

Lab Modules for PH2601

Spectra, Absorption, and Fluorescence

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Abstract: Through a process of trial and error four lab modules were created to fill a gap in WPI's undergraduate physics optics and photonics lab PH2601. The first is a pre-requisite module that serves as an introduction to using the equipment and data analysis of spectra. The three other separate modules then are: measuring the attenuation coefficient of water, constructing an energy level diagram of Ho and Er doped glasses using absorption and fluorescence spectra, and band gap measurements of Si, InP, and As₂S₃.

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Introduction

In WPI's undergraduate optics and photonics lab run by professor Quimby, PH2601, there are not currently any labs that deal with taking spectra. This is an important skill to have in the optics and photonics field, so the purpose of this MQP is to create lab modules to fill this gap. There exist many pre-built lab kits that are offered, with an example ranging from simple kits such as the Absorption Spectroscopy Kit available from Flinn Scientific¹, to more advanced sensor-based kits from Pasco². These kits however did not suit professor Quimby's needs. Most that were found were geared towards chemistry instead of physics, in addition to being expensive

It was decided that Professor Quimby had enough resources in his lab, including the spectrometers he uses for his own research and various samples of interesting materials he has gathered over the years, to create a set of lab modules from scratch. The following sections detail the setup, experiment process and procedure, and sample analysis using my own data, of each lab module. Instructional handouts will also be included in this paper as appendices.

I. Introduction to Spectroscopy

Introduction and Setup

The purpose of this lab will be to introduce students to the process of taking spectra and how to parse & analyze the data they get. Students will take spectra from many different sources using two different kinds of spectrometers. A visible range spectrometer will first be used. It can see light with a wavelength of 380-950 nm, which includes a bit of the near infra-red. However for simplicity I will be referring to it through this paper as the "visible range spectrometer". They will then use an optical spectrum analyzer (OSA) which can see into the infrared (700-1600 nm). The data that I took and present in the following pages is only from the visible spectrometer. I did not use the OSA until a later experiment, and subsequently learned how to use it then. However it makes sense to give students an introduction to it here.

The spectrometers both use an input fiber to accept light to process. The light is passed through a diffraction grating which only allows light of one wavelength to pass. The light that gets through the diffraction grating is then has its power analyzed. The diffraction grating then moves slightly allowing the next wavelength through. The result is a power per wavelength interval. The main difference between the spectrometers, besides which wavelengths they can see, is their size and accuracy. The visible spectrometer is very small, about the size of two decks of cards. It interfaces with a computer via USB. The OSA is larger, roughly the size of a large CRT monitor. It uses a built-in floppy drive to store data. The OSA is also a lot more accurate than the visible

spectrometer. The visible spectrometer only measured relative intensity, whereas the OSA measured a true power per wavelength interval.

The setup of the experiment is as straight forward as it gets. Point the end of the input fiber for either spectrometer at any source. I came up with a large number of different sources for the students to take spectra of. They are: sunlight, two types of compact fluorescent bulbs, two types of incandescent bulbs, the room lights, 5 different colors of Christmas bulbs (red, orange, pink, green, blue), light emitting diodes (white, green, blue, red), and an led flashlight. Beyond familiarizing themselves with the equipment and analysis process; the students will discover (as I did) that our eyes cannot always be trusted when looking at light. Light that appears to be very similar to our eyes can actually be very different. More on that in the subsequent section.

In addition to all the "unknown" sources a tungsten filament bulb will be provided that will be presumed to be an ideal black body emitter. This is important as the visible range spectrometer is not calibrated. When the spectra are uncalibrated, you cannot say that because one point of the spectrum is higher than another point of the spectrum, the higher point has a higher power. The process of calibration compares a theoretical model to experimental data in order to correct the data. The students will need to obtain a correction function based on comparing the spectrum taken from the tungsten bulb to a theoretical black body curve. They can then use this correction function on the rest of their spectra to obtain true spectra of the sources. This is a critical step as this correction function will be used throughout the other two labs which use the visible spectrometer.

The Correction Function

The first step when working with any data from the visible spectrometer is background subtraction (figure 1). The spectrometer has a background or dark signal that is present even when no light is entering the input fiber. This needs to be subtracted from all data before we begin to work with it. All data shown after this point has already had the background subtracted from it.

