

# Project Proposal

## **VE-NUS**

# Visible Emission Near-Infrared Up-Conversion Spectrometer

An optical spectrometer that analyzes near infrared spectrums with a visible spectrum detector utilizing up-converting phosphors.



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# 1 Abstract

In this project a spectrometer that works in the near infrared (NIR) spectral range but utilizes a visible spectrum detector will be developed. This product is being developed with a local company, Ocean Optics, to fill a hole in their market of a relatively cheap spectrometer than can be used in the near infrared region. This can be accomplished through frequency up-conversion. By using the proper up-conversion mechanism, such a device would meet the simple, rugged, user friendly and cost effective parameters that are desired for so many applications while being able to analyze the infrared spectrum.

We will be choosing specific phosphors that can up-convert the near infrared light, emit in the visible range and be pumped with a high energy photon that does not interfere with the emission. A large scale test set up will be built to test the phosphors and determine which should be used, how best to pump and to detect. Once the phosphor is decided upon this test set up will be used to characterize the phosphor for final use.

The final set up will be a compact modified version of Ocean Optics current NIR spectrometer that uses Indium Gallium Arsenide detectors (InGaAs). The test bed will be modified to hold our components and the detector replaced with a simple silicon (Si) detector. This new design will prove to be a simple and extremely cost efficient method to do NIR spectroscopy for a wide gamete of applications.

## 2 Introduction

### 2.1 Summary

Spectroscopy is a standard and highly developed technique used to analyze the optical spectrum of an input light. There are many variations of this technique such as absorption or transmission spectroscopy and two much more complicated techniques such as Raman or mass spectroscopy. The applications of such techniques are almost limitless. Spectrometers are used in every day applications such as water testing all the way to more elaborate applications like explosive detection and nuclear radiation analysis.

The more common spectroscopy techniques of absorptions, transmission and emission spectroscopy will be the focus of this project. These relatively simple techniques are very important. Almost every optical company or lab has one available and in addition many non-optical companies utilize these devices because how widely they are used. For many applications, a simple, rugged, user friendly and cost effective spectrometer is a must. Many companies currently specialize in making such devices.

While each individual application has many specifications, one specification that is always of interest is the wavelength range of interest for the user. Theoretically, spectroscopy can be performed in all wavelength ranges but there has been a surge of interest in Infrared spectroscopy.

## 2.2 Motivation

With such interest in infrared spectroscopy, the market for such spectrometers is very large. The complication is that the higher the wavelength of the infrared signal, the more expensive the components get. The optical components such as lens coatings and grating periods are more complicated which leads to a higher cost but the main increase in price comes from the detector. In the visible spectrum Silicon (Si) detectors are used. These are simple, cheap and made in bulk. Once you move into the near infrared spectrum, Si detectors no longer work and the commonly used detector is Indium Gallium Arsenide (InGaAs). This is a much more expensive detector. Also, often detector arrays are used in spectrometers so the increase in cost of the detector is multiplied by the size of the array. In addition InGaAs detectors are usually cooled which adds another expense. It can easily be seen how a near infrared spectrometer can cost exponentially more than a visible spectrometer.

The near infrared spectral range has become of interest due to many reasons. For example more and more lasers are being developed in this range, gas molecules have much more prominent spectroscopic features here and the military uses NIR for most applications for safety and discreteness. A standard tool used for many things in developing the mentioned applications is a spectrometer. Almost every optical lab has a basic spectrometer. It is a unique and versatile tool. But in order to keep it so commonly used for infrared applications the cost is of concern.

It would be ideal to develop an infrared spectrometer that uses a visible spectrum Si detector. Attempting to push the sensitivity of the Si detector to further wavelengths is not an option because this has been done for many years and its limit of roughly  $1.1\mu\text{m}$  is well accepted. The key is to convert the incoming infrared light into visible light and be able to correlate the two different wavelengths. This change in light wavelength/frequency is called frequency up-conversion. There are many different methods to do this such as sum-frequency generation, non-linear optical processes and some unique materials. The option we have found to be most practical and will work the best is utilizing a unique material called a phosphor.

When the material is pumped properly by a light emitting diode (LED), impinging near infrared light can linearly be converted to visible light. In addition, these materials are relatively cheap and simple to work with.

In order to do this the proper phosphor must be found, and an efficient manner to pump it, control the system, detect/amplify the signal, analyze/correlate the

spectrum must be designed. This will encompass the disciplines of optics, photonics, electrical engineering and computer science.

Such a device will fill a place in the market for a cheap and simple near infrared spectrometer.

## 2.3 Team Members

### 2.3.1 Sean Crystal

Sean Crystal studies Photonic Science and Engineering at The University of Central Florida within CREOL where he has a focus in lasers and laser beam applications. He is a senior at the university and will be graduating in spring 2017. Sean has done research in photonic properties of optical materials, optical and electrical test equipment, Ultra-fast fiber lasers, mid-infrared frequency combs and mid-infrared gas detection. Sean plans to continue his studies in lasers and laser beam applications after graduation in graduate school and then take his experience to industry.



### 2.3.2 Jason Owens

Born in Orlando in October of 1994, Jason Owens was raised by his aunt and his uncle in Mount Dora, Florida. By the age of 10 he was inspired by his uncle to pursue a degree in science and engineering. He graduated Mount Dora High School in 2013 and later earned his associates degree from Lake Sumter State College the same year. During his first year at the University of Central Florida he enrolled in the optics program at CREOL and started research under Dr. Ayman Abouraddy in 2014. He is currently working under Dr. Delfyett in the Ultrafast Photonics group at CREOL. He hopes to later continue his studies with high powered lasers and upconversion technology in graduate school.



## 2.4 Faculty Mentor



Dr. Stephen Kuebler will be a faculty mentor assisting us with the technical science and design aspects of this project. He is a faculty member in CREOL, The College of Optics and Photonics as well as in The Department of Chemistry. Dr. Kuebler's research areas include materials and processes for 3D nano- and microfabrication, use of these techniques for creating nanophotonic structures and devices, nonlinear optical materials and photochemistry. This project, while primarily optical and electrical has some chemistry components and due to Dr. Kuebler's co-appointment with CREOL and the chemistry department along with his chemistry research areas we felt he would be a great fit to advise us through this project.

## 2.5 Industry Customer

For this project our team will be working with a local company, Ocean Optics. Ocean Optics is a dominating player in the world of practical spectrometers. Their products are based on being high quality, but relatively inexpensive, compact, portable, and customizable. Ocean Optics will be the customer setting their desired specifications/requirements for the device. Ocean Optics will also be providing equipment for this project.



Figure 1: Ocean Optics logo and Ocean Optics standard flame spectrometer

## 2.6 Market Analysis

### 2.6.1 Market/Engineering Requirements

In the engineering world, while innovation is extremely important, it rarely can be done for no reason at all. There are two components, there are engineering requirements and market requirements. Where these two components cross is usually where the engineering project stems from. Below is a table that analyzes the engineering and market requirements for this project and shows where the cross happens

		Marketing Requirements						
		1) Phosphor Response	2) LED Pulse Speed	3) Spectrum Range	4) Resolution	5) Sensitivity	6) Cost	7) Output Power
		+	-	+	+	+	-	-
Engineering Requirements	1) Phosphor Responses	+	↑	↑	↑		↑	
	2) LED Pulse Speed	+	↓				↑	
	3) Spectrum Range	+	↓		↑		↑	
	4) Resolution	+	↓	↑		↓	↑	
	5) Sensitivity	+	↓	↑	↓	↓	↑	↑
	6) Cost	-	↓		↓	↓	↑	↑
	7) Output Power	+	↑				↓	↑

**Figure 2: Marketing/Engineering requirement correlation chart.**

It can be seen that the majority of requirements, both engineering and market related are positives which indicates this is a product worth putting together. The negative of cost in the engineering requirements is pretty common and the hope is that after efficient design and research this will come down and become a positive. The negatives in the market requirements should also, after more design and optimization, become significantly less of a concern.

### 2.6.2 Current Products

There are two products that currently exist that accomplish spectroscopy in the near infrared worth highlighting. First is the NIRQuest spectrometer from our customer, Ocean Optics and the second is an up-converting spectrometer from Stellar Net. These two work in very different manners but accomplish the same task of near infrared spectroscopy. Before describing these two devices it should be noted that the up-converting product from Stellar Net has been discontinued because it was a poor product (this will be explained). By looking at the advantages and disadvantages of these two systems we can explain what our system will accomplish.

The NIR spectrometer from Ocean Optics is a great product that is as robust, reliable and simple as all spectrometers from the Ocean Optics team. It is available as a standard USB spectrometer and in some cases phone application controlled. The spectral response can be pushed over  $2\mu\text{m}$  still with good resolution but usually closer to  $1.7\mu\text{m}$ . This system is usually cooled with a TEC and/or fan due to the heat created by the detector.

This system uses InGaAs detectors, in an array, must be cooled, and all the components must be designed for the near infrared. So overall there is a great product with very little wrong with it but, as gathered from the previous sections, it is quite expensive.



**Figure 3: Ocean Optics NIRQuest near infrared spectrometer with InGaAs detector.**

The second product, from Stellar Net, is an up-converting spectrometer much like the system we have proposed. It uses phosphors as the up-converting mechanism and a Si detector. While this product is less expensive than their NIR spectrometers, it does not work nearly as well for most applications. The only application this has been suggested for is basic laser characterization when you don't care about the wavelength as much and you have very high intensities. Neither of these limitations are good for a spectrometer.



**Figure 4: Stellar Net NIR up-conversion spectrometer.**

The issues with this particular spectrometer are relatively trivial. The reason high intensity was needed (usually short pulse duration) and the wavelength was unable to be properly correlated was because a non-pumped phosphor was used. If a non-pumped phosphor is used the up-conversion process is non-linear and this non-linear process does not allow for accurate determination of what energy photons are causing what up-conversion.

In addition to not working well this system was still relatively expensive. An expensive system that does not work well is a bad combination and explains why the product was discontinued.

These two products give a good idea of what current products exist for the near infrared region. We believe our design will allow us to stay low cost but by using a pump we believe we can create a linear system that corrects the issues with the system Stellar Net produced.

### 2.6.3 Ocean Optics Current Market Presence

Ocean Optics is one of the largest providers of rugged, simple to use and compact spectrometers. Their technology was developed by a pair of oceanographers who needed a field ready spectrometer. This need was not just for their application though. Over the years they have grown into the large market gap. Many competitors do exist but it is hard for anyone to compete with, not only Ocean Optics technology, but mainly there customization and speed of purchasing.

Ocean Optics was purchased in 2004 by Halma, the leader in safety and environmental technology. This is a German holding company and this acquisition expanded Ocean Optics market presence even further internationally. They now have over 5 locations in multiple different countries. Nearly every optics lab has a basic spectrometer and many of those are Ocean Optics products.

## 3 Specifications

### 3.1 Device Usage

As mentioned above, there are many different types of spectrometers used for a wide variety of applications. Ocean Optics spectrometers are designed to be used for any transmission, absorption spectroscopy. The device we are developing will be similar. It will be based on the basic transmission and absorption techniques.

For senior design our device will be designed for the purpose of characterizing laser spectrums. Lasers can have very narrow simple spectrums all the way to complicated and varying outputs. Knowing this specific output can be very important. The near infrared regime is becoming more and more popular in the laser arena and being able to characterize these new developing lasers is a must.

In fact, as will be discussed later, the only other product that was made similar to ours was used almost solely for this purpose.

A key reason we have chosen to use this device for this use is the complication of the phosphors. The key to this whole project is the success of our phosphor up-converting materials. This will be the most time consuming and scientifically complicated part but by using a more intense and coherent laser source we have more confidence in the success of our phosphors. In the future we do plan of continuing to develop this device to work with other test lights that are not as powerful or coherent.

### 3.2 Detection Wavelength Range

The desired wavelength detection range was determined based on multiple factors between our group and Ocean Optics. The factors that were considered were, where do standard Silicon detectors currently cut off, what wavelengths does the commercially available NIR InGaAs detector analyze, what wavelength ranges to laser scientists care about and what wavelengths are we confident our phosphors can work at. With all this being considered the wavelength range of 900nm to 1500nm was set. While this range may cut off slightly below what Ocean Optics current NIRQuest cuts off at, this is a developing product and the range of this system is purely limited by the phosphor technology. With further exploration and research in phosphor up-conversion, such as other materials, temperature dependence or pumping mechanism, this up-converting spectrometer wavelength range can easily increase in the future.

### 3.3 Resolution

Resolution of a spectrometer is defined as the number data points collected per wavelength (usually per  $\mu\text{m}$  or nm) that can be differentiated from each other for an incoming unknown source of light. The resolution is dependent on a number of factors depending on the type of spectrometer and this will be explained in greater detail in chapter 5. With this being a prototype of technology, we believe a resolution of 5nm to 40nm is a reasonable benchmark to show the technology works efficiently.

### 3.4 Device Size

Size is a major factor in the design of this device. Ocean Optics makes field ready spectrometers that are simple to transport so compact is a must. Ocean Optics currently has a bed for their NIR spectrometer not utilizing phosphors that is 182mm x 110mm x 47mm and we plan to fit our system into this same bed. The original device will be built on optical and electrical breadboards much bigger than this but once the design is complete it will be downsized from optical bench pieces to custom mounts and electrical breadboards to PCB's.

## 4 Research

### 4.1 Gratings

A diffraction grating, or grating as it's more commonly known, is a engineered material (typically a glass) that separates out any spectrum of light that passes through it into individual wavelength components. This is taking advantage of the diffractive nature of light and causing the different wavelengths to separate out. This is done by creating a periodic pattern on the diffraction grating separated by a certain distance. There is typically a designation wavelength for the gratings which they are best used at and a range for how far out they can go. The amount of frequencies the diffraction is able to separate out will be dependent on the spacing in terms of lines/mm.

All different wavelengths are diffracted at different angles. This means that depending on the wavelength range of interest the angle of incidence can be changed to refract different wavelengths at different angles. This is useful when focusing on to a detector.

An ideal grating works by having uniform slits of a spacing  $d$  with period wider than that of the incident wavelength. By assuming one has plane waves of discrete wavelengths, each slit will act as an equivalent "point source." When the incident light hits the slits diffracted light is reflected or transmitted composed of the sum of the interfering waves at each "point source." The path length to each slit will vary and there for the sum of interfering waves will create maximum and minimums. The maximum will occur with the path distance is different by  $\lambda$  and minimum will occur where the path distance is different by  $\lambda/2$ . There are multiple orders of diffraction but the first order is usually used [1]. From these phase relationships the grating equation can be derived which shows the effect of the slit period, order, angle of incidence and wavelength.

$$d = \textit{period}$$

$$\theta_m = \textit{maximum interference angle}$$

$$m = \textit{order}$$

$$\lambda = \textit{wavelength}$$

$$d \sin \theta_m = m \lambda$$

The resolution of a grading depends on the slit concentration. The more slits covered by your incident light source will result in higher resolution. With this, one can maximize resolution for their particular application.

There are two basic different forms of grating, transmission and reflection gratings. Typically it is common to use reflection diffraction grating in spectroscopy. Reflective diffraction gratings is what Ocean Optics currently uses and they act as a mirror surface which is convenient for a compact design. In addition, these two forms can come in multiple types such as plane, concave, echelle, holographic, and grisms [2].

A plane grating utilizing blazed grooves at a specific blaze angle. They are used in Littrow configuration which means light is diffracted back toward the source. This is best for maximum energy at specific wavelengths. Concave gratings are used for ultra-violet (UV) applications (sub 250nm). These gratings are concave in nature and are used in many applications to diffuse or focus light in the UV wavelength. Echelle gratings are a specific type of plane grating with high blaze angles. This is mainly used when high diffraction orders are desired. These types allow for high dispersion and resolution. Holographic gratings work in a much different manner. The slits or blazes are, instead are sinusoidal groove shaping's holographically added to the material. The diffraction efficiency is controlled by varying the ratio of groove depth and groove spacing. The last type of grating, a grism, is a combination of a grating and prism, both with separate varying wavelengths of light. In this case a period is holographically placed on the face of a prism. The advantage of this system is that it allows light of a chosen wavelength to pass straight through the system.

Diffraction gratings are very important for spectroscopy. Light sources of varying wavelengths can be decomposed and using various detecting schematics, individual wavelengths can be individually analyzed.

## 4.2 Up-Conversion

Up-conversion is the process where a material absorbs light of a certain frequency and converts it up to a higher frequency (frequency being inversely proportional to wavelength). This process is extremely useful for many applications and can be accomplished in numerous manners such as frequency mixing, and material up-conversion.

For the most part these up-conversion processes are complicated non-linear processes that require high energy density, and/or short pulse duration. These phenomena have been and are currently extensively studied. They will be described below.

Of high interest is the simpler up-conversion processes such as material phosphor up-conversion. This in some cases is non-linear but does not require the same high energy density and short pulse duration requirements. This is ideal for applications. In addition, there are phosphors that can be pumped (charge to a specific energy) which makes the up-conversion process relatively linear. This is important for this design and will be explained.

Since frequency is proportional to energy, the photon energy of the light is reduced in this process. However, there are ways to amplify the emission using techniques such as frequency mixing, using materials like quantum wells and quantum dots, and using phosphors.

### 4.2.1 Frequency Mixing

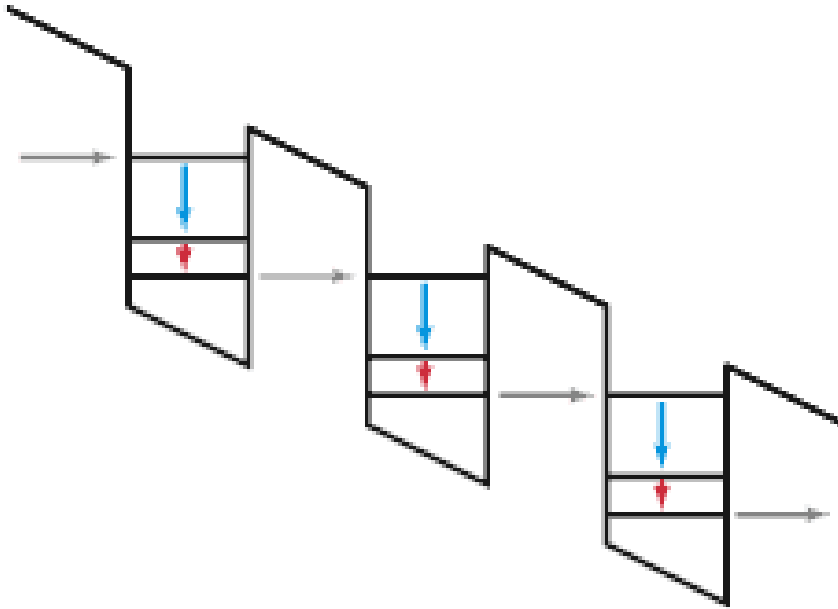
The idea of converting infrared to visible light for better light detection criteria is not a new idea. This has been attempted before by other companies but has been unsuccessful in practice. These products have used in the past a technique known as frequency mixing. Frequency mixing is a nonlinear process where two photons mix together in a nonlinear medium (typically a crystal) to generate a new frequency. The process used in other products to create visible light from infrared light was specifically sum frequency mixing. This meant the medium would absorb light with a low frequencies (for example 1064 nm and 1550 nm) and add together to create light with a higher frequency (for example 630 nm). Since this is a nonlinear process high intensity light is needed and the spectrum created from this is a nonlinear dependent spectrum which makes it a non-ideal method for generating an accurate model of a spectrum. Due to this, other methods are pursued and nonlinear methods are avoided.

