiency of 70.70% at a length of 3.16 m. NRL solution co-doped fiber 170901 was less efficient with a slope efficiency of 56.58% at a length of 3.31 m. NRL 171107 is a relatively good fiber with high erbium absorption and high slope efficiency. Future work (further discussion in Chapter 5) for these suspensions will include comparing the exact concentrations and dopants using traditional solution doping techniques versus nanoparticle doping techniques.
REFERENCES:


CHAPTER FOUR
CONCLUSION

This Thesis investigated the fabrication of optical fibers, generally designed for use in directed energy (high energy) laser systems based on nanoparticle doping instead of conventional salt solution doping. In order to achieve such fibers, a systematic study of the rare earth (RE) nanoparticle (NP) suspensions, doped preforms, and doped fibers was conducted. More specifically, lanthanum fluoride (LaF₃) nanoparticles were selected based on their high rare-earth doping capability, low phonon energy, and solution processability in nanoparticle form. LaF₃, doped with Eu and Er were synthesized at selected doping levels. X-ray diffraction (XRD) confirmed the successful formation of the LaF₃ by comparing sample spectra to the ICDD standard powder diffraction files. Transmission electron microscopy (TEM) confirmed nanoparticle size with an average diameter of about 10 nm, well below the wavelength of light such that scattering in the resultant fiber should be low. Dynamic light scattering (DLS) data showed that a pH value of 6 was optimal for particle stability of the LaF₃ nanoparticle in water compared to either more acidic (pH 4) or basic (pH 9) conditions.

Energy-dispersive x-ray spectroscopy (EDX) using a Hitachi SU6600 scanning electron microscope (SEM) confirmed the successful incorporation of the rare earth (RE) dopants into the nanoparticle and of the nanoparticles into the preform and fiber. Fibers were drawn from selected¹ NP-doped preforms and those fibers studied for their optical and

¹ By “selected” we mean that not all of the nanoparticles, preforms, or fibers fabricated during the course of this Thesis will be discussed herein. The reasoning for this is both to make for a more coherent narrative
spectroscopic properties. Attenuation spectra of the NP-doped fibers were measured over the wavelength range from about 1450 to 1600 nm. Attenuation values away from erbium absorption signatures were about 125 dB/km, which is too high for a practical high energy fiber laser (< 20 dB/km) but is more than sufficient for the purposes of this Thesis. This somewhat high background attenuation also explains the reduced slope efficiencies for the fabricated fiber lasers. Attenuation values at the peak erbium wavelength of about 1530 nm, values between 35.7 dB/m were measured, which are lower than optimum. NRL 171107 NP co-doped fiber had a relatively high slope efficiency of 70.70%, when the fiber length was 3.16 m. NRL 170901 solution co-doped fiber had a relatively low slope efficiency 56.58% at an approximately similar length. One of the possible reasons for the decreased efficiency in NRL170901 is assumed to be due to high Er$^{3+}$ ion clustering in the fiber. One possible way to improve the slope efficiency of these fibers includes increasing the Al concentration.

Active optical fiber fabrication using RE NP doping has proven successful. More work is to be done with this research and will be discussed in the following Chapter. Further work needs to be done to optimize NP suspensions. The exact synthesis pH for nanoparticle suspensions with host materials should be determined using the zeta potential measurements. Further NP characterization needs to be done to determine what species (e.g., the amount of residual ligand) are actually present in the suspension, to determine how the ions are interacting in the suspensions, and compare this data to what happens once ion NP are doped into the preform and then drawn into fiber.

---

as well as because several of the preforms and fibers were fabricated and tested at the US Naval Research Laboratories, which subsequently were used in programs that have restricted access.
CHAPTER FIVE
FUTURE WORK

This chapter will discuss future work for the nanoparticle-doped fiber research initiated in this Thesis. It will begin by discussing alternative rare earth dopants, holmium and thulium, and then discuss other topics for further research.