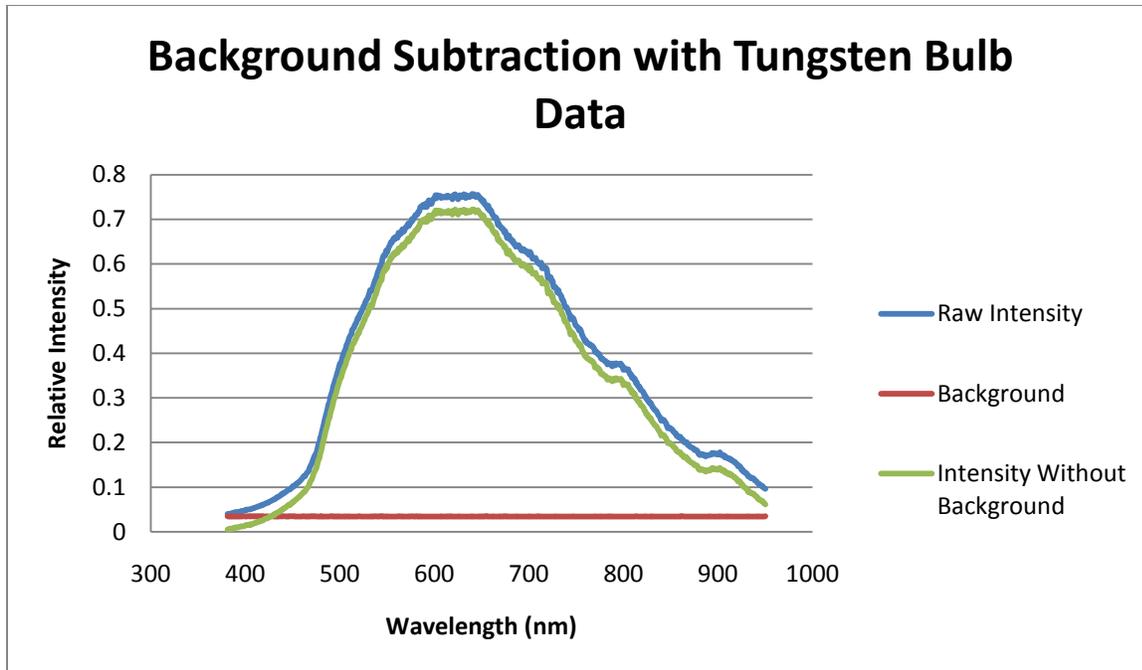


Figure 1: Demonstrating background subtraction with the raw data from taking the spectrum of a tungsten bulb.

Now we need to plot a theoretical black body spectrum. The following is Planck's Law³, which states that the power per unit wavelength that is given off by a black body as a function of wavelength is:

$$I(\lambda, T) = \frac{2\pi hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda kT}} - 1}$$

Where λ is the wavelength of interest, T is the absolute temperature of the source, c is the speed of light, h is Planck's constant, and k is Boltzmann's constant. The temperature of my tungsten bulb is assumed to be 2900K.⁴ Plotting Planck's law at 2900K on the same interval as the spectrometer can see (figure 2):

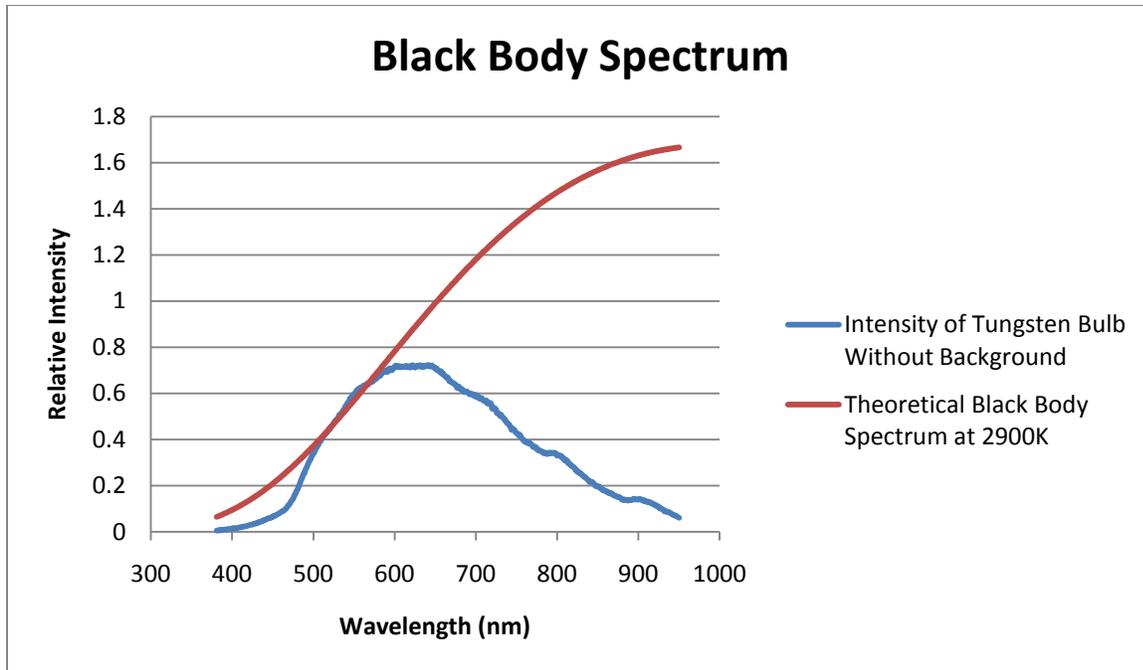


Figure 2: The theoretical black body spectrum and data taken from the tungsten bulb.