### 4.2.2 Material Up-Conversion

#### 4.2.2.1 Quantum wells

Quantum wells are double hetero-junction semiconductor lasers that confine an electron via potential energy barriers. Quantum wells come from the idea of finite quantum square wells. Quantum square wells tell us we can have different states or eigenvalues for different potential energies. A quantum well is essentially a quantum square well that has been confined in one dimension. As a quantum well becomes more confined in length the larger the spacing becomes in energy eigenvalues. The larger the spacing, the more range of frequencies can be supported by the quantum well. If the potential energy barrier between quantum wells is small enough, an electron can tunnel through the barrier and end up at a higher energy level. Such a technique is known as a quantum cascade laser shown in the figure below.





**Figure 5: Quantum cascade well.** The following diagram shows the process in which an electron can tunnel through a finite quantum square well and increase in energy level to cause up-conversion.

This process can be repeated by confining a quantum square well in three dimensions. This is what is known as a quantum dot. A quantum dot can cover wider range of wavelengths than a quantum well since it is more confined.

#### 4.2.2.1.1 Process

Quantum cascade lasers can be created by confining a quantum well in one dimension. Quantum dots can be created by confining a quantum well in three spatial dimensions. The chemistry of how to create quantum dots is quite complex.

#### 4.2.2.1.2 Materials

Common materials for quantum cascade lasers are InGaAs and GaAs. Common materials for quantum dots are PbSe/CdSe/CdS. It is important to note that these quantum dot materials can be quite toxic.

#### 4.2.2.2 Phosphors

The word *phosphor* comes from the Greek which means “light bearer” and in the Greek myths is personified by the goddess Venus. Phosphors are solid luminescent materials (often rare earth or transition metals) that emit a specific light frequency after absorbing or being excited at a different light frequency. Phosphors have been used since the beginning of the 20<sup>th</sup> century for a wide range of optical and electrical engineer applications. From cathode ray tubes to fluorescent displays, LED coatings, semiconductor lasers, plasma and LCD displays, biomedical devices and agricultural usages, to name a few, phosphors

have found a wide range of applications due to their optical and electrical properties. Due to the nature and the practical applications of phosphors it is plausible that phosphors could be the ideal material for the up-conversion process desired.

#### 4.2.2.2.1 Process

The mechanism that is of interest to us is the mechanism known as phosphorescence. Like semiconductors, phosphors have a conduction and valence band, and can be doped with impurities to add donors and acceptors to the lattice structure. Light can come in and interact with an exciton to create an electron-hole pair. There is a process known as quenching, which decreases the amount of luminescence in a phosphor. The process we are interested in is known as photostimulated luminescence through electron trapping, which is the increase of the amount of luminescence in a phosphor. The process is simple, the electron-hole pair gets created like normal but decays down to another, more stable energy level where the electron is [3] then trapped and does not decay back down to the ground state. Instead it stays there until it is stimulated by another photon where it is excited to a higher energy band then decays down to lower energy bands, releasing another photon. For our interests we want a material that has electrons which are stimulated, or charged, up to the first conduction band by ultraviolet light, fall down to the electron trapped energy band, then are stimulated by near-infrared light to release visible light. This process removes any nonlinearities involved and should yield more reliable results.

#### 4.2.2.2.2 Materials

As stated in section 4.2.2.2, most phosphor materials are doped with rare earth or transition metals. The different concentrations will affect the efficiencies of the light absorption and the emission. We examine the different phosphors available to us that could potentially work for the application we have in mind. Likewise, we examine the different concentrations of dopants in each to determine most desirable phosphor for our needs.

##### 4.2.2.2.2.1 ZrO<sub>2</sub>:Er<sup>3+</sup>

Strong visible emission under UV (320 nm) and IR (967 nm) excitation on ZrO<sub>2</sub>:Sm<sup>3+</sup> and ZrO<sub>2</sub>:Er<sup>3+</sup> nano-phosphors. Green (545 nm) and red (680 nm) emissions bands were observed under IR excitation through an up-conversion process.

The effects of Er<sup>3+</sup> concentration in ZrO<sub>2</sub> on the red (680 nm) and green (545 nm) upconversion emission from Er<sup>3+</sup> under near infrared radiation (NIR) excitation (at both 1438 and 962 nm) are presented. For the highest Er<sup>3+</sup> concentration used, the red band is almost quenched under VIS (489 nm) excitation, whereas it is enhanced under NIR excitation. This is shown in the figures below.

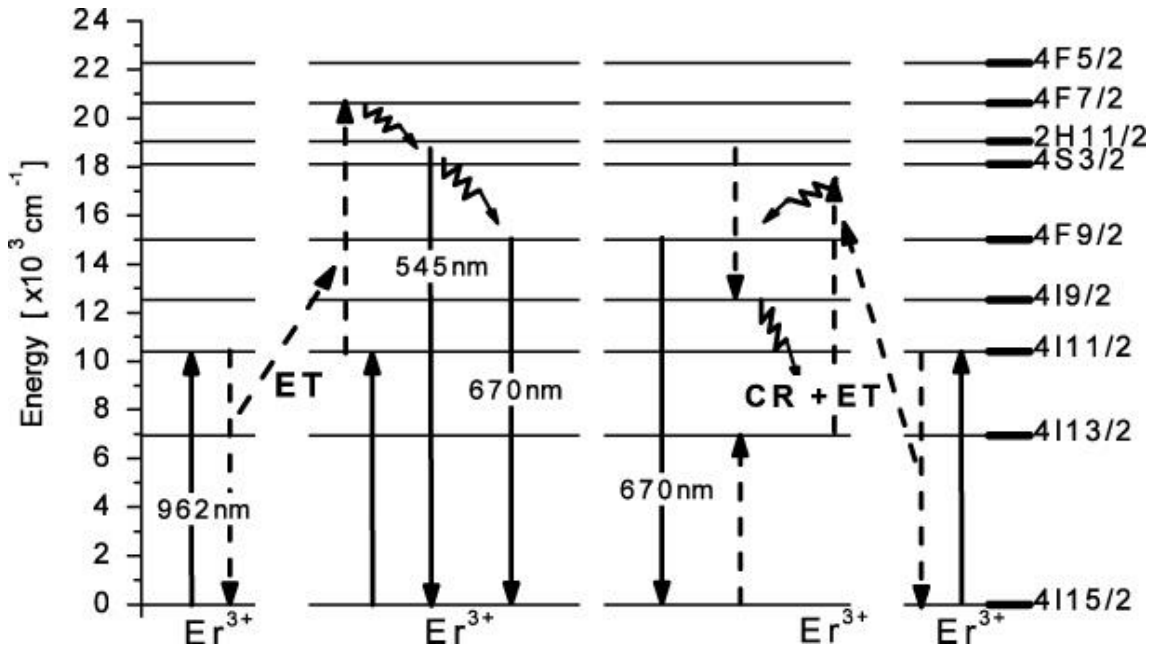


Figure 6: ZrO<sub>2</sub> band diagram for 962nm absorption.

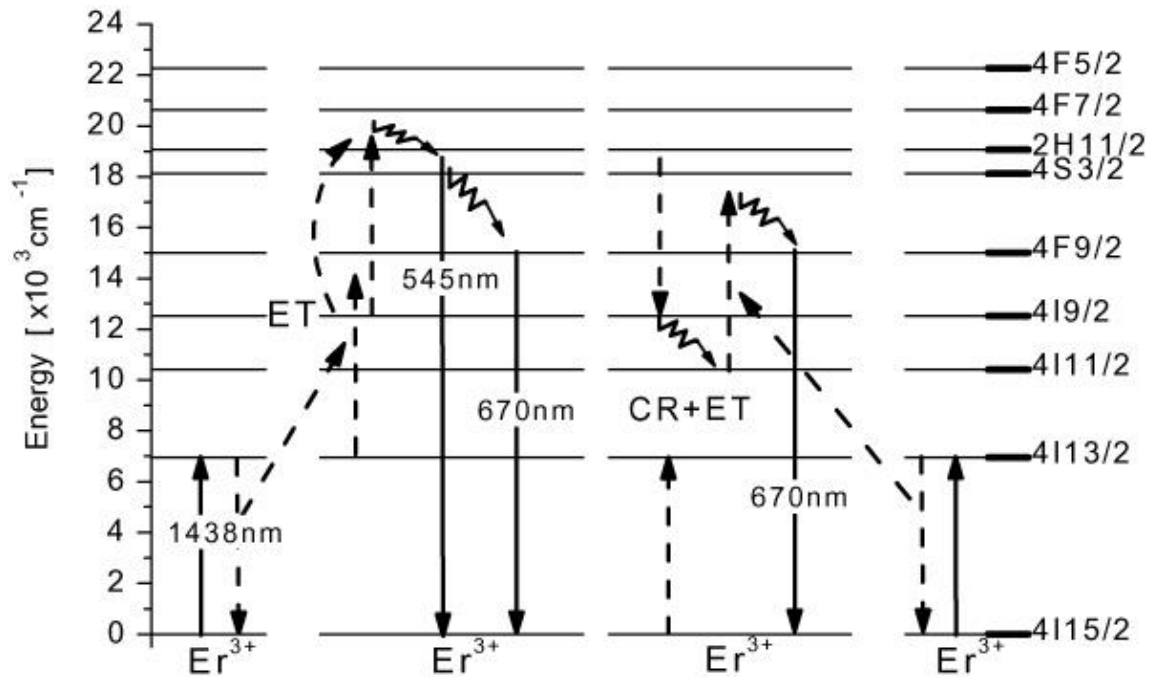
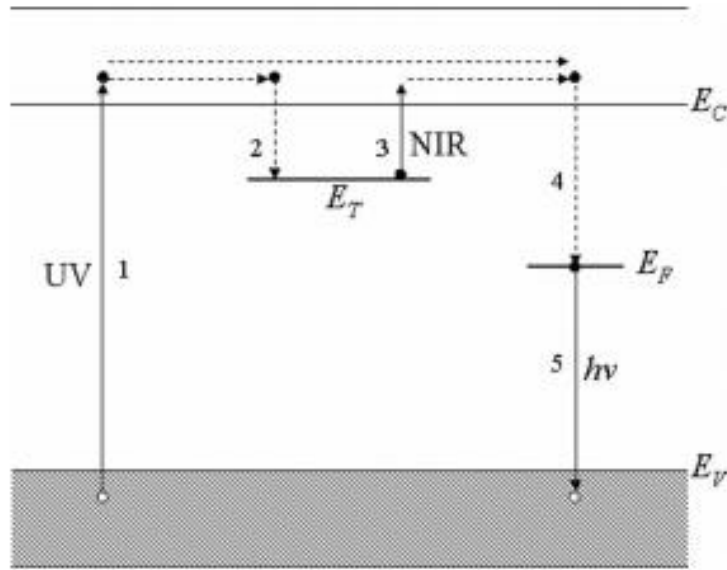


Figure 7: ZrO<sub>2</sub> band diagram for 1438nm absorption.

#### 4.2.2.2.2 ZnS:Cu,Mn

ZnS:Cu,Pb is very promising phosphor. It is most notable for its usage in infrared detector cards. It is charged by blue and ultraviolet wavelengths around 400 nm,

is stimulated by near-infrared wavelengths 700-1500 nm, and emits visible light at 490 nm. The process can be seen in the figure below.

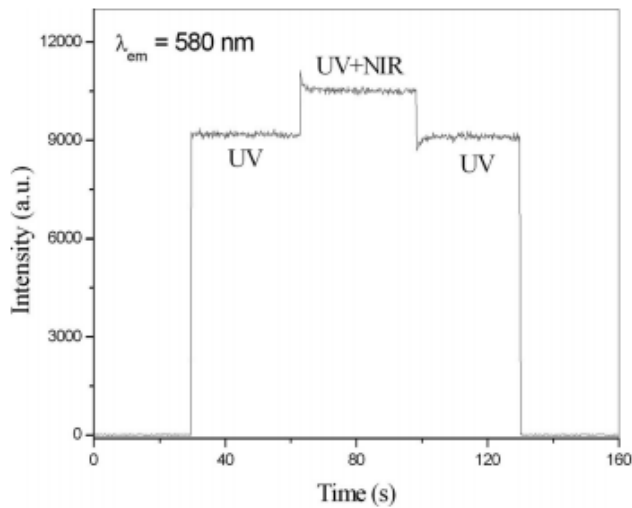


**Figure 8: ZnSu:Cu,Pb electron tapping band diagram.**

In the preceding figure, a 365 nm LED and a 980 nm LD were used as the UV and the NIR light sources.

#### 4.2.2.2.1 ZnS:Cu,Pb

ZnS:Cu,Pb is also very promising phosphor. It is charged by blue and ultraviolet wavelengths around 400 nm, is stimulated by near-infrared wavelengths 700-1500 nm, and emits visible light at 580 nm. The process can be seen in the figure below.



**Figure 9: ZnSu:Cu,Pb,Mn electron tapping band diagram.**

In the presence of a relatively high percentage of lead or certain other agents and after the usual excitation, zinc sulfide phosphors become capable of storing luminescence energy at such a high potential that, unlike phosphorescence, it can be released only by radiation with the near infra-red. There are two stimulating bands—a strong one at  $1.25\text{--}1.60\mu$  and a weaker one adjoining the visible. The resulting luminescence is increased by a small content of Manganese.

#### 4.2.2.2.2 YbF<sub>3</sub>:Er<sup>3+</sup>

A synergistic effect between UV down-conversion and IR up-conversion is witnessed in YbF<sub>3</sub>:Er<sup>3+</sup> phosphors by employing the dual wavelength (369 nm and 980 nm) excitation source. The green (548 nm) and red (656 nm) emission bands of YbF<sub>3</sub>:Er<sup>3+</sup> can be observed under 980 nm excitation at room temperature.

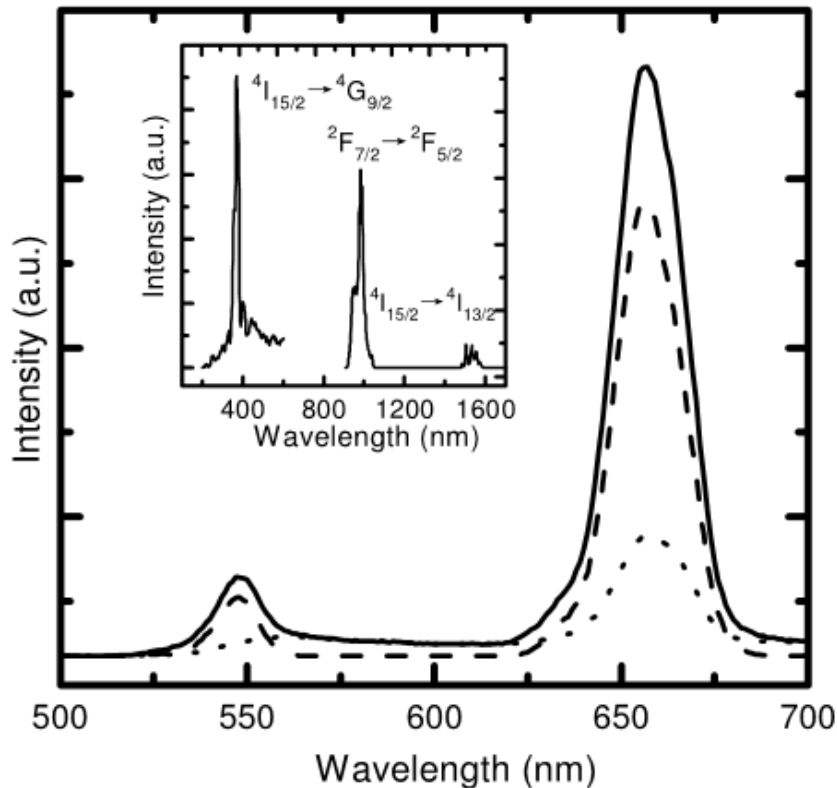


Figure 10: Absorption and emission plot of YbF<sub>3</sub>:Er<sup>3+</sup>.

### 4.3 Pumping

When using phosphors that must be charged, an external pump source should be used for best efficiency. The pumping mechanism plays an important role. If the phosphor is not charged properly then the impinging test near infrared photons will not cause emission of visible light photons. For many phosphors room light is

enough to keep the material charged but external pumping is still a better option. In addition in dark locations (important for this design) it is absolutely necessary.

The external pump is usually relatively high energy light, such as ultra-violet. This allows the electrons to be moved to a higher level. It is important the high energy pump does not pump the electrons higher than the band gap because that would cause emission directly from the ultra-violet light. This design will be explained in more detail in chapter 5, "design constraints". By energizing the electrons to this level the low energy infrared light is able to give the electrons the last bit of energy they need to pass the band gap and cause visible light emission. This can be seen in the figure below. Visible light has an energy that is less than ultra-violet but more than infrared. This makes this process very logical because a very high energy photon combine with a low energy photon will emit a medium energy photon.