5.1 Different Rare Earth Ions of Interest

The following two sections will discuss two other rare earth ions that are also of interest for high energy lasers, Holmium (Ho$^{3+}$) and Thulium (Tm$^{3+}$). Both of these ions emit in the eye-safer region.

5.1.1 Holmium (Ho$^{3+}$)

![Ho$^{3+}$ energy level diagram](5.1)

Figure 5.1 Ho$^{3+}$ energy level diagram [5.1]
Holmium doped optical fiber lasers operate near 2 µm (Figure 5.1) in an eye-safer wavelength region free of significant atmospheric water absorption, are efficient, and have good potential for power scaling with high beam quality [5.2]. A major concern for holmium-doped fibers is that OH- absorption in the glass is a significant loss mechanism [5.2,5.3,5.4]. OH- incorporation through reaction with the silica soot occurs during preform fabrication and thus gives an added complication for holmium doping [5.3]. Alternative techniques for holmium doping must include considerations for reducing the OH- contamination and extensive drying to remove any residual OH [5.5].

The silica lattice of the fiber can be detrimental to achieving optimum RE\textsuperscript{3+} properties. The fluorescence lifetime of a RE\textsuperscript{3+} transition is governed by the sum of all probabilities for both radiative and non-radiative relaxation pathways [5.6]. SiO\textsubscript{2} has a phonon energy at 1100 cm\textsuperscript{-1}, which is relatively large compared to the energy spacing between many RE\textsuperscript{3+} excited states. It is particularly detrimental for long-wavelength transitions, such as the $^5I_7 \rightarrow ^5I_8$ transition near 2 µm in Ho\textsuperscript{3+}, which non-radiatively couples energy to the glass host through a multiphonon relaxation of the ions at a much greater rate than radiative relaxation. Phonon quenching reduces fluorescence lifetimes for RE\textsuperscript{3+} dopants and therefore reduces lasing efficiency. Since the combination of radiative and non-radiative processes results in decreased lifetimes for RE\textsuperscript{3+} ions in high phonon energy hosts for longer wavelengths transitions, hosts with a smaller phonon energy than SiO\textsubscript{2} are desirable (e.g. LaF\textsubscript{3} with a phonon energy $\sim$350 cm\textsuperscript{-1}). While employing an alternate glass host is possible to achieve lower multiphonon quenching and higher efficiency, typically these low phonon glasses are difficult to fabricate and have higher losses than silica [5.5]. However, the host can be used to tailor the local environment, thus phonon energy, about the RE\textsuperscript{3+} by
incorporating it within a suitable nanoparticle that is dispersed into the silica matrix. The result is a fiber exhibiting the low loss and high strength of silica with the spectroscopic benefits of the reduced phonon energy from the NP [5.5]. Friebele, et al., demonstrated the first lasing in a Ho-NP-doped fiber with a record slope efficiency $>82\%$ [5.4].

In the future, it would be beneficial to study the effects of different low phonon energy oxide host NPs and NP suspensions in order to further reduce multiphonon quenching. These low phonon energy NP allow the RE to be “shielded” from the silica matrix, which can be detrimental for Ho. Friebele, et al., suggest that the oxide-based nanoparticles may be able to survive the high lathe temperatures [5.4].

5.1.2 Thulium ($\text{Tm}^{3+}$)

![Thulium energy level diagram](image)

Figure 5.2 Thulium energy level diagram depicting “two-for-one process” [5.7]

Another ion that operates in the eye-safer region is thulium ($\text{Tm}^{3+}$) which also operates in the 2 $\mu$m region. Although Tm is not a current ion of interest for this Thesis, it is
an attractive ion due to the “two-for-one” cross-relaxation process. Tm-doped fiber lasers have a much larger nonlinear threshold, and a much larger fiber damage threshold. Tm-doped fiber laser can exhibit larger mode area while still maintains single-mode output [5.8] in comparison to either Yb or Er fiber lasers operating at 1 µm and 1.55 µm respectively. These factors make the Tm-doped fiber laser promising to offer much higher laser output.