As is clearly seen there is a major discrepancy between the shapes of these two graphs. Between the wavelength range of 500nm to 630nm they are a pretty good match. However outside of that range the lack of calibration coupled with the device's inability to see very well towards the edges of its detection range necessitate a correction function. This is simply the theoretical black body spectrum divided by the measured black body spectrum.(figure 3):

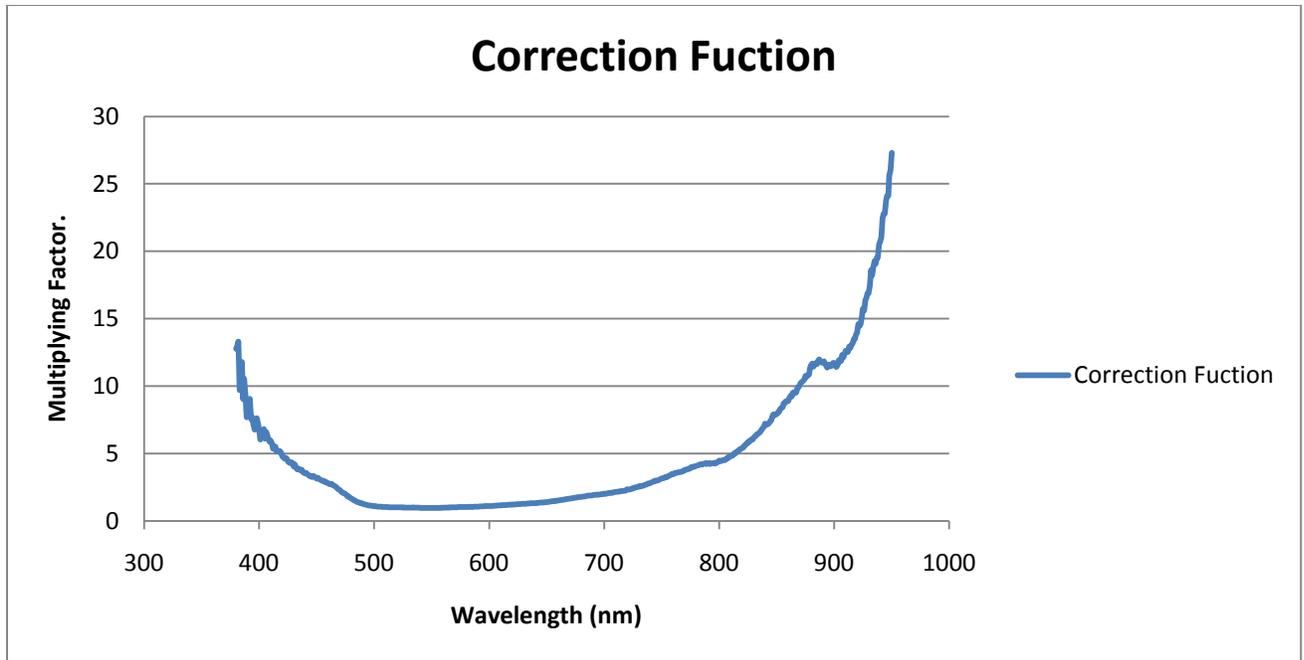


Figure 3: The finished correction function.

This correction function $C(\lambda)$ will be used on all data henceforth. All graphs shown in the other two labs have had the correction function applied without being explicitly shown or stated.

$$S(\lambda)_{\text{actual}} = S(\lambda)_{\text{meas}} * C(\lambda)$$

Data and Analysis

The required analysis after a correction function is attained is relatively straight forward. All that needs to be done is to first subtract the background signal, multiple by the correction function, then plot the resulting data.

$$S(\lambda)_{\text{actual}} = (S(\lambda)_{\text{raw}} - \text{Background}(\lambda)) * C(\lambda)$$

I have included both corrected and uncorrected data to show the (sometimes drastic) difference. All data has been normalized to 1, meaning the maximum value for each graph is set to 1, and all other data points are scaled accordingly. This is done simply for uniformity across graphs, making them easier to compare. All the data is relative, so scaling doesn't affect anything.

The first thing we take a look at is daylight coming through a window, figure 4.