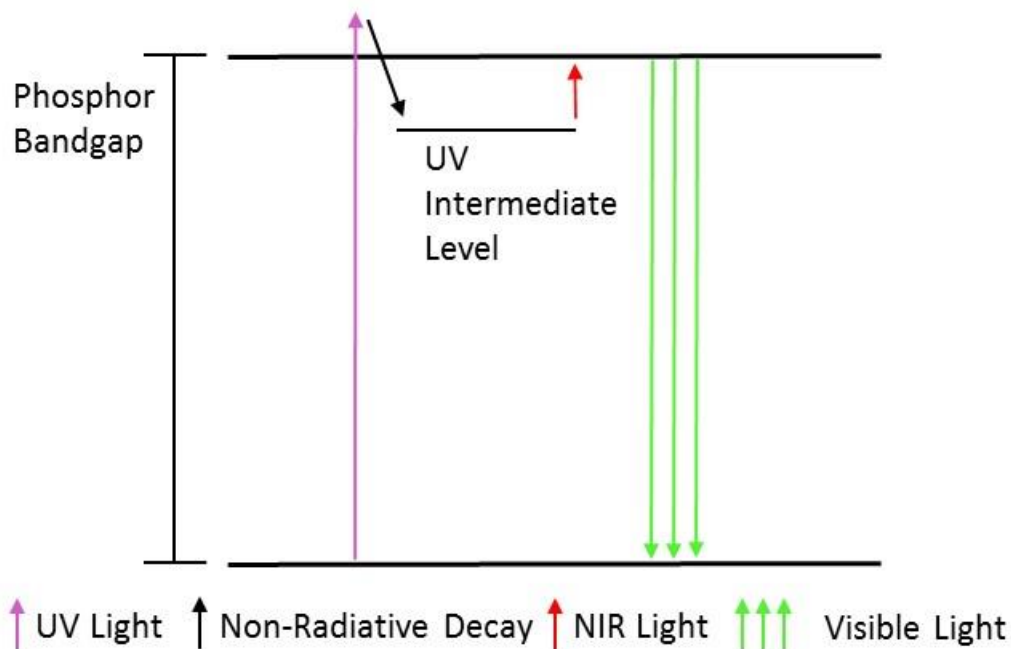


Figure 11: Band-gap representation of the UV light pump exciting the electron to an intermediate level, the IR light exciting the electron past the band gap and the visible light emission.

By using a pump the usually non-linear up-conversion process becomes relatively linear. This is very important and will also be explained.

There are two different options for pumping devices, laser diodes and light emitting diodes. In addition to these two different devices there are multiple different modulation methods for pumping. If previous experimental tests performed (test results were provided to us) this played a large role in the efficiency of the phosphor. We will test all these methods and some additional methods we feel are promising and missed in their testing.

### 4.3.1 Laser Diode

A laser diode, or LD, is an electrically pumped pn or pin diode. These are often done with a double heterostructure to get the best gain and also to act as a waveguide for the light. The wavelength of the light generated is dependent on the bandgap of the material used. The cleaved ends of the diode act as a resonator for the cavity. The longitudinal modes, or the amount of modes that can be supported by the cavity, will be dependent on the length of cavity.

### 4.3.2 Light Emitting Diode

A light emitting diode, or and LED, is a pn diode. It generates light much in the same way a laser diode does, however the light is not guided by a waveguide and the spectrum is much larger. The light emitted is incoherent which can be bad for certain applications. In this particular case as long as the photons impinge on the phosphor, coherently or incoherently, the charging will be accomplished. The plus side of LEDs is that they are simpler and cheaper compared to LDs. Adding another source into a spectrometer is met with some challenges, so the simpler the better.

### 4.3.3 Pumping Process

Based on previous work done by Ocean Optics, we have four different methods for illuminating the phosphors. In addition to these four we will be trying two new methods, which are combinations of the first three and the fourth. The advantages and disadvantages, as well as a description, of each method is provided below.

#### 4.3.3.1 Method 1: Direct Continuous Illumination (DCI)

The ultraviolet LEDs are left on to charge the phosphor at all times. Likewise, in combination with the ultraviolet LED light, the infrared light signal is added to the phosphors.

The advantage of this method is that it is by far the simplest method to implement. The disadvantage of this method is that it has a high noise ratio and adds a lot of dark current to the photodetector. This reduces the dynamic range of the photodetector which reduces the ability to differentiate the spectrum.

#### 4.3.3.2 Method 2: Discrete Pulsed Illumination (DPI)

The ultraviolet LEDs flash once to charge the phosphor, then, after a certain amount of time after the light fades and the phosphor needs to be charged again, flashes once more.

The advantage of this method is that it is suitable for infrequent measurements and with very low signal levels. Likewise this process had little autofluorescence

which yielded the highest dynamical range compared to all the other methods. This disadvantage is that it required a long amount of time (up to ten seconds for one second of integration time). It also required new dark current measurements with the fading auto-fluorescence which changes the baseline. As the signal hits the phosphor it discharges over time causing it to decay and reduce the emission intensity. When the infrared signal is turned off, there still remains an afterglow on the phosphor for minutes, making dark current measurements difficult.

#### 4.3.3.3 Method 3: Continuous Pulsed Illumination (CPI)

The LEDs are pulsed once then as the auto-fluorescence decays to a useable level then it takes one integration time. The integration time in this method begins sooner than it did in the DPI method.

The advantage here is that, especially compared with the DPI method, the integration time is considerably shorter. Likewise, since the integration time starts at a fixed amount of time after the LEDs flash, the background level is constant. The signal level and the charge level are eventually balanced and reach an equilibrium point. The disadvantage is that the dark signal level is higher than in the DPI method, and the time it takes to reach an equilibrium point is very long. Also, when changing integration times, the “duty cycle” of flash time versus “period” (which is different from integration time) must remain consistent, otherwise, the material charges or discharges to equilibrium slowly, and measurements appear to drift.

#### 4.3.3.4 Method 4: Filtered Direct Illumination (FDI)

The IR coating is applied over a base coating that blocks the charge wavelength from reaching the detector. The charging LEDs are always on.

The advantage of this method is that there is no firmware changes required and no time settings required. Also there is not a long wait time for the data to be collected. The disadvantage is that all autofluorescence from the charging LEDs reaches the detector, resulting in dark noise. The draft reports that they are “not sure if this problem also exists for the continuous pulsed mode.” Likewise the draft reports that they are unsure if it is possible to apply two coatings.

#### 4.3.3.5 Method 5: Filtered Discrete Pulsed Illumination

Filtered discrete pulsed illumination is a modification of method two. This method takes the advantages of discrete pulsing of the LED and adds a filter. This filter will help the detection because it will decrease the noise caused by the high energy UV light. This method has not been tested before.



### 4.3.3.6 Method 6: Filtered Continuous Pulsed Illumination

Filtered continuous pulsed illumination is a modification of method three. This method takes the advantages of the continuous pulsing of the LED and adds a filter. This filter will help the detection because it will decrease the noise caused by the high energy UV light. This method also has not been tested before.

## 4.4 Filter

### 4.4.1 Purpose

In our system we will have both near infrared light (the test light) and ultra-violet light (the pump light). The UV light will impinge on the phosphor and the majority will be absorbed to charge the electrons to the specific energy level the UV photons cause. It is inevitable that not all of these photons will be absorbed.

These unabsorbed photons are useless to the up-conversion process and if they are seen by the detector on the other side of the phosphor, this can cause a problem. These UV photons are significantly high in energy for the visible detector and in comparison to the emitted visible photons. This can cause a lot of noise for the detector. The higher the noise in the detector system, the less sensitive our system can be. With efficiency of phosphor being the main concern, any extra noise must be eliminated.

It should be noted that in addition to UV photons not all being absorbed, it is likely not all NIR photons will be absorbed. This light is less of a concern to us for multiple reasons. The first reason being that these photons are much lower in energy and will cause less dark noise. The second reason is that Si detectors will not see light of this wavelength. The cut off wavelength for Si detectors is from roughly 300nm to 1100nm. The NIR photons will not be absorbed and will not cause much noise. But this wavelength does include the UV pump photons which is why they must be eliminated.

Optical filters are natural or engineered that cut off certain wavelengths of light. Much like electrical filters, there are different types such as low pass, high pass and band pass. Just like the term “up-conversion”, these types are categorized by frequency they pass. We will use these to eliminate the high energy UV photons. This method will be explained below.

### 4.4.2 Science

Filters work due to very basic principles in light and matter interaction. To explain the principal behind how filters work let’s first start with Maxwell’s equations in a source free system, i.e.:

$$\nabla \cdot \mathbf{E} = \rho_s = 0 \quad (1)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (2)$$

$$\nabla \times \mathbf{E} = -\partial \mathbf{B} / \partial t \quad (3)$$

$$\nabla \times \mathbf{B} = \frac{1}{c^2} \partial \mathbf{E} / \partial t \quad (4)$$

The only operators we have on our system that give us nonzero values are equations (3) and (4). If we take the curl of the curl of the electric field (and remember our basic calculus identity  $\mathbf{A} \times \mathbf{B} \times \mathbf{C} = \mathbf{B}(\mathbf{A} \cdot \mathbf{C}) - \mathbf{C}(\mathbf{A} \cdot \mathbf{B})$ ), we have:

$$\nabla \times \nabla \times \mathbf{E} = -(\nabla \times \partial \mathbf{B} / \partial t)$$

$$\nabla(\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E} = -\partial / \partial t (\nabla \times \mathbf{B})$$

$$\nabla^2 \mathbf{E} = \frac{1}{c^2} \partial^2 \mathbf{E} / \partial t^2 \quad (5)$$

Equation (5) is what's known as the wave equation. We recognize this as a partial differential equation where the solution can be:

$$\mathbf{E} = f(\mathbf{z} \pm \mathbf{vt})$$

or, more specifically:

$$\mathbf{E} = E_0 \exp(i(\mathbf{kz} - \omega \mathbf{t})) \quad (6)$$

where  $\mathbf{z}$  is the spatial vector,  $k$  is the wave number,  $\omega$  is the angular frequency,  $\mathbf{t}$  is the time vector, and  $E_0$  is the electric field amplitude. We verify this is a solution,

$$\partial^2 \mathbf{E} / \partial t^2 = -\omega^2 E_0 \exp(i(\mathbf{kz} - \omega \mathbf{t}))$$

$$\nabla^2 \mathbf{E} = -k^2 E_0 \exp(i(\mathbf{kz} - \omega \mathbf{t}))$$

$$k^2 E_0 \exp(i(\mathbf{kz} - \omega \mathbf{t})) = \frac{1}{c^2} \omega^2 E_0 \exp(i(\mathbf{kz} - \omega \mathbf{t}))$$

and obtain the dispersion relationship:

$$k^2 = \frac{\omega^2}{c^2} \eta(\omega)^2 \quad (7)$$

where the complex refractive index,  $\eta(\omega)$ , is  $\eta(\omega) = n(\omega) + i\kappa(\omega)$ , and  $n(\omega)$  is the frequency dependent refractive index, and  $\kappa(\omega)$  is the frequency dependent extinction coefficient.

Now let's consider the equation of motion:

$$m \frac{d^2 \mathbf{r}(t)}{dt^2} + m \Gamma \frac{d\mathbf{r}(t)}{dt} + m \omega_0^2 \mathbf{r}(t) = -e \mathbf{E}(t) \quad (8)$$

where  $m$  is mass,  $\omega_0$  is the resonance frequency and  $\Gamma$  is the dampening. We take the Fourier Transform of both sides and solve for  $\mathbf{r}(\omega)$ :

$$\mathbf{r}(\omega) = -e/m \left( \frac{\mathbf{E}(\omega)}{\omega_0^2 - \omega^2 - i\Gamma\omega} \right) \quad (9)$$

If we define the dipole moment  $\boldsymbol{\mu}(\omega) = -\frac{e}{m} \mathbf{r}(\omega)$  we have:

$$\boldsymbol{\mu}(\omega) = \frac{e^2}{m} \left( \frac{\mathbf{E}(\omega)}{\omega_0^2 - \omega^2 - i\Gamma\omega} \right) \quad (10)$$

If the atomic polarizability  $\alpha(\omega)$  is related to  $\boldsymbol{\mu}(\omega)$  by the relationship,

$$\boldsymbol{\mu}(\omega) = \alpha(\omega) \mathbf{E}(\omega) \quad (11)$$

we have:

$$\alpha(\omega) = \frac{e^2}{m} \left( \frac{1}{\omega_0^2 - \omega^2 - i\Gamma\omega} \right) \quad (12)$$

We will from here on consider  $\alpha(\omega)$  as a scalar.

With  $N$  atoms per unit volume  $V$ , we have a net dipole moment per unit volume  $P(\omega)$  which is:

$$\mathbf{P}(\omega) = \frac{1}{V} \sum_{i=1}^{NV} \boldsymbol{\mu}_i(\omega) = N \langle \boldsymbol{\mu}(\omega) \rangle \quad (13)$$

We can relate this to  $\alpha(\omega)$  using equation (11) and (13). In scalar terms, we have:

$$P(\omega) = N\alpha(\omega)E(\omega) = \epsilon_0 \chi(\omega) E(\omega) \quad (14)$$

Where  $\chi(\omega)$  is the susceptibility of the material. Hence,

$$\chi(\omega) = \frac{Ne^2}{m} \left( \frac{1}{\omega_0^2 - \omega^2 - i\Gamma\omega} \right) \quad (15)$$

Note that this has real and imaginary terms. In order to simplify, we'll rationalize the denominator by multiplying by the complex conjugate to separate these terms and make the identity for the plasma frequency,  $\omega_p = \frac{Ne^2}{m}$ .

$$\chi(\omega) = \omega_p \left[ \frac{(\omega_0^2 - \omega^2) + i\Gamma\omega}{(\omega_0^2 - \omega^2)^2 + \Gamma^2\omega^2} \right] \quad (16)$$

Now we have the real and imaginary components ( $\chi'(\omega)$  and  $\chi''(\omega)$  respectively).

$$\chi'(\omega) = \omega_p \left[ \frac{(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \Gamma^2 \omega^2} \right] \quad (17)$$

$$\chi''(\omega) = \omega_p \left[ \frac{\Gamma \omega}{(\omega_0^2 - \omega^2)^2 + \Gamma^2 \omega^2} \right] \quad (18)$$

These equations are Lorentzian and can be related to each other using the Kramer's Kronig relationships:

$$\chi'(\omega) = -\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\chi''(\omega')}{\omega - \omega'} d\omega' \quad (19)$$

and

$$\chi''(\omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\chi'(\omega')}{\omega - \omega'} d\omega' \quad (20)$$

Now we can consider the dispersion relationship:

$$k^2 = \frac{\omega^2}{c^2} (1 + \chi(\omega)) \quad (21)$$

along with equation (7) to relate the complex refractive index to the complex susceptibility.

$$\eta(\omega) = n(\omega) + i\kappa(\omega) = \sqrt{1 + \chi'(\omega) + i\chi''(\omega)} \quad (22)$$

This leads to the relationships:

$$n(\omega) - \kappa(\omega) = 1 + \chi'(\omega) \quad (23)$$

$$2 n(\omega)\kappa(\omega) = \chi''(\omega) \quad (24)$$

Since we were able to relate the real and complex susceptibilities to each other through the Kramers – Kronig relationship, we can calculate  $n(\omega)$  and  $\kappa(\omega)$  from the above relationships and relate them. Likewise, we call the absorption coefficient,  $\alpha(\omega)$  (different from the atomic polarizability mentioned in equations (11) – (14)), and relate it using:

$$\alpha(\omega) = 2\omega \frac{\kappa(\omega)}{c} \quad (25)$$

So far, we have come up with equations for the refractive index, extinction coefficient, absorption coefficient, and how they relate with frequency, and shown how they can be related to each other. That being said, we can model the reflection, transmission and absorption of different materials. We already have an equation for the absorption coefficient  $\alpha(\omega)$ . For the reflection coefficient we have:

$$r(\omega) = \frac{1-n(\omega)-i\kappa(\omega)}{1+n(\omega)+i\kappa(\omega)} \quad (27)$$

For the reflectance we use:

$$R(\omega) = r(\omega)r(\omega)^* = \frac{(1-n(\omega))^2 - \kappa(\omega)^2}{1+n(\omega)^2 + \kappa(\omega)^2} \quad (28)$$

Note that the reflectance can have a value between 0 and 1 for it is a percentage of light reflected. If we add together the reflectance, transmittance and absorbance (and in some cases scattering) we will always have a value of 1, meaning a certain percentage of light can either be reflected, transmitted or absorbed by a system or material and adding together the percentages of light reflected, transmitted or absorbed gives us the 100% of the we put in to the system or material.

#### 4.4.3 Filter Materials

Different types of materials will reflect, transmit and absorb at different frequencies. Table (xxx) depicts how these types of materials are different.

Material Type	Material Properties
Dilute Gases	<ul style="list-style-type: none"> <li>• Refractive index near 1.</li> <li>• Narrow absorption lines.</li> <li>• Low reflection, mostly transparent.</li> </ul>
Insulators	<ul style="list-style-type: none"> <li>• Refractive index above 1, typically below 2.</li> <li>• Low absorption throughout the visible range.</li> <li>• Higher absorption in the ultraviolet and higher frequency range.</li> <li>• Low reflection.</li> </ul>
Semiconductors	<ul style="list-style-type: none"> <li>• Refractive index typically between 2.5 – 4.</li> <li>• Absorption starts at the ultraviolet and continues with lower frequencies.</li> <li>• High reflection.</li> </ul>
Metals	<ul style="list-style-type: none"> <li>• Refractive index less than 1 and large <math>\kappa</math> at low frequencies.</li> <li>• Very high absorption in the visible and infrared range.</li> <li>• Very high reflection in the visible range.</li> </ul>

The table above is the relationship in how dilute gases, insulators, semiconductors, and metals refract, absorb, and reflect light.

Most filters used are insulators, typically glass, plastics, polyester, or gels. The common types of these filter materials are longpass, shortpass, bandpass, and dichroic filters.

Longpass, shortpass and bandpass filters all absorb light at different wavelengths and transmit light at other wavelengths. The key word to remember here is that they absorb the light. A longpass filter will pass longer wavelengths and absorb shorter wavelengths. A shortpass filter, as one might imagine, will pass shorter wavelengths and absorb longer wavelengths. A bandpass filter will absorb wavelengths shorter one of its cutoff points, transmit specific wavelengths within a certain range, then cutoff again at longer wavelengths.

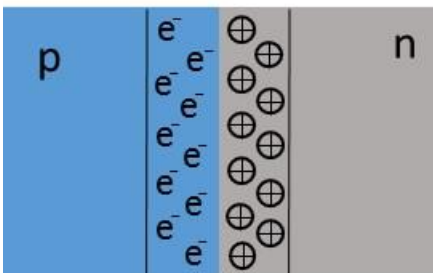
A dichroic filter (also known as an interference filter) on the other hand reflects certain wavelengths instead of absorbing them. In order to reflect the specific wavelengths, dichroic filters are made by depositing layers of thin films unto a glass substrate. The differences in refractive indices causes some wavelengths to transmit and others to reflect, and when they reflect they interfere destructively for unwanted wavelengths to try to eliminate them, while simultaneously interfering desired wavelengths constructively to reinforce them.