There are two main pump bands for Tm-doped fiber lasers, namely 790 nm and 1.6 µm. The 790 nm pump is most commonly used as efficient laser diodes and are commercially available. Pumping at 790 nm, a Tm-doped fiber laser only has about 40% efficiency at 2 µm. However, the cross-relaxation process occurs in the 790 nm pumping scheme allowing for 80% operational efficiency which is a quantum efficiency of 200% [5.8]. Figure 5.2 depicts the cross-relaxation process where the emission of two photons from the 3F4 manifold is achieved through cross-relaxation by pumping Tm3+ ions to the 3H4 manifold. The excited ions in the 3H4 manifold transfer energy to a neighboring ion in the ground state and decay to the 3F4 metastable manifold while exciting the other neighboring ion to the same metastable manifold [5.7,5.8]. When they both relax to the ground state, they emit photons creating a “two-for-one” process. One photon in, two photons out [5.7].

While not a focus of this Thesis, a TmF3 NP suspension was made using the same procedures as defined in Chapter Two and made into a multi-layer, double clad fiber at NRL following the process of Chapter Three (NRL 180914). The thulium oxide (Tm2O3) concentration in the resultant fiber, via EPMA, was ~ 0.14 mol% (~6.48x10^{25} Tm ions/m^3). There was possible clustering due to the high Tm concentration in the NP doped preform, even though the average (EPMA measured) concentration is quite low. The preform was
shaped into an octagon with 4 core layers having a 67 µm core and a 400 µm cladding shown in Figure 5.3.

Future work for thulium doped fibers for high energy lasers will consist of optimizing the Tm NP suspensions for doping to facilitate the most efficient 2:1 cross-relaxation while pumping at 790 nm. This optimization should help achieve the locally high Tm concentration while maintaining a low average concentration, so the fiber remains single mode.

![Image](image1.png)

**Figure 5.3 Tm doped octagon preform with 399.35 µm cladding**

### 5.2 Further Investigations

Rare earth (RE) nanoparticle (NP) doped optical fibers for high energy lasers continue to be of interest in the field of directed energy and much work remains to optimize the suspensions for doping into fibers. More testing needs to be performed on the nanoparticle suspensions, preforms, and fibers produced during this research. A direct comparison study needs to be done to test the effects of solution co-doping versus nanoparticle co-doping of these optical fibers.
The nanoparticle suspension’s host materials should be further studied to better understand the effect of the host on the RE and the glass structure, the optimal pH for the formation of NPs will be further studied, and finally, the optimized suspensions should be incorporated into fibers. Increased NP concentration while maintaining high efficiency will be the focus of future work in collaboration with the Naval Research Laboratory.

For fibers and preforms, this includes using electron probe microanalysis (EPMA) to find the exact RE concentration in the preforms, lifetime measurements, attenuation in the fibers, and high energy laser characterization. Other factors to look into with the preforms and fibers are the doping levels, sizes of the preforms and fibers along with different shapes of the core and cladding.
REFERENCES:


APPENDICES
APPENDIX A
NANOPARTICLE BATCH SHEETS

Table A.1 lists the rare earth compounds used in this research. Copies of the batch sheets employed for the rare earth nanoparticle synthesis are included in this Appendix.

Figure A.1 is the batch sheet for the basic nanoparticle synthesis. Figure A.2 is the nanoparticle batch sheet for the nanoparticle synthesis discussed in Chapter 2.3.