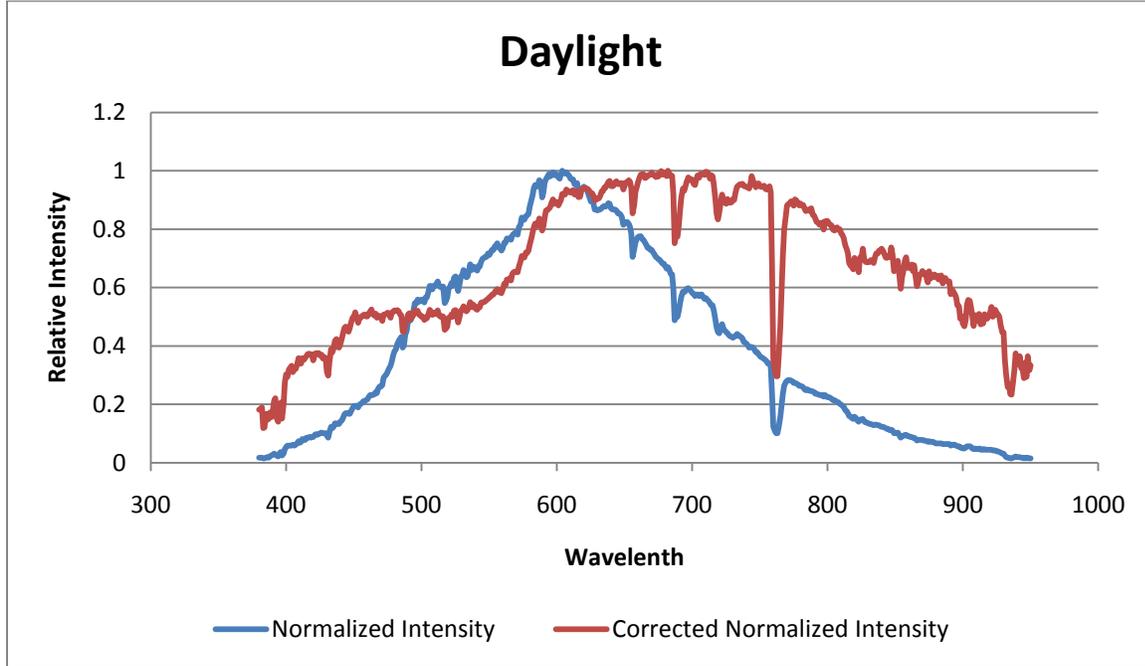


Figure 4: Spectrum from 380nm-950nm of daylight through a window.

Daylight coming through the window glass is riddled with interesting curves and dips. These dips are due to absorption of the light at those wavelengths, mostly due to the earth's atmosphere. One interesting thing is the drastic dip at 760nm. This is due to O₂ absorption in our atmosphere.⁵

Next we will take a look at several different types of Christmas bulbs, figures 5-9.

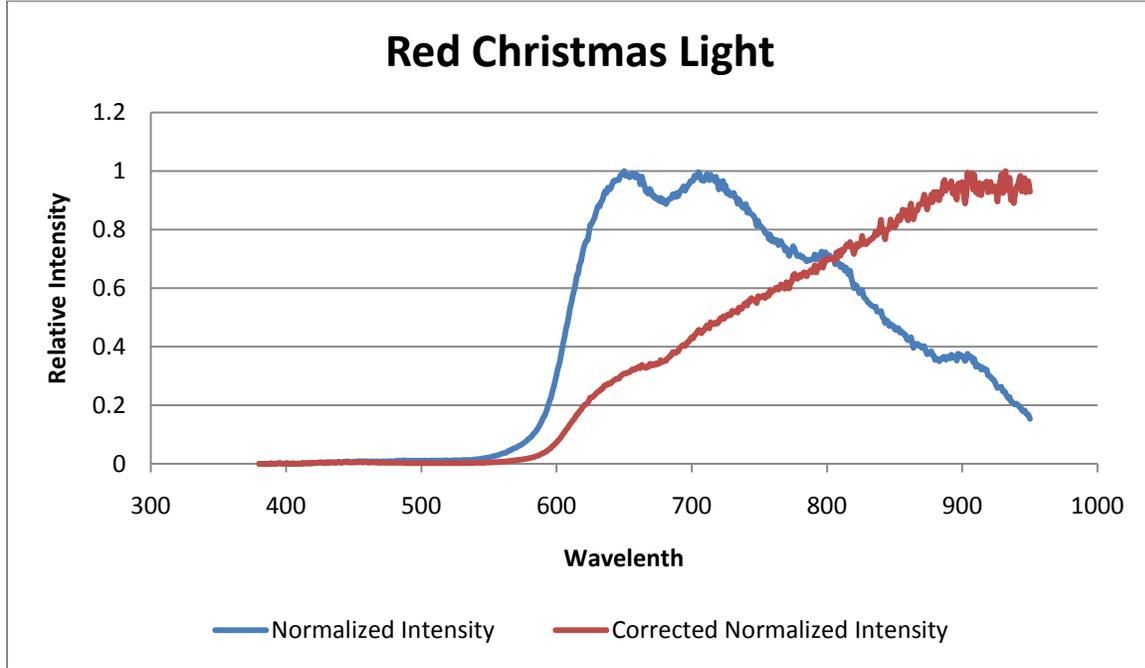


Figure 5: Spectrum from 380nm-950nm of a red Christmas bulb.