## 4.5 Detection

### 4.5.1 Photodiode

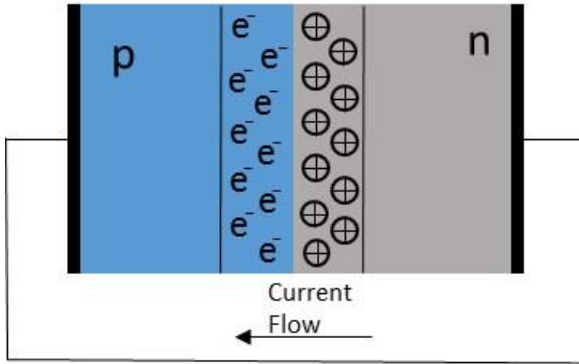
In order to detect the incoming light, photodiodes are needed in the circuit to convert said light into current. Photodiodes are semiconductor devices that take incoming light and convert the energy to electrons and holes.

Photodiodes are usually pn junctions. The the p-type and the n-type semiconductors come together, the holes and electrons will flow to their respective lower potential and create a small charge in the “depletion region”. The electric field in this region opposes that of the electron flow so no current is created [4].



**Figure 12: Representation of pn photodiode. P side (acceptor doped) in blue and N side (donor doped) in grey. The center area between the two vertical lines is the depletion region and negative ions form to the left of the junction and positive ions to the right.**

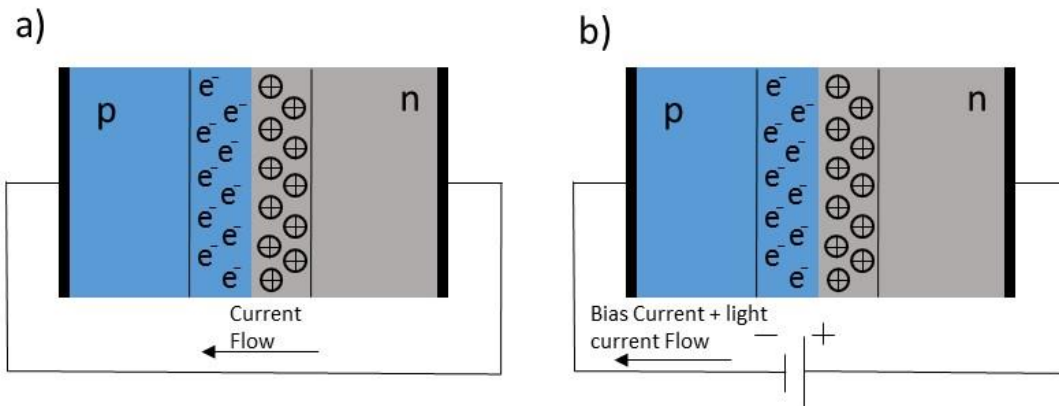
This is a steady state system that is changed when photons hit the pn junction depletion region. If these photons have substantial enough energy for the particular material to be absorbed, they will create an electron hole pair [4]. The electrons and holes will drift to their respective terminals. When the terminals are connected together this will create a current flow.



**Figure 13: The same pn photodiode but with terminals connected. The current flow can be seen from n to p side.**

This current flow can be measured. This allows for detection of light on the pn junction. When the light intensity varies up and down the current flow will vary up and down respectively. It is typical to measure the current but voltage can be measured as well.

Such devices can be operated in photovoltaic or photoconductive mode. In photovoltaic mode there is no voltage applied and the measured current is simply proportional to the light. In photoconductive mode a reverse bias is applied. This is opposite of optoelectronic devices such as LED's and lasers. This is because these type of optoelectronics are designed to take electrical current to emitting photons. When a reverse bias is applied the additional current created by the light is proportional to the light intensity not the total current (including the bias).



**Figure 14: a) pn photodiode in photovoltaic mode, with no applied bias and b) pn photodiode in photoconductive mode, with applied bias.**

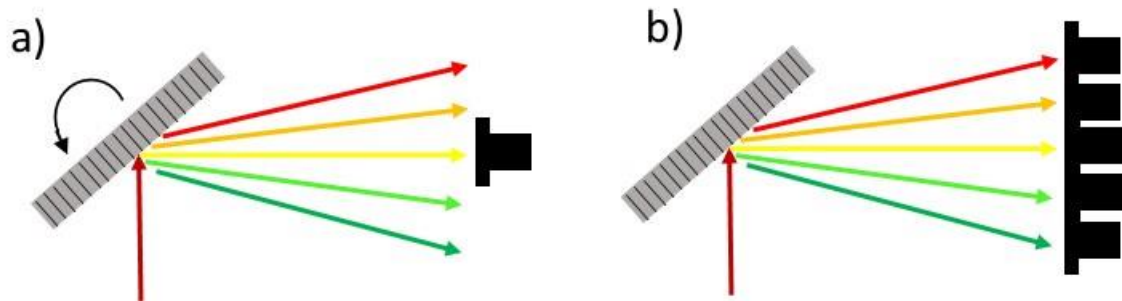
Even when there is no light, the photodiode will produce a current known as dark current. However, if the photodiode is used in photovoltaic mode (the diode is connected to the ground), then there is no dark current. This mode is used more for precision and not speed, and allows low noise and a linear output. It is advantageous to operate in the photoconductive mode because the bias increases the width of the depletion region which increases responsivity.

#### 4.5.2 Single Photodiode vs. Photodiode Array

In any standard grating based spectrometer there are two techniques used to detect the signal of each wavelength. One method involves a single photodiode while the other uses an array.

In a single photodiode set up the grating is rotated so that the reflecting/transmitting light is varying as rotated. This means that in any instance in time a different wavelength light with a different signal is hitting the photodiode. This data is analyzed and recorded then plotted over the varying wavelengths. To change wavelength ranges the beginning and ending rotation points on the gratings are changed.

The second method is to use an array of photodiodes. In this case the grating is fixed. The split wavelengths are, all at once shined on the array of photodiodes. The data at each photodiode is analyzed and recorded. The data is plotted over the varying wavelengths in the same manner as the single photodiode design. To change wavelength ranges with the photodiode array, again, the beginning and ending rotation points on the gratings are changed.



**Figure 15: a) Method one where the grating is rotated and only one wavelength at a time is detected by the single detector. b) Method two where the grating remains locked in position but multiple detectors are used to see all the wavelengths at once.**

#### 4.6 Signal Amplification



There are multiple methods amplify a signal for detection. The signal can be amplified before, during and after detection. Before detection will be optical amplification, during will be specific types of detectors and after will be electrical.

### 4.6.1 Optical

Optical amplifiers are used in a wide variety of applications and in multiple different forms. The common factor is that light is usually somehow trapped in a cavity and makes multiple passes while created more photons of the same energy. Optical amplification is determined by the gain factor which follows the exponential relation below:

$$G = e^{\gamma(\nu)*L}$$

The first method is to physically take the signal, create a free space cavity out of two, or more, mirrors and a gain medium. The entering photons will have a round trip lifetime. This means they will bounce around the cavity a specific amount of times. Each time the photons make a round trip they pass through the gain medium and free up more identical photons from energized electrons in the medium. This set up is used in many applications and is very basic. This does not work well with simple compact systems because it is the equivalent of having a laser.

The second method is conceptually very similar but is not done in free-space. By using a fiber you can create the equivalent of a cavity. The ends of a fiber can be cleaved and made into dielectric mirrors. The light can enter one end of the fiber, interact in the fiber and exit with enough power. Instead of a gain medium in a free-space cavity, fiber amplifiers are doped. This allows the incoming light to excite electrons the entire length of the fiber. There are two main advantages to this method. One is that it is easier to align then a free space cavity and the second is that the fiber can be coiled. In referencing the formula above the gain factor is dependent of the length of the cavity. Because fiber can be coiled and compacted one can get a much larger gain factor with a fiber amplifier because in the same space as a free-space amplifier you can get more optical path length.

### 4.6.2 Amplifying Detectors

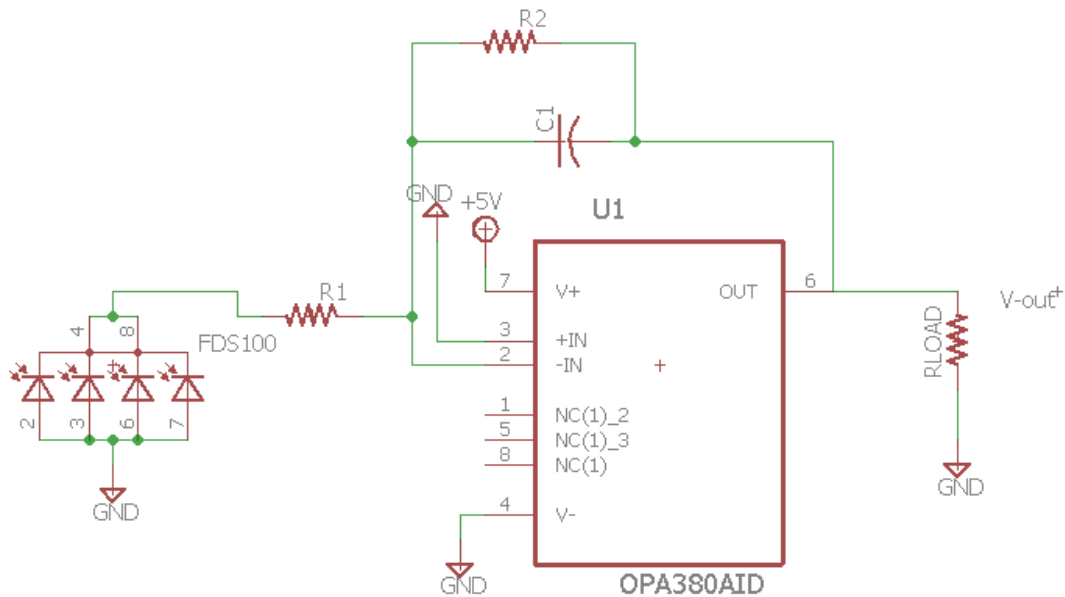
Two main types of amplifying detectors are avalanche photodiodes and photomultipliers. Avalanche photodiodes have a high reverse bias applied very near the breakdown voltage. With such a strong reverse bias the carriers in the semiconductor are accelerated by the impinging photons and multiple other carriers will emit identical photons. Photomultipliers work in a similar manner but operate similar to an old cathode ray television. They are vacuum tubes and instead of the light being absorbed by the semiconductor the photons are absorbed by a photocathode. A high voltage is applied which accelerates the photons which then generates more photons. All these photons are then detected on the detector. Both methods use a high voltage to accelerate and free more photons but the

difference is avalanche photodiodes amplify in the semiconductor while photomultipliers amplify before the semiconductor and use the semiconductor just to detect the multiplied photons.

### 4.6.3 Electrical

The signal can also be amplified in the electrical circuit. This is the most common and simplest method of amplification. A trans-impedance circuit can perform this operation. Such a circuit can convert the signal current into a voltage that can be later used in the analog to digital conversion. An operating amplifier, or op-amp is commonly used for voltage amplification and will also be used here. To minimize error an op-amp with little or no input offset voltage needs to be chosen. With higher input voltage offset, the higher the dark noise for the detectors. If we have high dark noise we will not be able to be as sensitive or precise in detection. Input-leakage current in another factor that must be minimized for the most sensitive and precise detection.

When one photodiode is used, this circuit is relatively simple. When multiple photodiodes are used, which is common in spectroscopy this circuit can get a little more complicated because each signal from each detector must be amplified. A simple schematic of the circuit is provided in the figure below:



**Figure 16: Simple trans-impedance signal amplifying circuit.**

## 4.7 AC to DC Conversion

In order to work with the data from the device, an ADC will be placed after the trans-impedance circuit. The ADC will allow the user to work with the analog data

that is being inputted. This is done by converting the voltage input into amplitudes and frequencies. The resolution of this device is determined by number of bits that it uses. The number of bits shows  $2^B$  distinct levels, where B is the number of bits. There are several architectures to consider when looking at ADC's.

#### 4.7.1 Delta-sigma

This type of architecture oversamples the input signal and then filters the wanted signal band. This is because in delta modulation the change in the signal is encoded. As a result a stream of pulses is generated. After this step, the signal goes through a 1-bit digital-analog converter (DAC) and adding a sigma signal, reducing the error made by delta modulation. This type of architecture allows for higher resolution but the sampling frequency suffers.

#### 4.7.2 Direct-Conversion

Also known as flash ADC, this architecture uses a bank of comparators to sample the input in parallel. This type of architecture is very fast in that it can sample in gigahertz, however the resolution suffers since it can only offer 8 bits or lower.

#### 4.7.3 Successive Approximation Register (SAR)

In this architecture the input analog waveform is converted using a binary search through all possible levels. This means that it looks up each bit one at a time. The comparator in this architecture must also be as fast and as accurate as the ADC. The latency in this architecture is only one cycle.

#### 4.7.4 Pipeline

This architecture combines the best of both flash and SAR in order to obtain both high resolution and sampling speed. This is done by comparing more than one bit at time. The drawback is that the latency is about 3 or more cycles.

## 5 Design Constraints

### 5.1 Resolution

The spectral resolution of our system will be determined by four main elements. These elements are the slit, the grating, the phosphor point spread function, and the number of detectors in the array.

#### 5.1.1 Slit

The slit is very important because it will determine the smallest possible size an object that can be imaged on the detector. A fiber optic input with a  $9\mu\text{m}$  core was used as the entrance slit.

### 5.1.2 Grating

The next element that will constrain our resolution is the grating. The grating determines the wavelength range of our spectrometer and how many wavelengths the grating will split the incoming light into. The higher the amount of wavelengths that get split up, the higher the resolution.

### 5.1.3 Phosphor Point Spread Function

The point spread function of the phosphor determines how much the point will spread. Meaning, if we take every single particle in the phosphor as a source that has its own spread and several of these particles are illuminated at once, how much the light will spread from its original beam width.

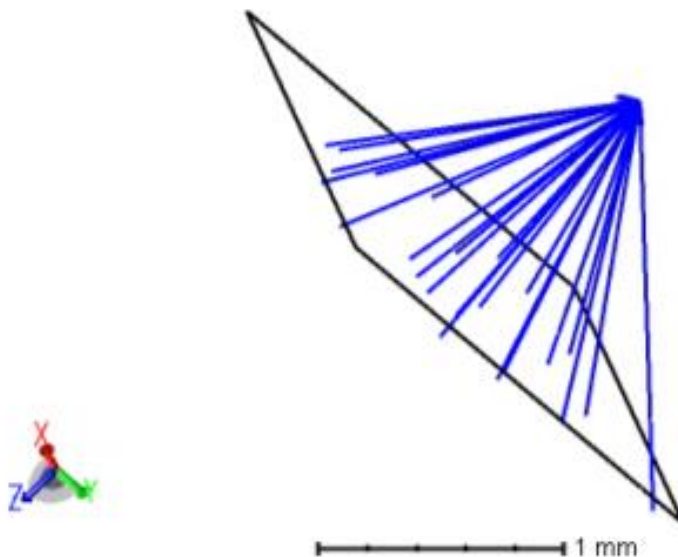
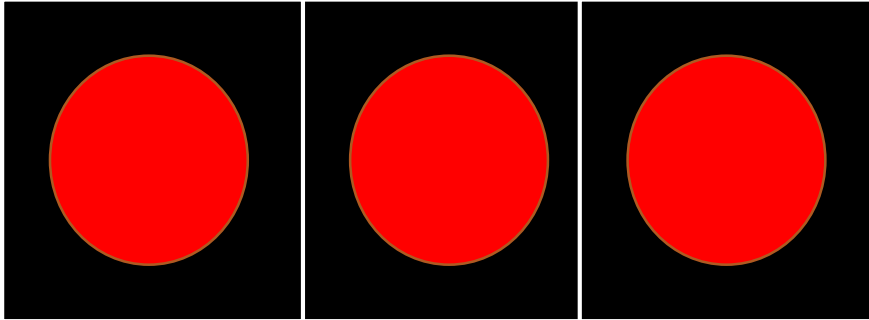


Figure 17: Zmax representation of point spread function.

### 5.1.4 Detector

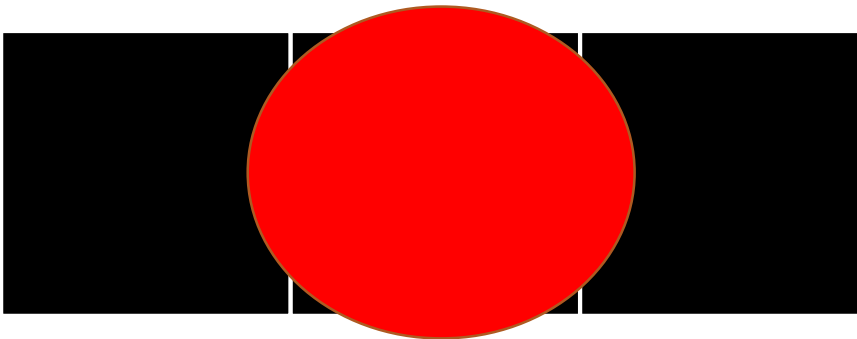
The final element is the detector. The detector will determine the amount of pixels available to us and how big each pixel will be. In the figure below is an example of

three detectors (three pixels) each being illuminated by three separate beams. In this case, we detect all three.



**Figure 18: An array of three detectors that each gets illuminated by their own, separate beams of light.**

The next figure, however, is an example where the beam is too big for the detector. In this case the beam hits the same three detectors and the detectors detect three beams even though there is only one.



**Figure 19: An array of three detectors that gets illuminated by one, single beam. In this case the detectors size is too small and the detector is detecting three separate beams when there is only one.**

It is important that we have as many detectors as we need, however if we are limited by the point spread function of the slit, phosphor, and the grating, it is unnecessary to have more detectors than points we can accurately detect. A good balance of detector size and number of detectors is needed

## 5.2 Device Cost/Size/Simplicity

It is important that this device is simple, compact, rugged and relatively cheap. We are working with Ocean Optics for this system and this is what their company is based off of. There are many ways to accomplish up-conversion, as seen in chapter 4 of this document but some of these manners such as frequency mixing or quantum well material up-conversion can be costly, big and complex.