<table>
<thead>
<tr>
<th>Rare Earth</th>
<th>Chemical Equation</th>
<th>Brand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Erbium (III) nitrate</td>
<td>Er(NO$_3$)$_3$*5$\text{H}_2$O</td>
<td>Aldrich, 99.9%</td>
</tr>
<tr>
<td>pentahydrate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Europium (III) nitrate</td>
<td>Eu(NO$_3$)$_3$*6$\text{H}_2$O</td>
<td>Alfa Aesar, 99.9%</td>
</tr>
<tr>
<td>hexahydrate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ytterbium (III) nitrate</td>
<td>Yb(NO$_3$)$_3$*5$\text{H}_2$O</td>
<td>Alfa Aesar, 99.9%</td>
</tr>
<tr>
<td>pentahydrate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Holmium (III) nitrate</td>
<td>Ho(NO$_3$)$_3$*5$\text{H}_2$O</td>
<td>Alfa Aesar, 99.9%</td>
</tr>
<tr>
<td>pentahydrate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thulium (III) nitrate</td>
<td>Tm(NO$_3$)$_3$*5$\text{H}_2$O</td>
<td>Alfa Aesar, 99.9%</td>
</tr>
<tr>
<td>hydrate</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table A.1 Rare earths used
LaF3 Nanoparticle Synthesis

5 mol% Er:LaF3

| Batch Size | 195 mg | Batch Ratio | 8.00 |

**Concentration (in Ln+3 mol %)**

<table>
<thead>
<tr>
<th>Rare Earth</th>
<th>Complex</th>
<th>atm wt</th>
<th>Rare Earths</th>
<th>Complex</th>
<th>atm wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er(NO3)3*5H2O</td>
<td>443.35012</td>
<td>167.259</td>
<td>Er(NO3)3*6H2O</td>
<td>446.07038</td>
<td>151.964</td>
</tr>
<tr>
<td>Sm(NO3)3*6H2O</td>
<td>444.46638</td>
<td>150.36</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd(NO3)3*6H2O</td>
<td>438.34638</td>
<td>144.24</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Precursors**

<table>
<thead>
<tr>
<th>Precursors</th>
<th>Complex</th>
<th>Ratio (mol)</th>
<th>Precursors</th>
<th>Complex</th>
<th>Ratio (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH4F</td>
<td>37.037</td>
<td>3</td>
<td>Tb(NO3)3*6H2O</td>
<td>453.02</td>
<td>158.92</td>
</tr>
<tr>
<td>La(NO3)3</td>
<td>433.011</td>
<td>0.96</td>
<td>Tm(NO3)3*5H2O</td>
<td>445.04</td>
<td>168.93</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>192.124</td>
<td>3</td>
<td>Yb(NO3)3*5H2O</td>
<td>449.05</td>
<td>173.04</td>
</tr>
<tr>
<td>Er(NO3)3*5H2O</td>
<td>443.35012</td>
<td>0.05</td>
<td>Ho(NO3)3*5H2O</td>
<td>441.01</td>
<td>164.93</td>
</tr>
<tr>
<td>Pr(NO3)3*5H2O</td>
<td>416.9894</td>
<td>140.91</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Adjust pH to 5.15 using NH4OH

**LaRE Solution**

<table>
<thead>
<tr>
<th>La(RE) Solution</th>
<th>La(NO3)3*6H2O</th>
<th>Er(NO3)3*5H2O</th>
<th>Ultra Pure Water</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4114</td>
<td>3.2909 g</td>
<td>0.0222</td>
<td>0.1773 g</td>
<td>8.0000 mL</td>
</tr>
</tbody>
</table>

Adjust pH to 5.15 using NH4OH

**LaF3**

<table>
<thead>
<tr>
<th>LaF3</th>
<th>Citric Acid</th>
<th>NH4F</th>
<th>Ultra Pure Water</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5764</td>
<td>4.6110 g</td>
<td>0.1111</td>
<td>0.8889 g</td>
<td>320.0 mL</td>
</tr>
</tbody>
</table>