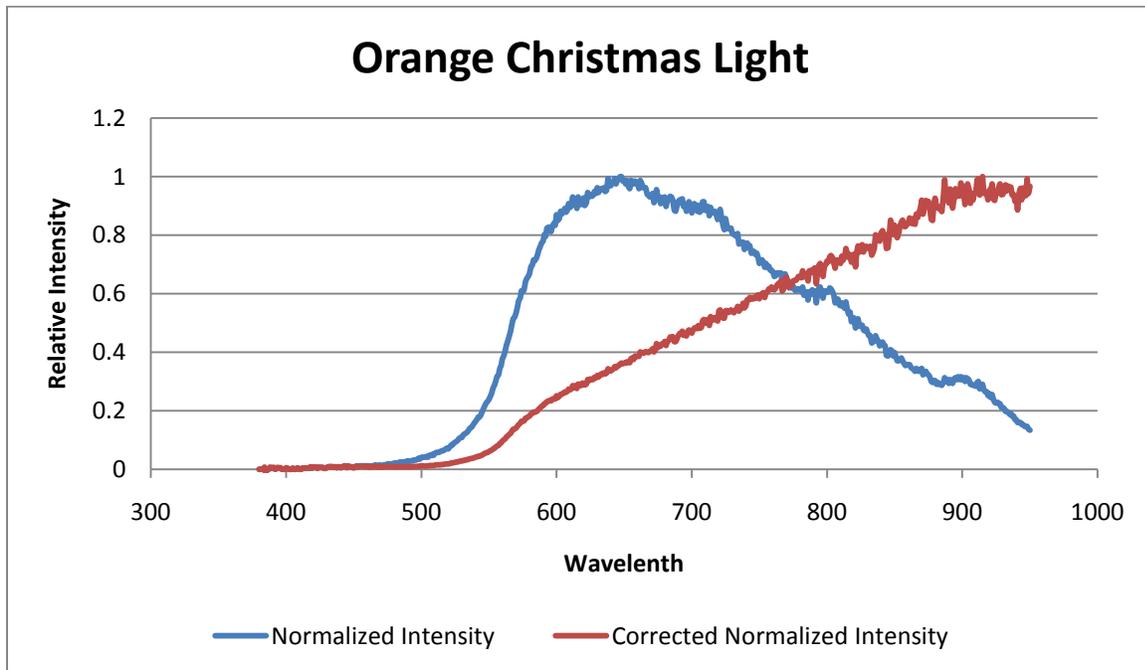


Figure 6: Spectrum from 380nm-950nm of an orange Christmas bulb.

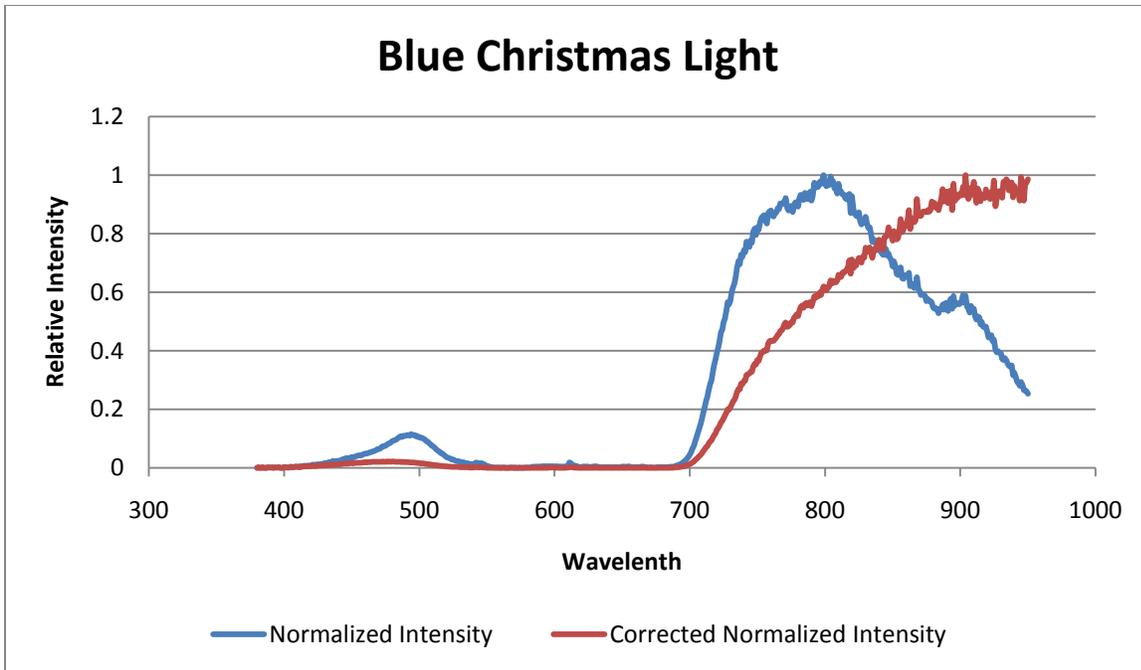


Figure 7: Spectrum from 380nm-950nm of a blue Christmas bulb.