### 5.2.1 Cost

To meet the needs of cost for this system we were constrained by making sure this system ends up being cheaper than a standard InGaAs detector spectrometer. The standard we set was from our sponsor, Ocean Optics, FlameNIR spectrometer. This is actually the entire motivation for this project because if cost was not a concern one would easily decide on using an InGaAs detector spectrometer because it is simpler and has less components in the system than our up-converting spectrometer.

When it came to quantum well materials, while they tend to be more efficient when it comes to up-conversion, they are less widely available. These materials are not found from standard material companies. In order to use these materials in this system we would have to have them specifically designed and prepared by a research lab. This is not viable for production and is also almost not viable for a single prototype.

There is no doubt that with a huge complicated fancy laser we could do frequency mixing to up-convert at almost any wavelength but with the cost of such a laser this method would make no sense. From a marketing perspective this is a product that would never sell except for the possibility of a few select specific customers. While it would be nice that just by changing the laser frequency we could up-convert for, theoretically, the entire infrared spectrum, we would also have to change the laser for each desired IR detection wavelength. In some cases this could be low but for the most part, IR lasers are very expensive. Frequency mixing also requires a second non-linear crystal. Not only is this one more component to spend money on but it is a complicated crystal that would need to be custom designed and anything custom designed is expensive.

The cost constraint is also what led to the decision to use an LED vs. an LD as a pump for the phosphor. As mentioned LD's are much more expensive and are not necessary for this system. LED's can be cheap as a dollar.

### 5.2.2 Size

The constraint of size for frequency mixing is that the lasers that would need to be used are not small. Especially when you compare their size to current Ocean Optics products. The only laser that could meet our needs for size are laser diodes and infrared laser diodes will not meet the design constraint for cost.

Size is also one of the constraints that caused us to design the phosphor and filter sandwich that will be described in chapter 6.

### 5.2.3 Simplicity

When it comes to simplicity both quantum well materials and frequency mixing were out of the question.

The quantum well material is much more complicated to design and manufacture. Like mentioned above it is only done in research labs right now. There is less known about these materials and to use them in this system could lead to problems later down the road that would not be realized at the time of prototyping.

In addition frequency mixing was also not an option due to its complexity. As mentioned, a laser and a non-linear crystal would need to be added into the system. When a laser diode and a non-linear crystal are used a whole new set of laser beam optical design complexities come into play. The optical design for this addition to the spectrometer would be more complicated than the entire optical design of a current Ocean Optics FlameNIR spectrometer. In addition this addition would require more optical components than the current Ocean Optics FlameNIR currently has.

The simplicity constraint is also what led to the decision to use an LED vs. an LD. As mentioned LD's are much more complicated to work with and are not necessary for this system.

#### 5.2.4 The Phosphor and LED Pump

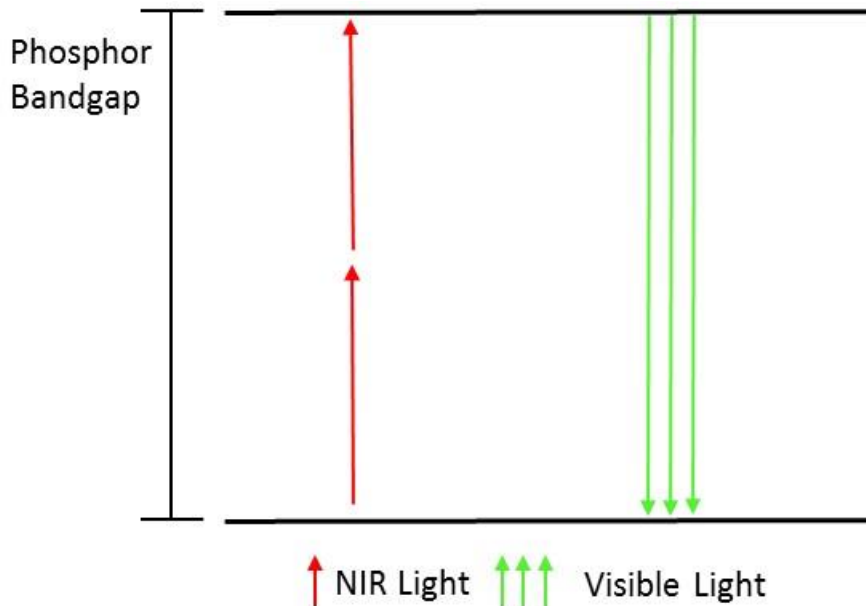
Using a phosphor with an LED pump quickly became the best option after considering the three constraints of cost, size and simplicity.

When it came to cost, phosphors are used in everyday IR cards that are laying around almost any optics lab that does even the slightest work in the IR. The phosphor itself is easily available, compact, cheap and simple.

The phosphor can be prepared as a coated layer which is obviously about as compact as can be attained in the z component. The length of the phosphor is determined by how far the grating splits up the wavelengths there for the phosphor does not contain the size in this component.

As far as simplicity, for up-conversion processes, phosphors is about as simple as it can get. The mechanism in which it works is described in chapter 4. Essentially the UV light pumps it, the NIR light hits it and is converted to visible light. This process only requires the addition of a pump LED and some filters.

There are phosphor that require pumps and phosphors that do not require pumps. The most common though is that a phosphor that works without a pump is simplest. In fact, this is not the case. Without a pump to charge the phosphor the up-conversion is done through a non-linear process. Non-linear optical science is a division of optic on its own. For the phosphor to work in this manner it would be dependent on the two-photon absorption non-linear process. This is visually described in the figure below:



**Figure 20: Representation of two photon absorption.**

From the figure it can be seen that two low energy NIR photons must hit the phosphor together to excite the electron past the materials band gap. Once this occurs visible light will emit.

This process is based on the random nature of the photons and leads to one more variable to determine what wavelength the light is. This variable leads to an inability to determine what wavelength of light exists. Having a non-linear process in the system leads to many problems and is the main reason the Stellar Net up-converting spectrometer was discontinued.

## 5.3 Power Supply

This system will have two electrical circuits that must be electrically powered from a USB or wall source. We must get enough power to run these circuits. Traditionally Ocean Optics spectrometers are powered by USB which is what we will aim for. Ocean Optics spectrometers also have less electrical components than our system due to the fact that they do not have a pumping LED circuit. Due to this we may need to use a 120V 60Hz wall source and with later more advanced electrical design a USB power source can be designed. Most of the components in this system require 5V.

### 5.3.1 120V 60Hz Wall

When considering AC to DC wall adapters what we need is fairly simple. Luckily a 5V output is a standard wall adapter that can be purchased from many electrical component companies. The only other factor to consider is that if there is any significant resistance in the circuit we would need a larger wall adapter and a regulator later in the circuit.



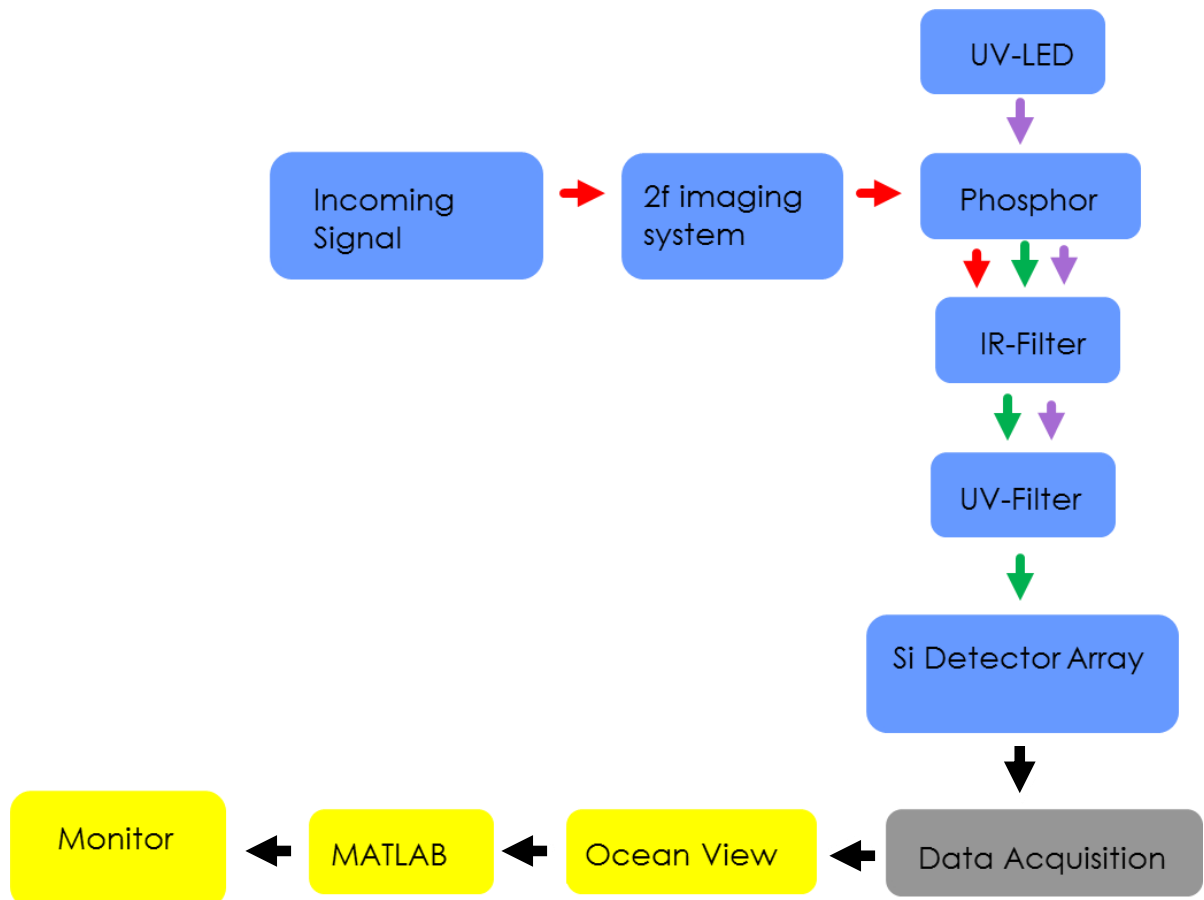
### 5.3.2 USB

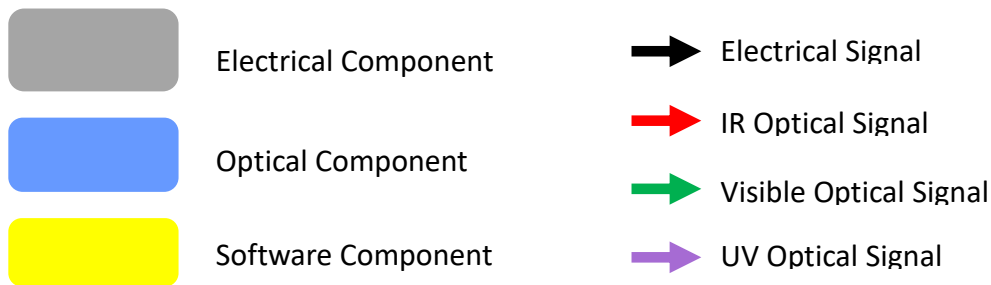
A standard USB from a computer, USB or USB 3.0, gives 500mA and 5V. Again this should be enough power assuming no significant resistance in the circuit occurs. It is nice to use a USB to power the device because the device must already be plugged into a computer to interact with the analysis software and to display the resulting spectrum.

## 6 Design

### 6.1 Block Diagram

The block diagram below gives a basic conception of how a test light source (in this case a tunable laser) will propagate optically through our system, where the UV pump will come into play and how this optical signal is converted to an electrical signal then analyzed.





**Figure 21: General block diagram of entire system with Legend.**

## 6.2 Grating

As mentioned in section 4.1 it is ideal for us to have a grating that spans the wavelength range of interest. We are looking for a grating that can not only cover this wavelength range, but that also has a large amount of lines/mm within our collimated test beam size, to help cover the resolution.

We will be using a standard holographic grating centered in the NIR. Standard diffraction gratings from places like Edmund Optics or Thor Labs will suffice. Likewise, for our optical setup we want a diffraction grating that will not only contain a large amount of lines/mm, but will also be transmissive rather than reflective for simplicity purposes.

The other diffraction grating types are not necessary for our set up. The diffraction grating element of this optical set up is tried and tested by Ocean Optics in the wavelength range of interest. Ocean Optics already uses NIR wavelength diffraction gratings in their FlameNIR and NIRQuest spectrometers and they will be providing the exact same grating for this set up.

## 6.3 Phosphor

For the phosphor design we want a phosphor that emits at a visible wavelength, charges from ultraviolet light and is stimulated by near – infrared light. It must work under the right conditions and work effectively. More importantly, we want a phosphor that is already commercially available and ready to order.

*STORAGE PHOSPHORS REQUIRING DAYLIGHT OR UV CHARGING PRIOR TO USE:*

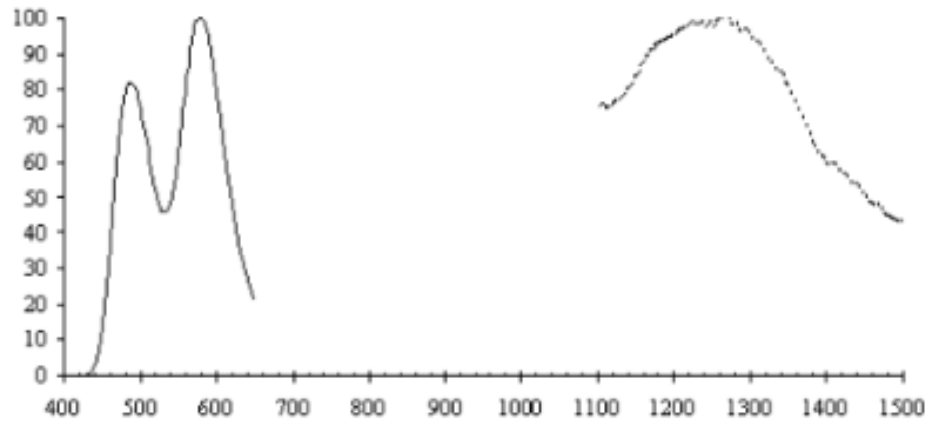
PTL CODE	CHEMICAL COMPOSITION	MEDIAN PARTICLE SIZE (µm)	EXCITATION MAX (nm)	EMISSION MAX (nm)
FL63S/F-11	CaS:Eu, Sm	5.0	800-1400	650
FL58S/F-11	CaS:Ce, Sm	5.0	800-1400	510
GL29P/B-11	ZnS:Cu, Pb	17.5	700-1500	490
GL29PM/B-11	ZnS:Cu, Pb, Mn	17.5	700-1500	580

**Figure 22: Particle size, excitation, and emission of different phosphors provided to us by Phosphor Technology.**

CaS:Eu,Sm which is calcium sulfide doped with europium and samarium is a relatively small phosphor that is charged by ultraviolet/visible light and is excited by 800 – 1400 nm light. This does not meet our design parameters which include going up to 1500 nm light so it is not of particular interest to us. The same problem exists for calcium sulfide doped with cesium and samarium CaS:Ce Sm. That being said, we narrowed down our phosphor list to two hopeful candidates. Both are derivatives of zinc sulfide, or ZnS.

The first one is ZnS:Cu,Pb,Mn which is zinc sulfide doped with copper, lead and manganese. ZnS:Cu,Pb,Mn is charged by ultraviolet/blue light, emits around 580 nm, and is stimulated by near – infrared light from 700 – 1500 nm. The particle size is roughly 17.5 microns. Below is the normalized sensitivity curve of the phosphor.

**Emission colour : Yellow**  
**Wavelength at peak, nm : 580**  
**Excitation, nm : 700-1500**



**Figure 23: Normalized sensitivity curve of ZnS:Cu,Pb,Mn**

The second one is ZnS:Cu,Pb which is zinc sulfide doped with copper and lead. ZnS:Cu,P is charged by ultraviolet/blue light, emits around 490 nm, and is stimulated by near – infrared light from 700 – 1500 nm. The particle size is roughly 17.5 microns.

Both of these phosphors require a very little amount of ultraviolet/blue light in order to be charged. One of the biggest differences, though, is the emission wavelengths. Since ZnS:Cu,Pb,Mn emits further from the ultraviolet/blue region, and also the silicon detector has a better response the closer you are to the 800 – 900 region. For this reason, it will be more likely that we will use the ZnS:Cu,Pb,Mn phosphor, however there are other factors to consider.

Both ZnS:Cu,Pb,Mn and ZnS:Cu,Pb phosphors have the same particle size so the point spread function of both phosphors should be roughly the same. An important distinction to consider might be the conversion efficiency of both phosphors. While it is important to have a phosphor that emits closest to where the silicon detector will respond most effectively, it is also just as important that the conversion efficiency for both is high. This is a factor that will be determined both theoretically and experimentally.

Similarly the afterglow of each phosphor and the decay time are important. How strongly the material continues to glow and for how long it glows will affect the integration time and dark current calibrations for our detector. Likewise, the bleaching, or saturation, of both phosphors is something that needs to be taken

into account so that we don't over saturate our phosphor and so we can keep a consistent and reliable dark current for calibration and a high signal to noise ratio.

## 6.4 Pumping

Due to the fact that LEDs are cheaper, simpler and easier to work with than LDs we will be using LED's as an illumination device used for the project. The idea of a pump in a spectrometer is not common so the simpler the better. Using a LD would be overkill and too complicated for this project especially sense the goal is to develop a simpler solution to NIR spectroscopy.

### 6.4.1 Process

The proposed method for implementing the LED is similar to those used in the report by Ocean Optics summarized in section 4.3.3. The idea is to use one or more LEDs being pumped into a waveguide. We have decided to use Kg glass as a waveguide because it can double for an IR filter and its refractive index  $n=1.53$  which is close to that of standard glass. The phosphor will be coated onto the surface of the Kg glass. When the LED's are pumped into the glass their evanescent wave will charge the phosphor coated on its surface.

The filter seemed advantageous for most cases so again in this case a filter will be applied to prevent the charge wavelength from reaching the detector. The biggest problem here is the dark noise from the autofluorescence, so that needs to be addressed. We could try combining it with the DPI method, however the autofluorescence causes the baseline measurement to change. The best method would be to combine it with the CPI method to keep the background level constant. This will yield a higher dark current than the DPI method, but it comes with fewer disadvantages that are more easily solved. The solution here would be to have a separate detector that senses and monitors the ultraviolet LEDs and adjusts the pulse intensity accordingly as needed. By doing this the autofluorescence is kept at a minimum, the dark noise will be adjusted and accounted for, and the integration time will be kept at a short interval.