Heat to 70°C

La/RE dropwise 2 | 16.0 mL |

**Notes**

**FINAL pH**

- Stir for 1.5 hours
- Let cool to room temperature
- Put in Nalgene container

Figure A.1 NP example batch sheet

\[
\text{Host nitrate (g)} = \frac{MW_{host}}{1000} \left( \frac{\text{Total moles of host}}{} - \frac{\left( \text{RE doping level in mole \%}\right) \left( \text{Total moles of host} \right)}{100} \right)
\]

\[
\text{RE nitrate (g)} = \frac{MW_{RE \, dopant}}{1000} \left( \frac{\text{RE doping level in mole \%}}{100} \right) \left( \text{Total moles of host} \right)
\]

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LaF3 Nanoparticle Synthesis

Project: 30 mol% EuLaF3

<table>
<thead>
<tr>
<th>Batch Size</th>
<th>195 mg</th>
<th>Batch Ratio</th>
<th>4.00</th>
</tr>
</thead>
</table>

| Concentration (in Ln+3 mol %) | 30 |

<table>
<thead>
<tr>
<th>Rare Earth</th>
<th>Complex</th>
<th>atm wt</th>
<th>Rare Earths</th>
<th>Complex</th>
<th>atm wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu(NO3)3*6H2O</td>
<td>446.07038</td>
<td>151.964</td>
<td>Eu(NO3)3*6H2O</td>
<td>446.07038</td>
<td>151.964</td>
</tr>
<tr>
<td>Sm(NO3)3*6H2O</td>
<td>444.46638</td>
<td>150.36</td>
<td>Nd(NO3)3*6H2O</td>
<td>438.34638</td>
<td>144.24</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Precursors</th>
<th>Complex</th>
<th>Ratio (mol)</th>
<th>RE Nitrate (g)</th>
<th>Complex</th>
<th>atm wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH4F</td>
<td>37.037</td>
<td>3</td>
<td>Tb(NO3)3*6H2O</td>
<td>453.02</td>
<td>158.92</td>
</tr>
<tr>
<td>La(NO3)3</td>
<td>433.011</td>
<td>0.7</td>
<td>Tm(NO3)3*5H2O</td>
<td>445.04</td>
<td>168.93</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>192.124</td>
<td>3</td>
<td>Yb(NO3)3*5H2O</td>
<td>449.05</td>
<td>173.04</td>
</tr>
<tr>
<td>Eu(NO3)3*6H2O</td>
<td>446.07038</td>
<td>0.3</td>
<td>Ho(NO3)3*5H2O</td>
<td>441.01</td>
<td>164.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pr(NO3)3*5H2O</td>
<td>416.9894</td>
<td>140.91</td>
</tr>
</tbody>
</table>

Adjust pH to 5.15 using NH4OH

<table>
<thead>
<tr>
<th>LaRE Solution</th>
<th>pH</th>
<th>g</th>
</tr>
</thead>
<tbody>
<tr>
<td>La(NO3)3*6H2O</td>
<td>0.3031</td>
<td>1.2124</td>
</tr>
<tr>
<td>Eu(NO3)3*6H2O</td>
<td>0.1338</td>
<td>0.5353</td>
</tr>
<tr>
<td>Ultra Pure Water</td>
<td>1</td>
<td>4.0000</td>
</tr>
</tbody>
</table>

Adjust pH to 5.15 using NH4OH

<table>
<thead>
<tr>
<th>LaF3</th>
<th>pH</th>
<th>g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citric Acid</td>
<td>0.5764</td>
<td>2.3055</td>
</tr>
<tr>
<td>NH4F</td>
<td>0.1111</td>
<td>0.4444</td>
</tr>
<tr>
<td>Ultra Pure Water</td>
<td>40</td>
<td>160.0</td>
</tr>
</tbody>
</table>

Heat to 70°C

La/RE dropwise | 2 | 8.0 mL |

Notes

- FINAL pH
- Stir for 1.5 hours
- Let cool to room temperature
- Put in NaIgene container
- DO NOT CRASH OUT PARTICLES

Figure A.2 Eu:LaF3 NP batch sheet

$$\text{Host nitrate (g)} = \frac{MW_{host}}{1000} \left[ \text{Total moles of host} - \frac{\text{(RE doping level in mole %) (Total moles of host)}}{100} \right]$$

$$\text{RE nitrate (g)} = \frac{MW_{RE dopant}}{1000} \left[ \frac{\text{(RE doping level in mole %) (Total moles of host)}}{100} \right]$$
Nanoparticles of a variety of host materials were synthesized even though this Thesis focused on lanthanum fluoride (LaF₃). Alkaline earth fluorides (AEF₂) and lead fluoride (PbF₂) specifically were synthesized and studied further in terms of colloidal stability.