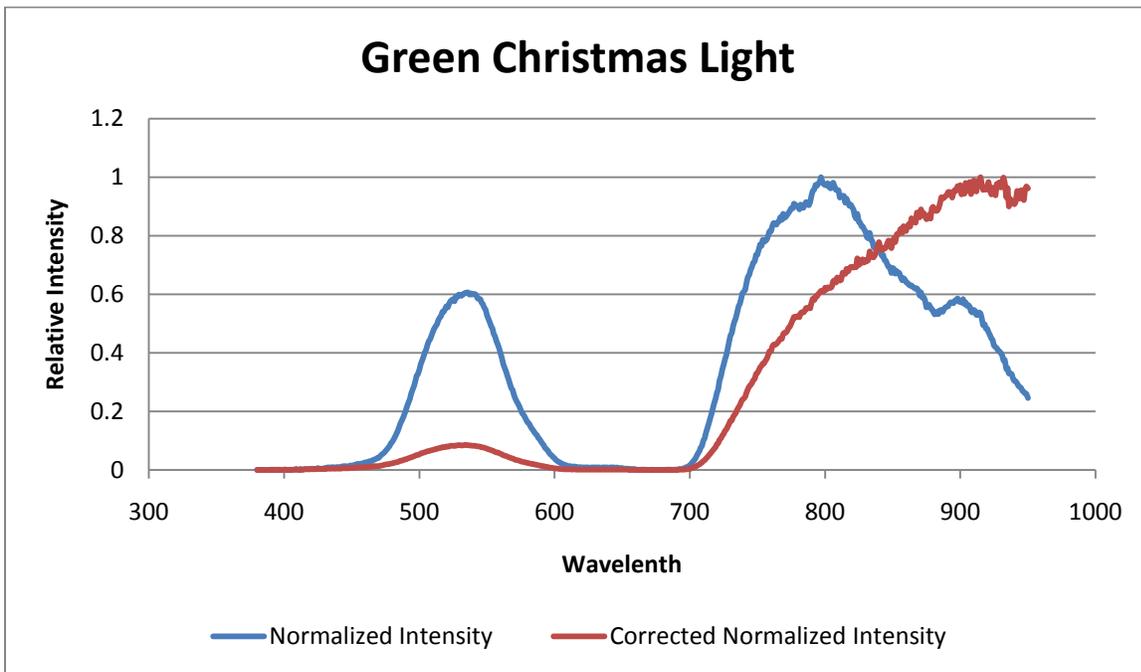


Figure 8: Spectrum from 380nm-950nm of a green Christmas bulb.

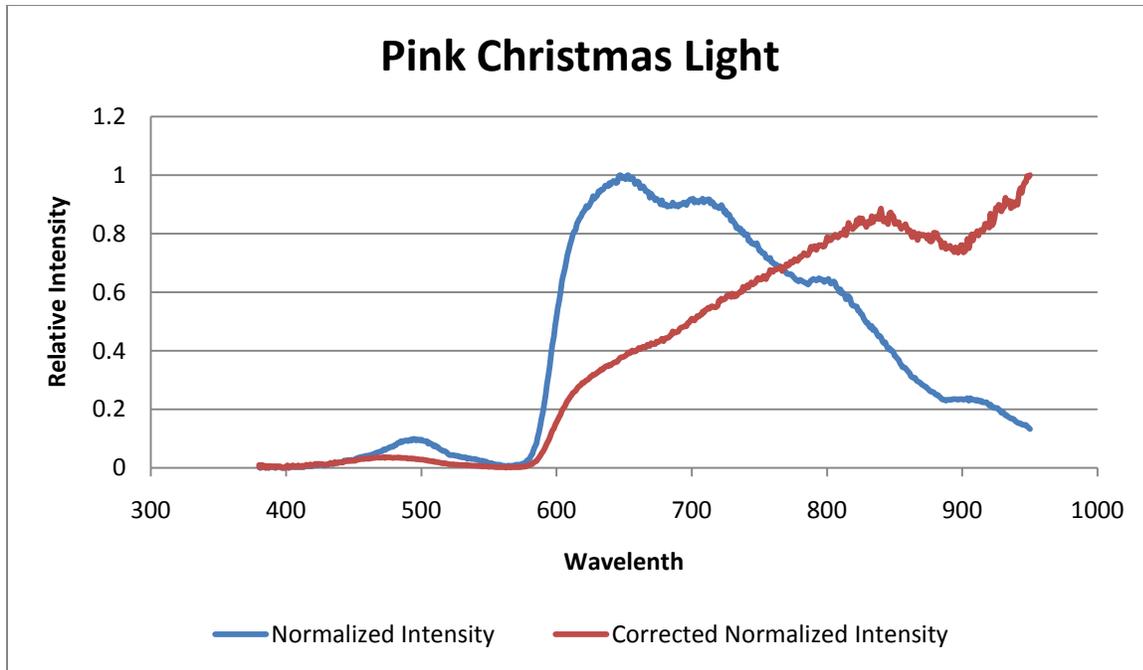


Figure 9: Spectrum from 380nm-950nm of a pink Christmas bulb.

Figures 2-6 are the spectra from the five different colors of Christmas bulbs. What is interesting is they all measure virtually a black body beyond 700nm. This tells me that the filament inside each of the bulbs is giving off the full black body spectrum, and that the colored glass that makes up the shell of each bulb is simply a cut off filter. What is also interesting is the manufacturer of these bulbs made no effort to block the infrared wavelengths. This is of course not needed as the human eye cannot see infrared.

The blue and green are similar. The green bulb lets through predominantly green light, cutting off everything below roughly 480nm, and again everything from 600nm to the infrared. The blue bulb similarly cuts off everything below roughly 410nm and 510nm to the infrared. The Red bulb cuts off everything below roughly 600nm, letting only red wavelengths through. The orange bulb only blocks wavelengths below roughly 520nm, letting both yellow, orange, and red wavelengths through.

Next we look at two different kinds of compact fluorescent light bulbs.