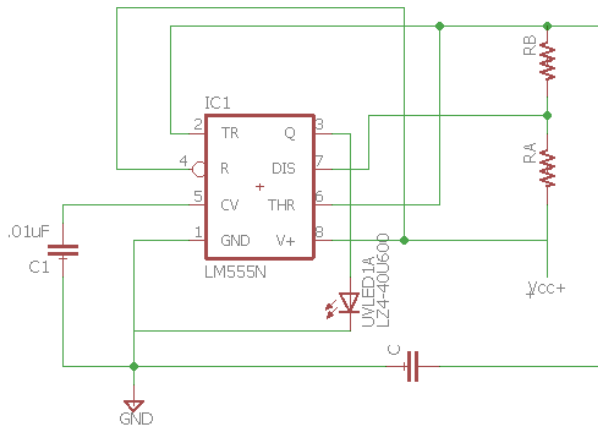
The UV pump process is very simple in the sense that we need to only oscillate the UV LED to meet our needs. This can be done in several different ways. For this project, we are considering the use of a timer integrated circuit, or a microcontroller.

### 6.4.2 Light Emitting Diode Circuitry

We decided on the use of a timer circuit for the purpose of the test set up since we can use variable resistor and capacitors to determine the values needed in the prototype of our device. The IC in mind is the LM555 from TI. It is a timer that can provide precise timing and pulse generation. The frequency and duty cycle can be adjusted based on the external resistors and capacitors. The output will be a UV

LED that will pump the phosphor that is also receiving another incoming light signal. Below is the circuit that will be used. It will operate in a stable mode so there is no need for a trigger on the circuit.

A timer integrated circuit will allow the UV pump to oscillate at a certain frequency which can be calculated based on the resistors and capacitors used. A microcontroller is also an option in which we can program the UV LED to oscillate at the desired frequency. However, this will require some coding, and in terms of what we need, a Timer IC is more feasible as we will not need to worry about adjusting the frequency in the final product. The Timer IC can be made to be stable, meaning it will trigger itself on. The duty cycle of the circuit can then be set by the external resistors.



**Figure 24: Timer IC Schematic**

### 6.4.3 Reference

When taking spectral measurements over time or even at multiple different times it is important that all the spectra can be compared. You want to be sure the only variable changing is what you are measuring. But it is important to note that this system does have one other variable that could change the spectrum over time and that is the pump power. If the pump power changes at all it will change the measured spectrum. If these spectrum change due to anything except a change in what you are measuring, multiple spectrum cannot be compared. It is important that we know of any variations in the pump signal while running scans in order to accurately reflect the true intensity of the spectrum. Though it should be noted that a standard LED is fairly stable and this is a subtle problem, but still worth addressing.

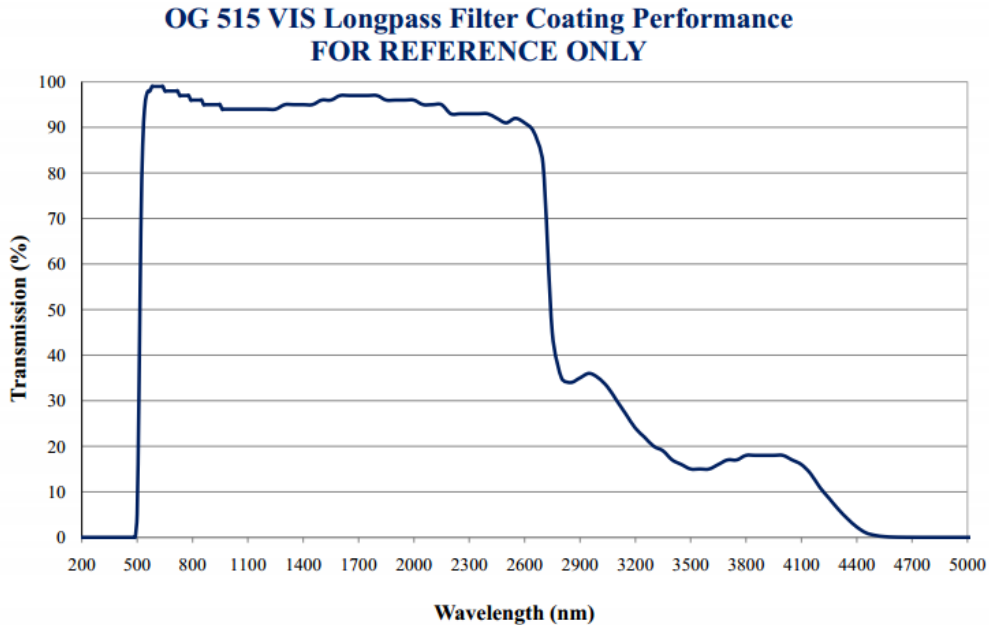
We will use a UV photodiode that monitors a portion of the pump beam for any fluctuations. This signal will be sent to the electronics that analyze the final up-converted signal. If any fluctuations in the pump occurs the final up-converted signal will be normalized to the reference. This will allow the system to compensate for any fluctuations.

## 6.5 Filter

### 6.5.1 UV Filter

For our long pass, or ultraviolet filter, we want a filter that cuts off and reflects the wavelengths that are not absorbed from the phosphor. The reason we want this is because the ultraviolet light will interact with the silicon detector since a silicon detector detects a spectrum from roughly 300 – 1200 nm. This overlaps with some of the ultraviolet light we will be using. Likewise, these high energy photons can disrupt the accuracy of our detector and cause dark current, which we want to limit as much as physically possible for the best measurements possible. The reason we want a reflecting filter is because we want to prevent the ultraviolet light from reaching the detector and likewise we want to utilize as much as the ultraviolet light as we possibly can toward charging our phosphors.

Edmund Optics' website features a multitude of filters that can be used to reflect ultraviolet light and emit at longer wavelengths such as visible, near – infrared, and mid – infrared. Having infrared light transmit through the ultraviolet filter won't be a problem when we use the near – infrared filter in tandem with the ultraviolet filter. We want a filter that reflects ultraviolet and blue light (anything below 500 nm), and transmits visible light (between 580 – 630 nm). One example featured on Edmund Optics' website is depicted in figure 18.



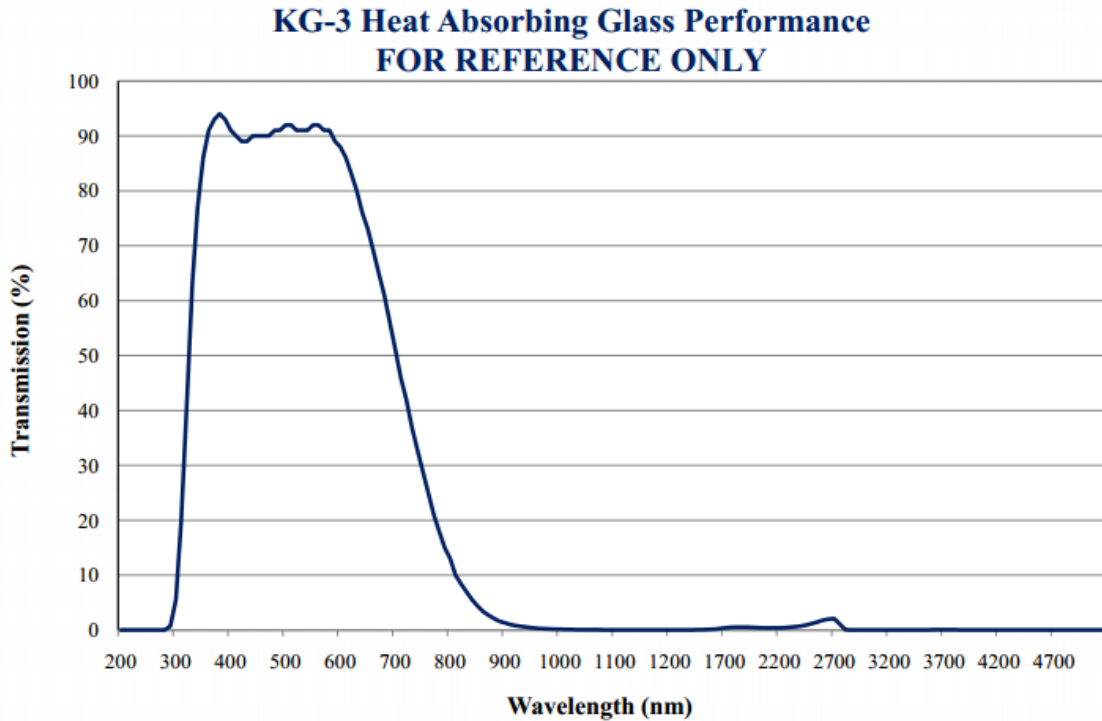
**Figure 25: Ultraviolet Filter, or Long Pass Filter. Spectrum of the transmission for an ultraviolet filter found from Edmund Optics’ website, the image shows a transmission of approximately 90% between the wavelength range of 500 – 2600 nm, and a transmission of less than 10% for wavelengths lower than 500 nm and wavelengths higher than 2600 nm.**

### 6.5.2 NIR Filter

For our short pass, or near – infrared filter, we want a filter that cuts off and absorbs the wavelengths that are not absorbed from the phosphor. The reason we want this is because the near infrared light will interact with the silicon detector since a silicon detector detects a spectrum from roughly 300-1200 nm. As one can see, this overlaps with some of the near – infrared light we will be using. We want an absorbing filter rather than a dielectric/dichroic filter because any reflections from the filter that interact with the phosphors will cause anomalies with our data measurements. Therefore, an absorbing filter would be ideal for this.

Edmund Optics’ website features a multitude of filters that can be used to absorb infrared light and emit shorter wavelength light such as visible and ultraviolet. We want a filter that transmits visible light (roughly 580 – 630 nm light for our phosphors), and something that eliminates any near – infrared light. One example of a filter featured on Edmund Optics’ website is depicted in figure 19.





**Figure 26: Near – Infrared Filter, or Short Pass Filter. Spectrum of the transmission for a near – infrared filter found from Edmund Optics’ website, the image shows a transmission of approximately 90% between the wavelength range of 400 – 700 nm, and a transmission of less than 10% for wavelengths lower than 300 nm and wavelengths higher than 800 nm.**

### 6.5.3 Filter packaging

For this system we are looking to pass a specific wavelength range. Essentially we want to combine the two filters mentioned above to create a band-pass/notch filter. In the research section multiple different types of filters are mentioned including dielectric reflecting and absorbing. The difference between these two is why we cannot simply purchase a band-pass/notch filter. As mentioned in 6.5.1 and 6.5.2, we want a NIR filter that absorbs and a UV filter that reflects. This is a combination of an absorbing and dielectric filter. If the UV light were to be absorbed it would not cause a problem necessarily but it would not create the light trapping component we desire. On the other hand, as mentioned, if the NIR filter reflects vs. absorbs it will cause a major problem for our system.

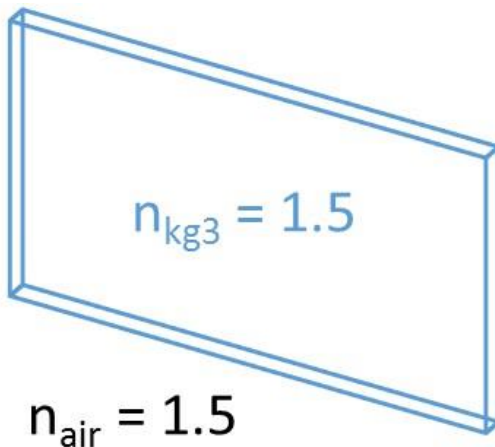
We are interested in passing the visible up-converted wavelengths and cutting of the impinging NIR and pump UV wavelengths. We want the UV 405nm pump to be cut off and NIR wavelengths down to roughly 800nm to be cut off as well. By properly packing these two types of filters together we can create a band pass filter that does not allow the NIR or UV light to pass, therefor not to be detected. The unique thing about this package vs. a standard band-pass filter is that it will allow us to create a light trap for the UV pump light. By reflecting the UV light and trapping it we can continue to pump the phosphor with UV photons that pass

through, and are not absorbed by the filter after their first pass until they decay/are absorbed.

The light trapping works as a normal waveguide. As can be seen in the figure below, the blue rectangle can be thought of as the Kg3 material with air around. When there is a difference in refractive index at a surface, at a certain critical angle, photons will reflect vs. transmit. This occurs when a photon is traveling from a material of higher refractive index to lower refractive index. This can be seen in the formula below:

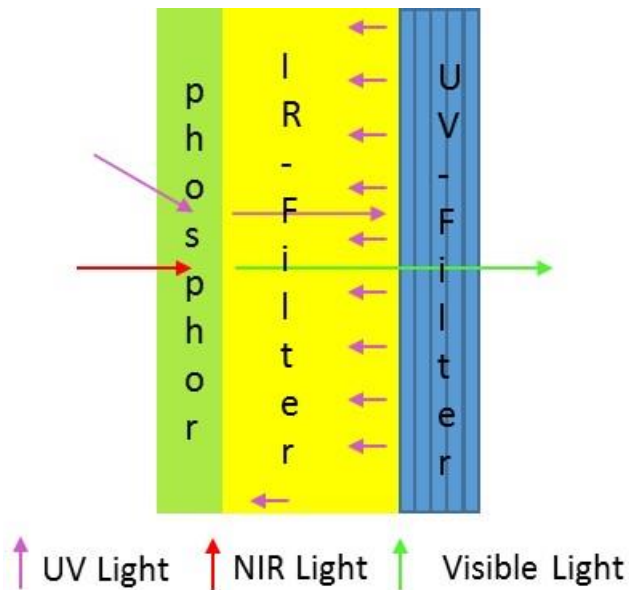
$$\theta_c = \sin^{-1}(n_2/n_1)$$

When a sandwich of lower refractive index, seen in figure 21, then higher refractive index then lower refractive index again is created, the photons under the critical angle will be trapped. They are trapped until they are either absorbed by the phosphor or strike an interface past the critical angle. This gives these UV photons many more opportunities to be absorbed by the phosphor.



**Figure 27: Waveguide and refractive indices of Kg-3 material (blue) and air (black).**

The phosphor coating, NIR absorbing Kg-3 glass and UV dielectric coating are sandwiched, as seen in figure 22. UV photons are actually reflected into this light trap by the UV dielectric filter coated on the back.



**Figure 28: Depiction of phosphor, IR-filter, and UV-filter sandwich that creates UV light trap/filter and IR-filter but transmits the generated visible light from the phosphor.**

It can be seen that the UV light is charging the phosphor while impinging NIR light is converted to green visible light. The majority of the NIR and UV light will be absorbed in the phosphor but some will pass through along with the converted green visible light. The NIR absorbing filter will absorb the NIR light and only allow the UV and visible light to pass. The next layer the dielectric UV filter will allow the visible green light to pass but reflect the remaining UV light. This light is then trapped in the IR filter and can hit the surface of the IR filter where the phosphor is coated beyond the critical angle and have a chance to charge the phosphor more with UV photons that were originally not absorbed during the first pass.

This sandwich design is being prototyped as a collaboration between us and Edmund Optics prototyping division. By working with Edmund Optics we will be able to design a single part that can be used in our system rather than ordering the IR absorbing filter from one party, having the UV dielectric coating with another party and the phosphor coated with another party. Due to varying material interactions this process could get complicated and cause problems. By working with Edmund optics the number of potential issues is significantly reduced.

## 6.6 Detector

### 6.6.1 The Detector

A detector works by taking advantage of a phenomenon known as the photoelectric effect, which states that electron – hole pairs can be created by shining light onto a material, or to be more specific, a semiconductor material. The now freed electrons and holes move freely which creates a current. This current can be detected and can be used to determine how much light is hitting a specific

area. This is explained in more detail in section 4.5.1. The key components to take into consideration when looking at detectors are the responsivity, or quantum efficiency, of a material (meaning how many photons contribute to creating electron – hole pairs and in turn, create an electrical current), dark current (which is the amount of current that is produced when there is no incoming signal on the photodiode – we want this to be as low as possible for better low signal measurements), and the speed or bandwidth (which determines the highest or fastest frequency component that can be interpreted as a signal).

A silicon detector works by absorbing light within a range, 300 – 1200 nm, and producing an electrical current from the incident light. The bandgap of silicon is very large, and indirect, so it is virtually impossible to detect near – infrared light with it. For these kinds of near – infrared detections other detectors are used, most notably indium gallium arsenide, or InGaAs, detectors. InGaAs detectors have relatively low dark current, high response time, and good sensitivity for near – infrared light. However, the major disadvantage of using InGaAs detectors is that they are far more expensive than silicon detectors.

Like InGaAs detectors, silicon detectors have a relatively low dark current and high response time. Silicon detectors have high sensitivities for visible light. They are cheap and are very common. There is a growing field in optics and photonics known as silicon photonics which seeks to unionize optoelectronic devices and silicon. This is because, as previously mentioned, silicon is very cheap and everywhere, especially in electronics. To be able to use silicon devices in optoelectronic fields or areas is major, since, for the most part, silicon has a large, indirect bandgap that is not easily utilized for visible light purposes. This is the aim of our project, to use a silicon device for something that normally a silicon device couldn't detect.

### 6.6.2 Single Photodiode vs. Photodiode Array

While both of these two different detection methods mentioned in section 5.5.2 accomplish the same thing there are advantages and disadvantages to each.

The single photodiode set up is “technically” simpler seeing as how it involves a basic rotation motor, one photodiode and easy point by point data analysis. The disadvantages is that it involves a mechanical part (it is always better to have the least or no mechanical parts) and it takes longer because the grating has to scan.

The photodiode array set up is a much more fluid method. There are no mechanical parts which is very important for our design. As mentioned, Ocean Optics makes field ready spectrometers. Field ready means they need to be simple and rugged. Motorized components are generally not considered rugged making the array a better option. Also the array allows for much faster spectrum capturing which is also nice but not as crucial. The disadvantage of course is the cost. Clearly an

array contains many diodes, up to 1064. The more diodes the higher the cost and in order to get high quality resolution more diodes are needed.

This explains the main motivation for this project. The reason current NIR spectrometers are so much more expensive than visible spectrometers is due to the cost of InGaAs (NIR) vs. Silicon (Visible). If one has a single photodiode it is an expense increase to change to a InGaAs detector but when one has an array of photodiodes it is more expensive by the cost of one InGaAs detector times the number of elements in the array. By utilizing this up-conversion process we can keep the costs very close to that of the visible silicon spectrometer.