Different pH levels were employed to stabilize the aqueous suspensions. The alkaline earth fluorides used were barium fluoride (BaF₂), calcium fluoride (CaF₂), and strontium fluoride (SrF₂). Fluorides made with the alkali earth ions have exhibited lower phonon energy than LaF₃. More specifically, relative to LaF₃ (350 cm⁻¹), the maximum transverse optical phonon energies for CaF₂, SrF₂, and BaF₂ are 257, 217, and 184 cm⁻¹, respectively [B.1]. Employing a lower phonon energy nanoparticle to encapsulate the NP inside the silica glass could be beneficial from the perspective of increasing radiative emission probabilities and quantum efficiencies. In the silica matrix, alkaline earth ions act as glass modifiers by occupying interstitial spaces which can reduce the overall glass connectivity improving the solubility of dopant ions [B.2]. In this section, additional research is discussed relating to colloidal stability of the suspensions. The effect of pH 4, 6, and 9 on the suspension will be studied by adjusting the pH one time versus the typical two times. The nanoparticle synthesis for these suspensions will be discussed in Section B.1.
B.1 Synthesis of Alkali-Earth and Lead Fluoride Nanoparticles and Their Suspensions

This section will discuss the recipe for one representative nanoparticle suspension for the pH study with different host materials (AV-47-56; Eu:CaF₂; pH4). All of the suspensions were 30 mol % Eu:(host nitrate). The relative amounts of host nitrate and Eu(NO₃)₃ will change depending on the doping concentration. To begin the suspension synthesis process, a triple neck flask was used to prepare a fluorinated ligand solution of 0.2222 g of ammonium fluoride (NH₄F; Fisher Scientific), 1.1527 g of citric acid (C₆H₈O₇; Alfa Aesar, anhydrous, 99.5%) and 120 mL of ultra-pure (UP) water. Ultrapure water was obtained from a Barnstead Nanopure Diamond water purifier. The fluorinated ligand solution was placed in a hot water bath at 70°C inside of a glass dish ¾ full of water and condenser balls to prevent the water from evaporating. A stir bar was placed in the triple neck flask to continuously stir the suspension, around 500 rpm, until the suspension appeared clear. The rare earth suspension was comprised of 0.8009 g of europium (III nitrate hexahydrate (Eu(NO₃)₃*6H₂O; Alfa Aesar, 99.9%), 0.9894 g of calcium nitrate (Ca(NO₃)₂; Alfa Aesar, 99.99%) as the host for the rare earth solution (RE solution), and 3 mL of UP water. The RE solution of host material nitrate, rare earth dopant nitrate, and UP water was made in a centrifuge tube while the fluorinated ligand solution was being stirred and reaching the appropriate temperature. The centrifuge tube was sonicated until the nitrates were completely dissolved. Before testing the pH of the fluorinated ligand solution, the pH reader was calibrated using buffer solutions of 4.01, 7.00, and 10.01. Then the pH of the fluorinated ligand solution, which was originally around 2.90, was adjusted dropwise to 4.00 using ammonium hydroxide (NH₄OH; British Drug Houses) to control particle size and
to create space for ligand to join. Once the pH is adjusted the first time, the rare earth solution was added dropwise close to the center of the vortex. The suspension typically appears to have a cloudy haze when dropping in the RE solution; this is due to the formation of the nanoparticles. The pH is measured again once all of the rare earth solution had been added and is readjusted to a pH of 4.00. The combined suspension then stirs for 1.5 hours at 70°C and is cooled to room temperature. The relative amounts of materials are listed below in Table B.1.