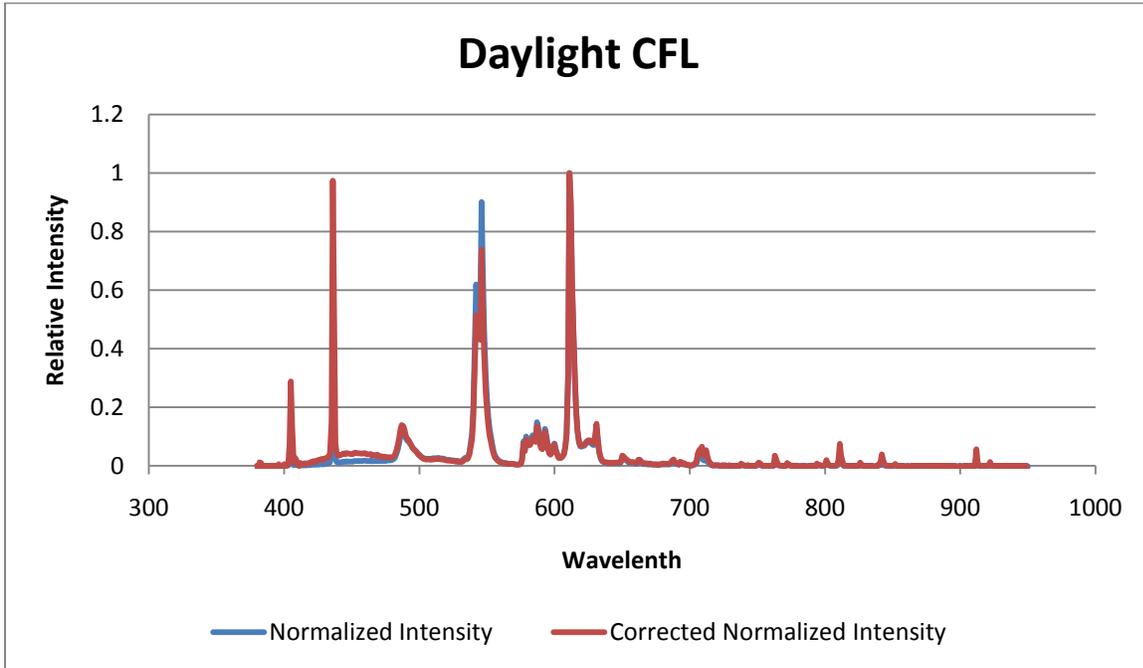


Figure 10: Spectrum from 380nm-950nm of a "daylight" CFL bulb.

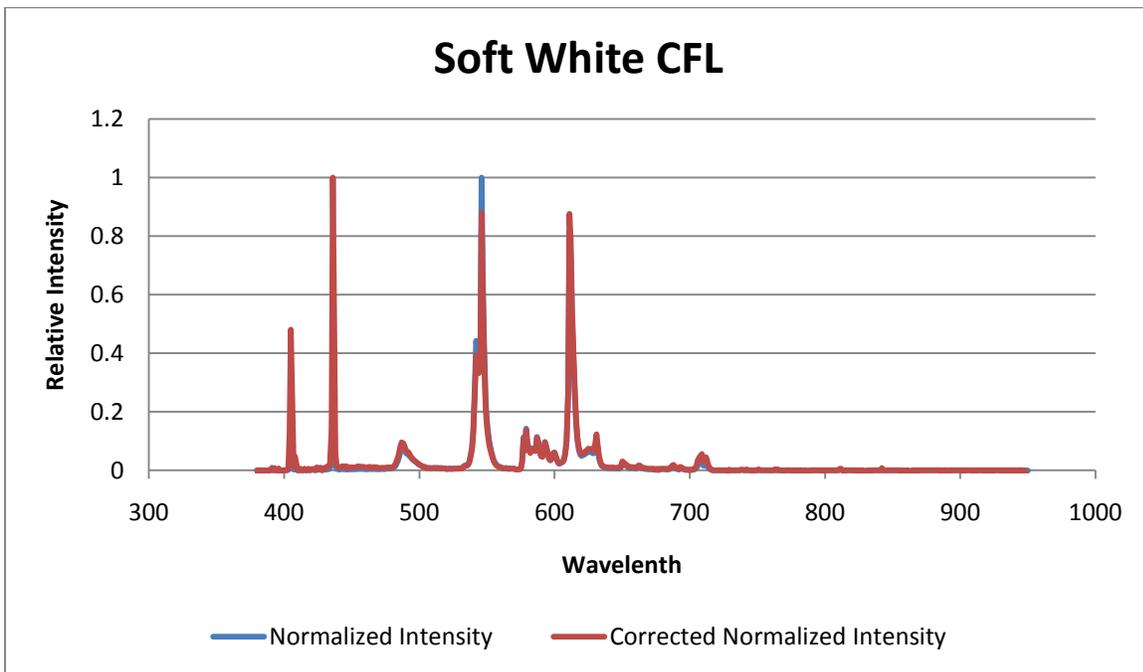


Figure 11: Spectrum from 380nm-950nm of a "soft white" CFL bulb.

As seen in figures 10 and 11, both CFLs spectra are remarkably similar. They appear to be slightly different to the naked eye. The daylight CFL has a bluish hue, and has a slight bump

between 430-470nm that the softwhite CFL does not have. What's more is that they are predominantly only a few wavelengths, the four big spikes of the graphs. These spikes are due to phosphorescence⁷. There is a coating inside the CFL which phosphoresces under the light given off inside the bulb. An interesting consequence of this is that the light our eyes see from fluorescence lights isn't the light being generated directly from the electricity the bulb uses, but rather the phosphorescence from the coating. Also it is clear the "daylight" CFL is absolutely nothing like real daylight (Figure 1).

Next we will look at two different kinds of incandescent light bulbs.