## 6.7 Signal Analysis

Once the optical signal is converted to an electrical signal, the signal must be analyzed. In order to do this an electrical amplifying photodetector circuit will be purchased that takes an analog input current and outputs a digital voltage signal for each individual detector of the detector array. This signal is sent to a standard spectrometer software. This software is set up to analyze spectrums but it will see the light as visible and will not adjust for the sensitivity of our phosphor. This file is then sent to Matlab to be adjusted. In Matlab the wavelength will be converted to the true IR signal. This is done by calibrating the device with at least two known wavelength lasers. With basic math we can figure out the wavelength per pixel and adjust any incoming signal appropriately. To adjust for the phosphors varying sensitivity per wavelength of light, the characterization data will be used and fit, most likely Gaussian fit. This curve will be used to normalize the data and account for the phosphors varying sensitivity.

The Matlab code will take the individual detector signals, there set wavelngths and place this information into a cell. The detector signal is normalized and plotted as a function of wavelength. This plot is then sent to the monitor.

The block diagrams below represent this with three detectors as an example.

### 6.7.1 Detector Block Diagram

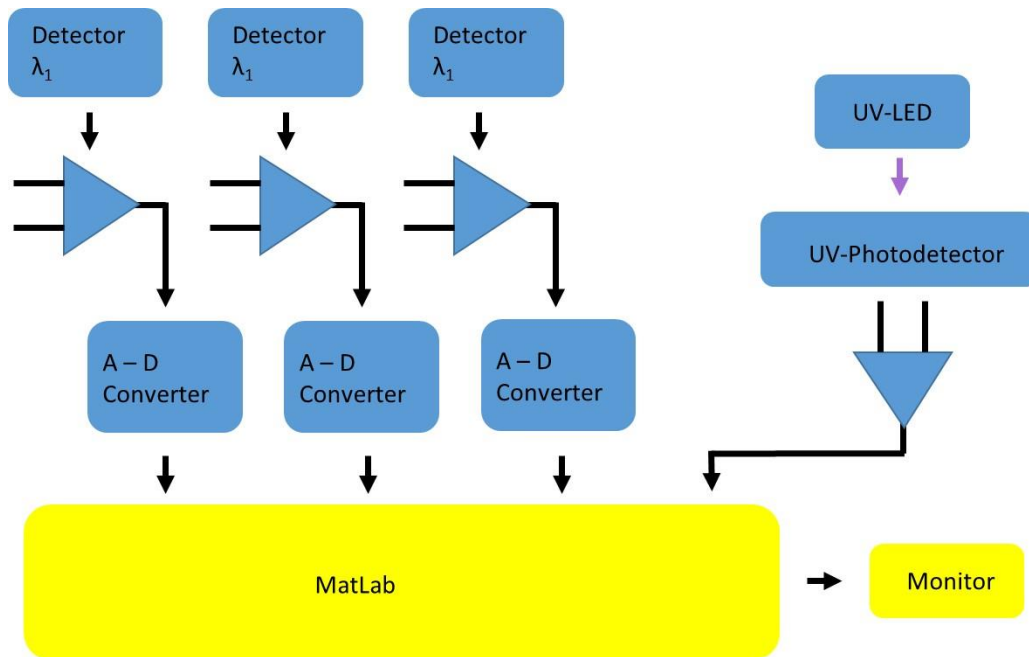
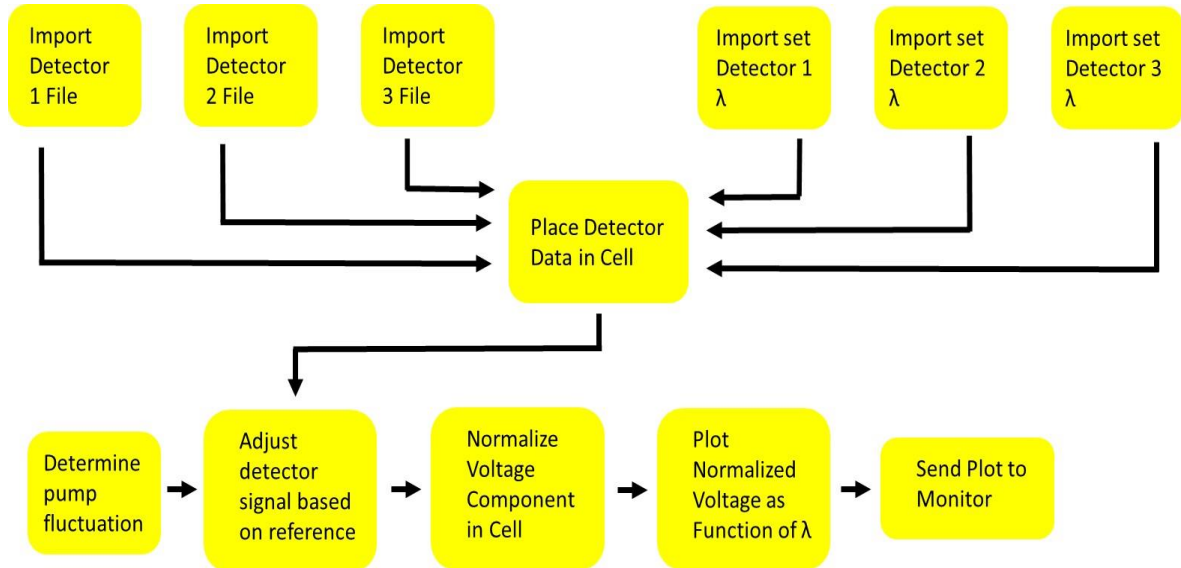


Figure 29: Electrical signal analysis block diagram

### 6.7.2 Matlab Block Diagram



### 6.8 Design Schematic

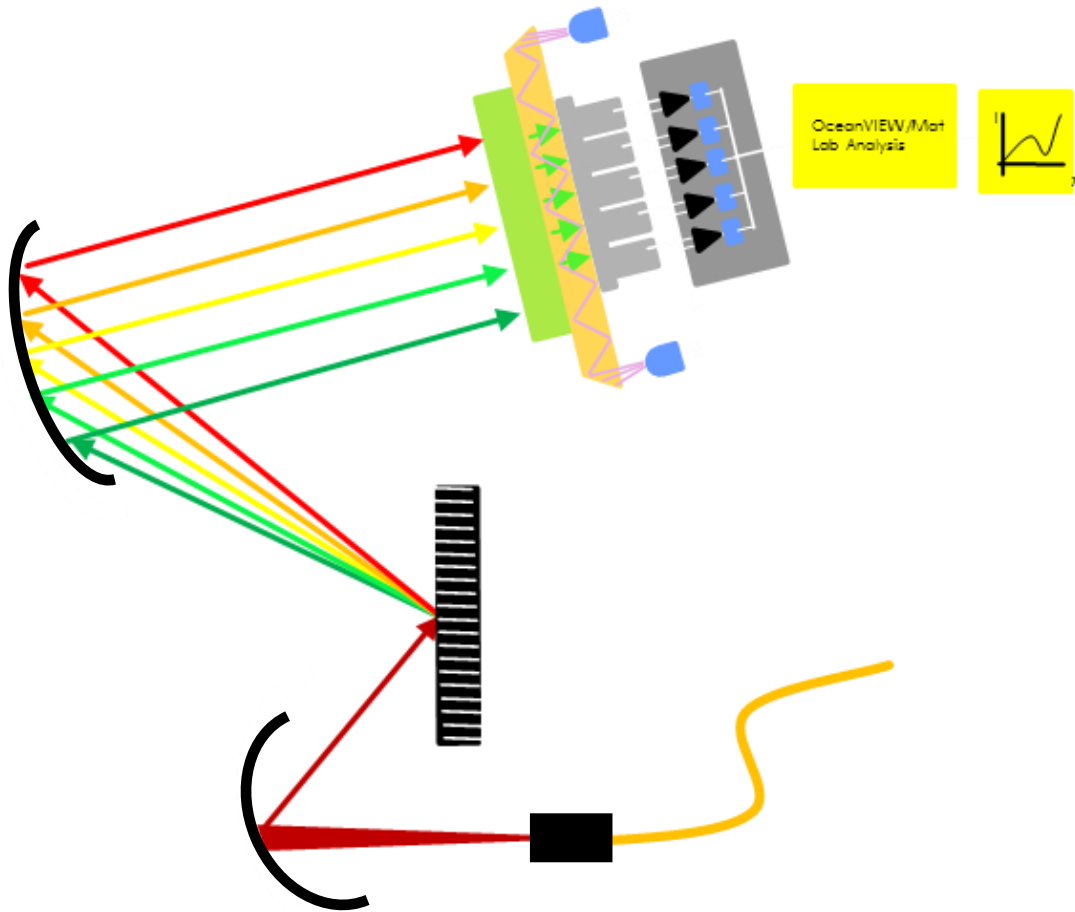


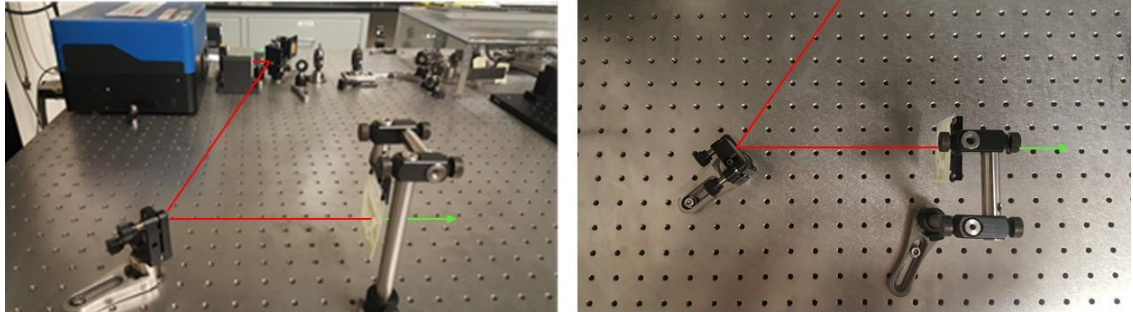
Figure 30: Schematic of full system.

## 7 Testing

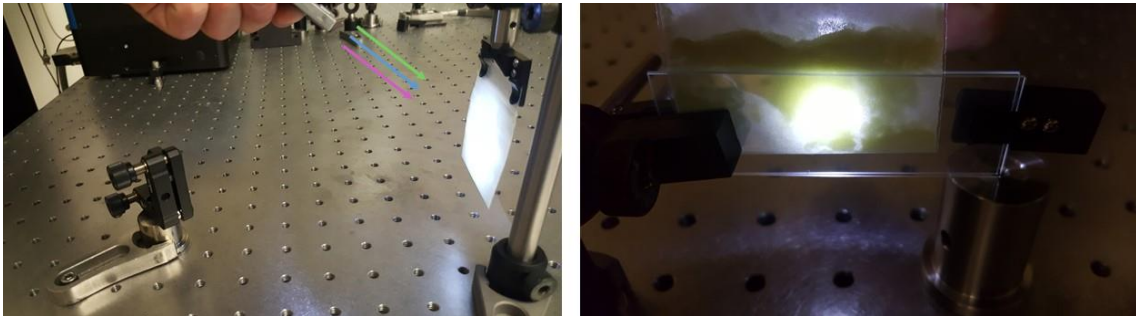
### 7.1 Primitive Current Test of Phosphor Functionality

First we must test the basic functionality of our phosphors. The objective of the phosphors in this system is to take an incoming NIR signal, which cannot be seen with the naked eye and convert it to a visible signal. We will test the functionality by impinging the near infrared test laser onto our phosphors and observing whether or not a visible signal is seen.

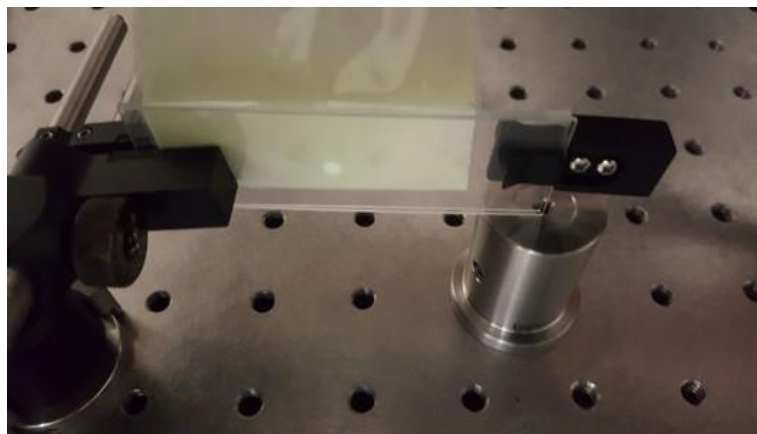
In order to do this simple test, the phosphor material, in powder form in a bag was charged with a broadband white light LED. After charging the material between 10mW and 20mW of 1560nm laser power with a spot size of roughly 1.2mm was impinged on the phosphor powder. Again this test is to purely test the basic concept. The set up and results are shown in the pictures below:



**Figure 31: Pictures with beam of the primitive current test set up for phosphor functionality.**



**Figure 32: Pictures of LED charging phosphor material.**



**Figure 33: Picture of visible green emission from phosphor with impinging 1560nm NIR light after pump has been removed.**

The pictures above, while very basic do prove that this material can easily convert invisible NIR light into visible green light. These results were actually surprisingly good due to the un-ideal parameters of this test. First, the pump was merely a white LED flashlight, far from the higher energy 405nm UV pump proposed. In addition this pump source was either on, or off. None of the different pumping methods mentioned in chapter 4 were implemented here. Finally the converted NIR signal was 1560nm. This wavelength is not only out of the realm we claim to be able to detect for our system but it is also outside of where Phosphor Technology (the phosphor manufacturer) claims the phosphor can perform up-conversion to. If you look at the sensitivity curve for this material in chapter 4, you can see the response is much lower between 1400nm and 1500nm and this source was even past this. With this being said, we have high confidence that with further



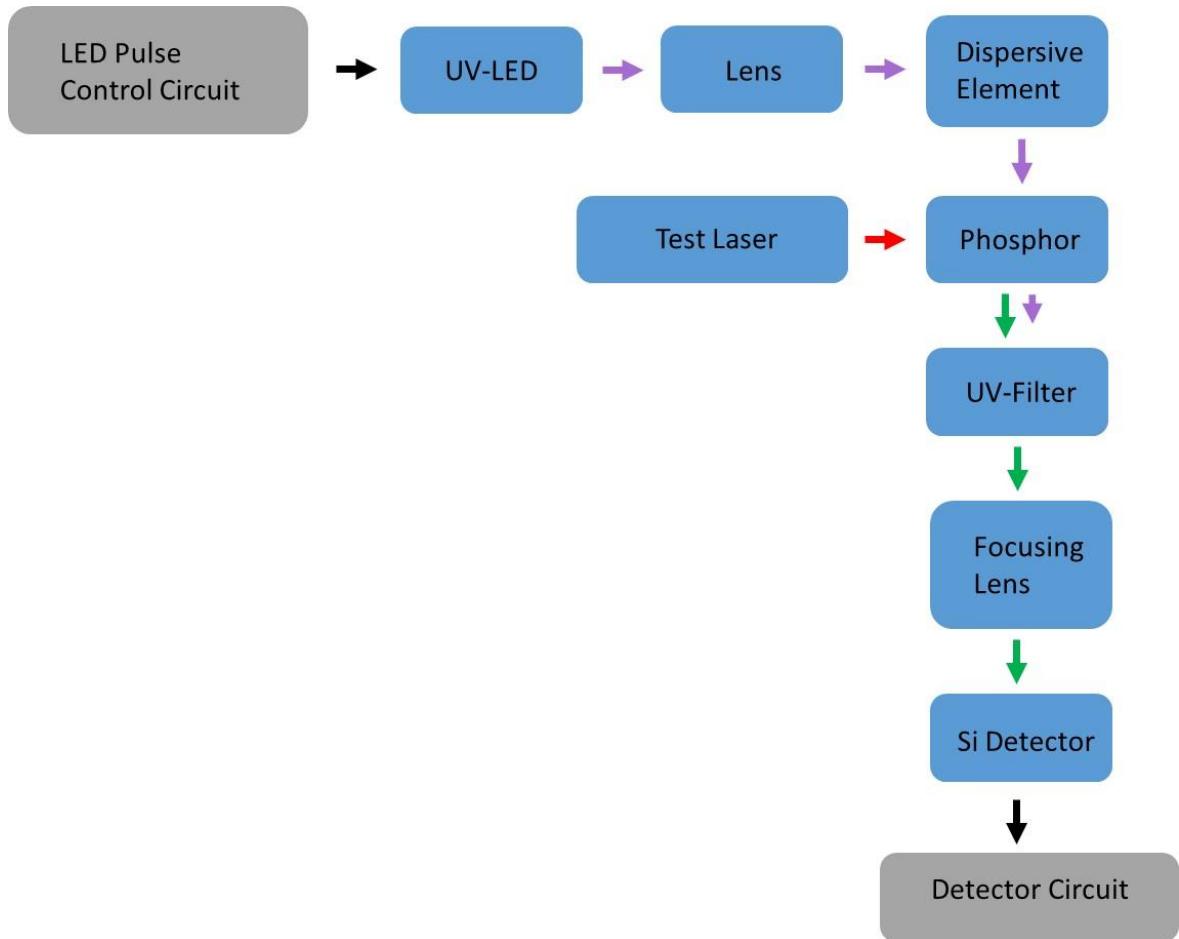
testing and by implementing the planned, more proper, conditions, we will be able to develop an efficient up-converting spectrometer system.

## 7.2 Main Test Set-up and Purpose

In order to successfully design the VE-NUS, a proper test of the key elements, the pumping mechanism and up converting phosphors, needs to be conducted. We will test five different pumping methods, a couple different pump diffusing techniques and four-five different phosphors, from different manufactures to see which one fits our specifications best. The pumping mechanisms will be tested for uniform illumination efficiency and ease of use while the phosphors will be tested for sensitivity over our desired wavelength range, efficiency, linearity, and ease of preparation.

In testing the phosphors we will be concerned with a few different parameters. First is the absorption curves over varying wavelength to be sure we can meet the specified wavelength range. Second will be the emission curves to determine the photodiode needed. Lastly will be the sensitivity curves and efficiencies. This will be done by building a large scale simple version of our compact design on an optical breadboard with standard opto-mechanical components. The specifics will be discussed in the proceeding sections.