<table>
<thead>
<tr>
<th>Host material</th>
<th>Amount (g)</th>
<th>RE</th>
<th>Amount (g)</th>
<th>Citric Acid (g)</th>
<th>NH₄F (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba(NO₃)₃</td>
<td>0.5488</td>
<td>Eu(NO₃)₃*6H₂O</td>
<td>0.4015</td>
<td>1.1527</td>
<td>0.2222</td>
</tr>
<tr>
<td>Ca(NO₃)₂</td>
<td>0.9894</td>
<td>Eu(NO₃)₃*6H₂O</td>
<td>0.8009</td>
<td>1.1527</td>
<td>0.2222</td>
</tr>
<tr>
<td>Sr(NO₃)₂</td>
<td>0.8866</td>
<td>Eu(NO₃)₃*6H₂O</td>
<td>0.8009</td>
<td>1.1527</td>
<td>0.2222</td>
</tr>
<tr>
<td>Pb(NO₃)₂</td>
<td>1.3876</td>
<td>Eu(NO₃)₃*6H₂O</td>
<td>0.8009</td>
<td>1.1527</td>
<td>0.2222</td>
</tr>
</tbody>
</table>

Table B.1 Host material amounts

B.2 Dynamic Light Scattering pH Study with Different Hosts

This section discusses the results of a pH study using DLS with different host material. DLS was described more fundamentally in Chapter 2 as relates to LaF₃ NP stability. The results are shown in Figures B.1 (a-d). Although alkaline earth fluorides can be beneficial due to their low vibrational energies, they were difficult to work with than LaF₃. All of the (AE)F₂ suspensions tended to precipitate out the particles. As a reminder, it is desirous to have NPs with diameters of less than 100 nm, preferably about 10 nm, to
minimize scattering in the resultant optical fiber, which would increase loss and reduce laser efficiency. As can be seen from the DLS data below, the pH of 4 was not optimal for any of the suspensions with its low intensity and a broad spectrum of sizes. For the SrF$_2$ (a), a pH of 9 appears to have the best particle size formation along with the highest intensity. BaF$_2$ (b) has the smoothest distribution and good particle size with pH 6. PbF$_2$ (c) also has the smoothest distribution and good particle size with pH 6. CaF$_2$ (d) has the smoothest distribution and good particle size with pH 6. There is more work to be done to find the optimal pH for the alkaline earth fluorides and lead fluoride before they are doped successfully into optical fibers.

a) SrF$_2$  

b) BaF$_2$
Figure B.1 Dynamic light scattering with different host material and different pH levels. a) Strontium fluoride (SrF₂), b) Barium fluoride (BaF₂), c) Lead fluoride (PbF₂), and d) Calcium fluoride (CaF₂)

B.3 Dynamic Light Scattering pH Study with Different pH Adjustments

Nanoparticle synthesis for this study was completed as mentioned in B.1 except the pH was adjusted twice during nanoparticle formation compared to the initial pH change before the RE nitrate was added. Results are shown in Figures B.2, B.3 and B.4. Figures B.2, B.3, B.4 show the hydrodynamic diameter particle size distribution over a 12 hour period with pH 4, 6, 9, respectively, adjusted once vs. twice. The results show that solutions adjusted once generally were more stable over the course of the 12 hour time period. The pH 6 adjusted once showed preferable hydrodynamic diameter size and highest stability through the run. Adjusting the pH twice leads to agglomerates forming and particles precipitating out of suspension. From the data collected it can be concluded that pH 6
adjusted once was the optimal pH for this study. This data can be used to further optimize the nanoparticle synthesis process in the future.