## 7.3 Block Diagram

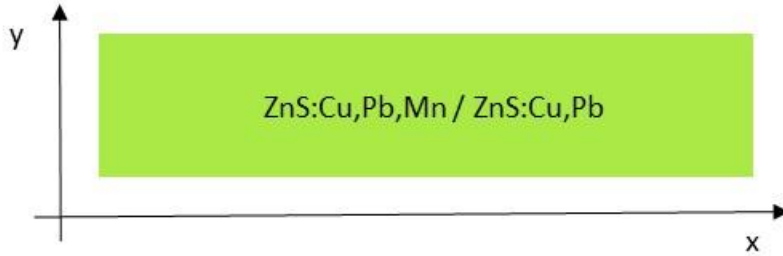


**Figure 34: General block diagram of test set-up.**

## 7.4 Tests/Procedures

### 7.4.1 Pump Uniformity

The different incoming test NIR wavelengths will be split up on the grating and sent to the phosphor. This means that the phosphor will have incoming light hitting various x-axis points. It is important that the pump uniformly charges all these x-axis points therefore the up-conversion will be relatively the same for the varying light across the x-axis (the varying diffracted wavelengths from the grating).



**Figure 35: Phosphor up-converting material spatial axis representation.**

To test the uniform illumination of the pump source we will simply try the different dispersive techniques and measure their intensity over varying distance. This will be accomplished with a photodiode moved by a translation stage while recording the intensity. We will do this in x, y and z axis but the main axis of concern is the x.

### 7.4.2 Pumping Method

The phosphor must be pumped with a high energy photon source, such as UV light, to charge it for emission with NIR light. There are multiple different ways to do this. We will examine them individually and determine which will work the best for our system. Four of these methods were previously tested by Applied Scintillation Technologies. We will replicate these tests for verification and perform one method that was not tested. The 5 pumping methods are:

- Discrete Continuous Illumination
- Direct Pulsed Illumination
- Continuous Pulsed Illumination
- Filtered Direct Illumination
- Filtered Continuous Pulsed

### 7.4.3 Sensitivity and Efficiency

We need to test the sensitivity of our phosphor over the wavelength range set in the specifications of the project. Not only do we need to know the material can up-convert over these wavelengths but we need to know how the emission intensity changes so our software can compensate for this and display an accurate intensity of our infrared light.

The efficiency was determined experimentally and calculated as seen below:

$$\begin{aligned}
 \text{Quantum Efficiency} &= 100 * \frac{\text{Visible Emitted Photons}}{\text{IR Absorbed Photons}} \\
 &= \frac{n_{vis\ emitted}}{n_{IR\ abs}} = \frac{n_{vis\ emitted}}{n_{IR\ total} - n_{IR\ transmitted}} = \frac{\frac{P_{vis\ emitted} \cdot t}{h \cdot \nu_{visible}}}{\frac{P_{IR\ total} \cdot t}{h \cdot \nu_{IR}} - \frac{P_{IR\ transmitted} \cdot t}{h \cdot \nu_{IR}}}
 \end{aligned}$$

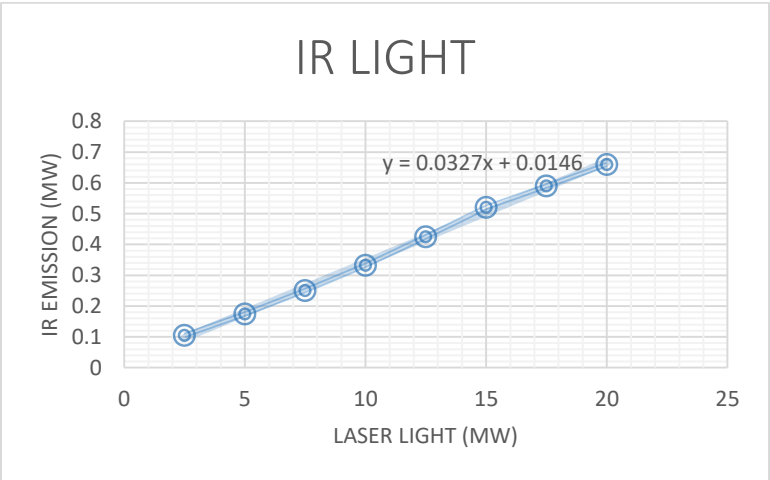
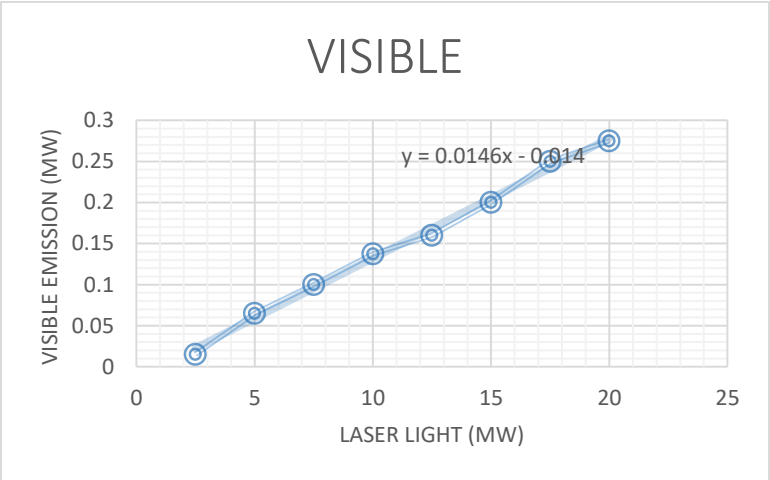
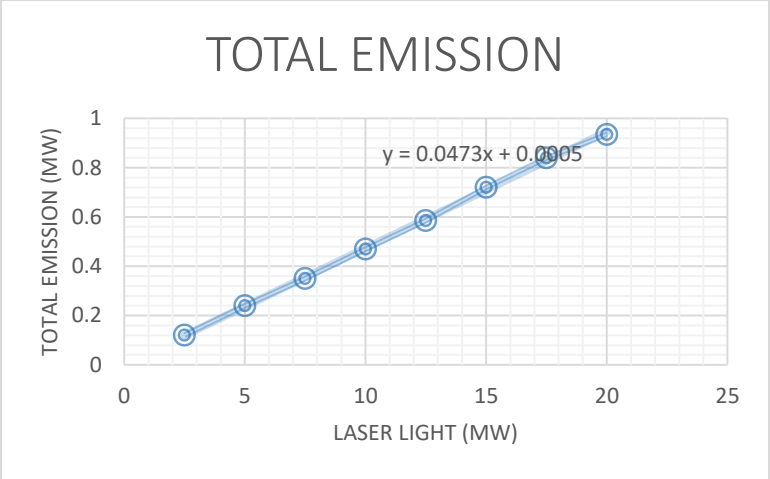
$$\begin{aligned}
&= \frac{\left(\frac{t}{h}\right) \cdot \frac{P_{vis\ emitted}}{\nu_{visible}}}{\left(\frac{t}{h}\right) \cdot \left(\frac{P_{IR\ total}}{\nu_{IR}} - \frac{P_{IR\ transmitted}}{\nu_{IR}}\right)} = \frac{\frac{P_{vis\ emitted}}{\nu_{visible}}}{\left(\frac{P_{IR\ total}}{\nu_{IR}} - \frac{P_{IR\ transmitted}}{\nu_{IR}}\right)} \\
&= \frac{\frac{P_{vis\ emitted}}{\nu_{visible}}}{\frac{P_{IR\ total}}{\nu_{IR}} - \frac{P_{IR\ transmitted}}{\nu_{IR}}} \\
&= \frac{P_{vis\ emitted} \cdot \nu_{IR}}{(P_{IR\ total} - P_{IR\ transmitted}) \cdot \nu_{visible}}
\end{aligned}$$

$$Quantum\ Efficiency_{1560nm} = 0.29\%$$

#### 7.4.4 Linearity

As mentioned in our proposal, a key factor in making this system work is that the visible light emission is very near linear. This was an issue that caused a previous product fail and we believe, this high factor of linearity due to having a pump LED, is the solution.

The linearity tests performed are shown below:



### 7.4.5 Detection

In order for this device to be useful we must be able to see the up-converted signal. A concern with using phosphors for this up-conversion process is the efficiency. If not enough light is converted we will not detect anything we care about. We believe the efficiencies should be fine for this use but it will be useful to know the minimum amount of input power needed and whether or not a coherent light source is required. We may be able to adjust components such as lenses and apertures to increase signal detection.

#### 7.4.6 Diode

While section 6.5.1 described why we will be using a photodiode array for our design for testing we will be using a single photodiode for the test set up. This is because a diode array is simply not necessary at this point. We want to show we can detect a visible signal at the desired wavelengths and with the use of a tunable laser source the array is un-necessary along with the grating. In addition because our test source is tunable we can gather the sensitivity curves with a single diode. This is the case for both testing the phosphor and pumping the LED. We will also use a standard visible spectrometer to analyze the emission spectrum of our phosphor (this visible spectrometer most likely utilizes a photodiode array).

### 7.5 Analysis

## 8 Budget

### 8.1 Testing

#### 8.1.1 Pump System

Component	Manufacture	Part #	Units	Price
Plexi Glass	Home Depot	LED 370E	1	\$11.00
405nm, 6mW LED	Thor-Labs	LED405L	1	\$11.30
Diode Mount Adapter	Thor-Labs	LMRA9	1	\$15.00
Lens Holder	Thor-Labs	LMR1	1	\$15.23
Electrical Breadboard	B&K Precision	GS-830	1	\$8.40
Timer IC	Texas Instruments	LM555	1	\$.93

Diffuser	Thor-Labs	DG20-120	N/A	N/A
Capacitors	DigiKey	N/A	N/A	N/A
Potentiometers	DigiKey	N/A	N/A	N/A

### 8.1.2 Imaging System

Component	Manufacture	Part #	Units	Price
Grating	Thor-Labs	47-823	1	\$47.00
Spherical Mirrors	N/A	N/A	1	N/A

### 8.1.3 Phosphors

Component	Manufacture	Part #	Units	Price
ZnS:Cu,Pb	MaxMax	IRSPG	1	\$41.94/5 g
ZnS:Cu,Pb,Mn	Phosphor Technology	N/A	1	Sample

### 8.1.4 Detection System

Component	Manufacture	Part #	Units	Price
Si Photodiode	Thor-Labs	FDS 100	1	N/A
Focusing Lens	Thor-Labs	LA1951	1	\$35.42
Lens Holder	Thor-Labs	LMR1	1	\$15.23
Short-pass Optical Filter	Edmund Optics	49-087	1	\$20.00
Custom Dielectric Long-Pass Filter	Edmund Optics	N/A	1	N/A
Electrical Breadboard	B&K Precision	GS-830	1	\$8.40

## 8.2 Device

Components from the Test set up will not be used for the main device because it will save little money and if there is a need to re-characterize the phosphors after the device is made it will be advantageous to have the test set-up still together. When “provided” is listed in the Price column, this indicates that our customer Ocean Optics is providing the part from there inventory.

<b>Component</b>	<b>Manufacture</b>	<b>Part #</b>	<b>Units</b>	<b>Price</b>
405nm, 6mW LED	Thor-Labs	LED405L	10	\$113.00
Diode Mount	Custom	N/A	1	\$100.00
Timer IC	Texas Instruments	LM555	1	Sample
Electrical Breadboard	B&K Precision	GS-830	2	\$16.80
Capacitors	DigiKey	N/A	N/A	N/A
Potentiometers	DigiKey	N/A	N/A	N/A
Diffraction Grating	N/A	N/A	N/A	Provided
Fiber Optic Patch Cable	Thor-Labs	N/A	1	Provided
Focusing Lens	Thor-Labs	LA1951	1	\$35.42
Silicon Detector Array	N/A	N/A	1	Provided

## 9 Schedule

<b>Date</b>	<b>Description</b>	<b>Member</b>
4/1/16	Initial project meeting with Dr. Stephen Kuebler	All
5/19/16	Initial project meeting with Ocean Optics spectrometer company	All
5/20/16	Submit Project Idea	All



6/3/16	Submit Initial Project Document outlining general concept of project	All
6/4/16	Finish analyzing "NIR Coating for Detectors" report from Ocean Optics	All
6/7/16	Breakdown components of project research areas	Sean
6/10/16	Begin researching phosphors	Jason
6/10/16 – 6/12/16	Pump Research	Sean
6/14/16	Delegate out project general area responsibilities and submit "divide and conquer"	All
6/22/16	Project update with Ocean Optics	All
6/25/16 – 6/26/16	Investigate Stellar Net Company's up-conversion spectrometer	Sean
6/28/16	Begin general research of components for proposal	All
7/1/16	Submit proposal table of contents/outline	All
7/5/16	Finalize Introduction for proposal	Sean
7/8/16	Proposal checkup; Submit proposal progress	All
7/14/16	Decide on phosphors to test	Jason
7/14/16 – 7/17/16	Research pump LED dispersing process/components	Sean
7/17/16	Determine status of CREOL senior design lab for project development	Sean
7/18/16	Decide on test photodiode and filters to test	Jason
7/18/16	Decide on pump photodiodes, LED's, lens's, mounts and diffusers to test	Sean
7/20/16	Submit "Phosphor Test Set-Up" document to Ocean Optics	Sean
7/22/16 – 7/26/16	"Phosphor Test Set-Up" Zmax optical design	Jason
7/22/16 – 7/26/16	Filter/absorption basic science description for proposal research	Jason
7/29/16	"Phosphor Test Set-Up" meeting and update with Ocean Optics	All

8/2/16	Submit VE-NUS proposal	All
8/3/16	Order all components for "Phosphor Test Set-Up"	Sean
8/3/16 – 8/6/16	Begin exploring phosphor preparation	All
8/4/16 – 8/5/16	Explore test source options	Sean
8/5/16 – 8/7/16	Design electrical pump circuit	Sean
8/8/16 – 8/22/16	Light budget	All
8/29/16 – 9/9/16	Build phosphor test set up	All
9/12/16 – 9/14/16	Prepare phosphors	All
9/19/16 – 9/30/16	Testing: <ul style="list-style-type: none"> <li>• Functionality of phosphors</li> <li>• Pump uniformity</li> <li>• Pumping method</li> <li>• Phosphor preparation and deposition</li> <li>• Sensitivity and efficiency</li> <li>• Linearity</li> </ul>	All
9/30/16	Determine and acquire needed parts based on testing	Sean
9/30/16	Update Ocean Optics on testing	All
9/27/16 – 9/30/16	Put together initial presentation	All
10/3/16 – 10/5/16	Design computer data acquisition and analysis method	Sean
10/6/16 – 10/11/16	Test array detector and coatings on array detector (phosphor and filter)	Jason
10/17/16 - 10/21/16	Optimize phosphor and filter coating for detector array	All
10/24/16 - 10/26/16	Adjust any optical design from testing information for final set up	Jason
10/3/16 - 10/14/16	Build final system	All
10/31/16 - 11/11/16	Test final system	All
11/16/16 - 11/23/16	Adjust final document	All

11/24/16 - 11/28/16

Finalize presentation

All

## 10 Conclusion

In this proposal the basic components and options of the proposed system were researched. The design constraints were outlined and from there a design was put together. A test was devised to allow for enhancing the design and a budget to develop this system was provided. With all this information we have proposed an efficient and cost effective manner to up-convert and detect NIR optical signals.

NIR spectrometers are a highly desirable product. The ability to convert infrared light to visible light is a relatively simple technique we describe as up-conversion. This process can allow us to convert NIR light to visible light and detect it on a visible spectrum detector which is much cheaper than a NIR detector. Normally this process would be a non-linear, however we bypass this process through a phenomenon that occurs naturally in commercially available phosphors called electron trapping. We can do this by pumping our phosphor with a high energy LED that charges the electron to its trapped level and the NIR light cause the phosphor to emit a visible photon. This process is a near linear one that bypasses the complexities and extra variables of a non-linear process.

This project is being worked on with a local and internationally prominent spectrometer company, Ocean Optics. The Ocean Optics business model of, compact, portable, simple and relatively cheap can be seen in the design of this system.

In our current work we showed that it is possible to detect the transmission of phosphorescence and use it to perform spectroscopy. We will shortly begin in-depth testing of these phosphors, pumping mechanisms, filter methods and detection. After these tests are completed and we have gathered sensitivity curves for the phosphors the main component will be developed.

The biggest constraints that are affected from this process are resolution, conversion efficiency, and dark current from the added ultraviolet source. Work is still being done to show that these engineering challenges can easily be overcome and improved upon. For example, other phosphors exist that can continue farther into the near – infrared range and possibly into the mid – infrared range.

For our work we hope to show a proof of concept test setup that demonstrates all of this is possible, and eventually a final product that is compact and meets all of the engineering specifications. This will be developed on a breadboard.

Since previously existing devices have not worked as well as this device (since it used the nonlinear principle of doing the technique) and the expenses of other devices that directly measure infrared light are greater, there is a wide commercial demand for a product such as this device.

If the system works as expected we will begin the second stage of this project (post senior design II). This developed technology will be integrated for our customer. In addition we believe there is a way to develop this technology as an attachment that can hook to current visible spectrometers.

# Appendix a: References

- [1] "Wikipedia," [Online]. Available: [https://en.wikipedia.org/wiki/Diffraction\\_grating](https://en.wikipedia.org/wiki/Diffraction_grating). [Accessed July 2016].
- [2] "GratingLab," [Online]. Available: [http://www.gratinglab.com/Products/Supplemental\\_Information/Types.aspx](http://www.gratinglab.com/Products/Supplemental_Information/Types.aspx). [Accessed July 2016].
- [3] E. D. I. Rosaa, L. Diaz-Torresa, P. Salasb and R. Rodriguezc, "Visible light emission under UV and IR excitation of rare earth doped ZrO<sub>2</sub> nanophosphor," *Optical Materials*, vol. 27, no. 7, pp. 1320-1325, 2004.
- [4] L. Diaz-Torres, E. D. I. Rosa-Cruz, P. Salas and C. Angeles-Chavez, "Concentration enhanced red upconversion in nanocrystalline ZrO<sub>2</sub> : Er under IR excitation.," *Journal of Physics*, vol. 37, no. 18, 2004.
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- [7] G. R. Fonda, "Preparation and Characteristics of Zinc Sulfide Phosphors Sensitive to Infra-Red," *Journal of The Optical Society of America*, vol. 36, no. 7, pp. 382-389, 1946.