Figure B.2 Particle size over 12 hour period with pH 4 adjusted once vs. twice
Figure B.3 Particle size over 12 hour period with pH 6 adjusted once vs. twice

Figure B.4 Particle size over 12 hour period with pH 9 adjusted once vs. twice
REFERENCES


APPENDIX C

RARE EARTH EMISSION USING PHOTOLUMINESCENCE

Figure C.1 Jobin Yvon Horiba – Fluorolog 3-22 – Tau 3 / TCSPC

photoluminescence spectrophotometer

Photoluminescence (PL) is the emission of light from a material under optical excitation. When light of sufficient energy is incident on a material, photons are absorbed and electronically excited. The photoluminescence signal is created by the emitted light when the excited electrons radiatively return to a lower lying energy level, typically the ground state. The intensity of this signal gives a measure of the relative probability for radiative relaxation [C.1]. Europium (Eu) has strong red luminescence intensity, which corresponds to the radiative transitions from the $^5D_0$ to $^7F_2$ state [C.2]. Because this emission is both easy to view using the spectrometers available at Clemson and because Eu is a well-known spectroscopic probe into local structure [C.3], it is used here to gain more insight into the properties of the rare-earth-doped NPs.
In this Thesis, photoluminescence is the characterization technique used to verify rare earth emissions and incorporation using the Jobin Yvon Horiba – Fluorolog 3-222 – Tau 3 / TCSPC photoluminescence spectrophotometer pictured in Figure C.1. The most intense spectral lines in europium emission spectrum are due to the $^5D_0 \rightarrow ^7F_1$ transitions around 590 nm (magnetic dipole) and $^5D_0 \rightarrow ^7F_2$ in the 610-620 nm spectral range (electric dipole) [C.4]. Emission scans of all of the Eu samples were collected using excitation at 394 nm and the data was normalized to intensity of the 590 nm peak, which is characteristic of Eu and, being a magnetic dipole transition, is insensitive to the local environment [C.5]. An instrumental slit width of 5 nm, integration time of 0.1 sec, and a step size of 0.5 nm were used in all PL measurements. Figures C.2 shows the emission spectra results for comparison to LaF$_3$ (Eu:CaF$_2$, Eu: PbF$_2$, Eu:BaF$_2$, Eu: SrF$_2$). The dominant peaks of 590nm and 615nm are present in all of the Eu samples. Figures C.3-C.5 show that pH 6 has the highest intensity of the 615nm peak. A pH value of 6 also exhibited the best particle stability from Appendix B so this indicates it is the best pH for this study. This selection results from this pH yielding NPs that exhibited the most intense emission peak at 615nm, smaller overall particle size and stability of the solution (aggregation) over 12 hours. Adjustment of once or twice did not change the intensity a significant amount between all the samples. The sharp photoluminescence peaks confirm that the 30 mol% dopant of the RE$^{3+}$ ions have been successfully incorporated into the aqueous suspensions.

Figure C.6 displays the correlation between pH, particle size and intensity. This graph shows that pH affects both particle size and intensity. pH 4 yielded the largest particle and the lowest intensity level, pH 9 also yielded a larger particles and high intensity levels. The solution with a pH 6 was the smallest particle with the highest emission intensity. These
were key factors in determining optimal pH. The number of times the solutions pH was adjusted had little to no effect on intensity, but as the pH was adjusted there was a change observed in particle size. The pH 6 suspension showed very little difference in particle size as opposed to the other pH solutions. There was less than a 10 d.nm difference when looking at pH 6 adjusted once and pH 6 adjusted twice.

Figure C.2 Emission spectrum of Eu:LaF$_3$, Eu:BaF$_2$, Eu:SrF$_2$, Eu:PbF$_2$, Eu:CaF$_2$
Figure C.3 Emission spectra for Eu:LaF$_3$ pH 4 with excitation at 394 nm

Figure C.4 Emission spectra for Eu:LaF$_3$ pH 6 with excitation at 394 nm
Figure C.5 Emission spectra for Eu:LaF₃ pH 9 with excitation at 394 nm

Figure C.6 Relationship between particle size, pH, and photoluminescence (PL) intensity
REFERENCES