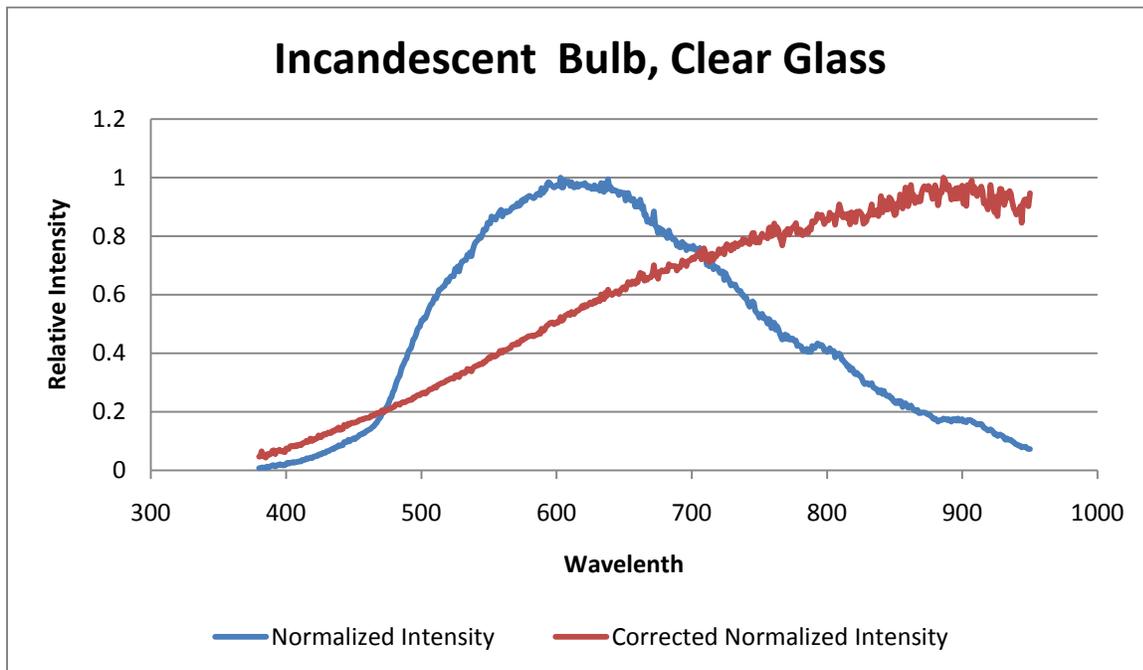


Figure 12: Spectrum from 380nm-950nm of an incandescent bulb, clear glass exterior.

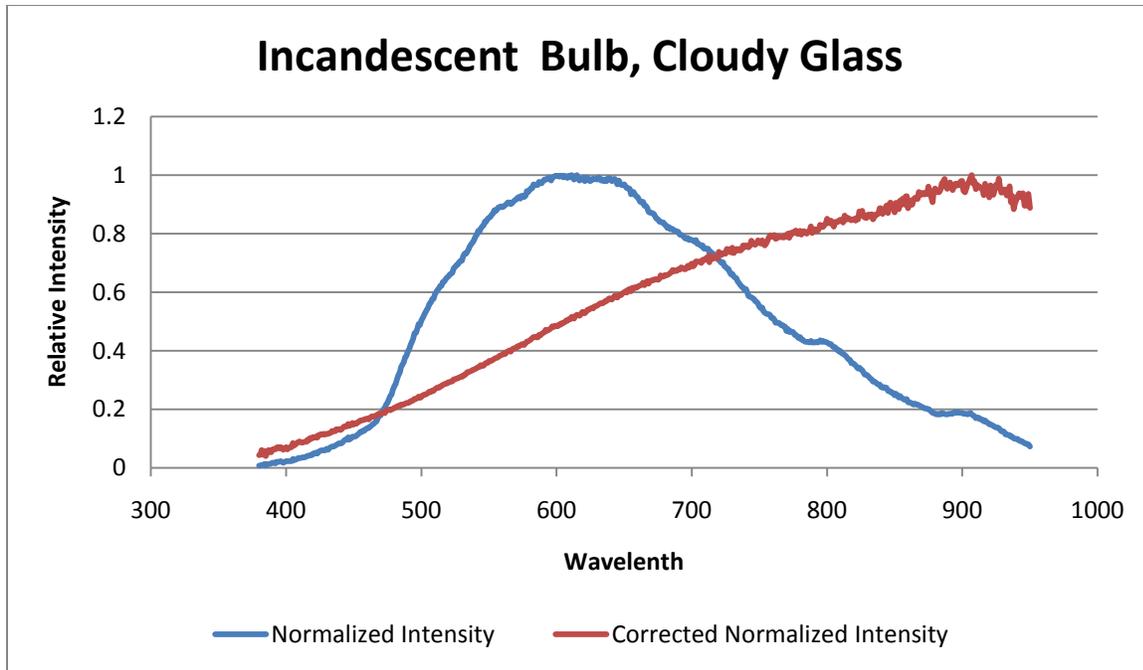


Figure 13: Spectrum from 380nm-950nm of an incandescent bulb, cloudy glass exterior.

Taking a look at figures 12 and 13, both these bulbs appear to be very close to the tungsten bulb I used to for my correction function (See figure 3). With a quick search of the manufactures' website⁶ I found they do in fact contain tungsten filaments. The only other thing to note is the cloudy glass does very little to the spectrum except perhaps reduce the noise measured ("smoother light?").

Next we look at sources of light that are much more efficient than incandescent bulbs, LEDs.

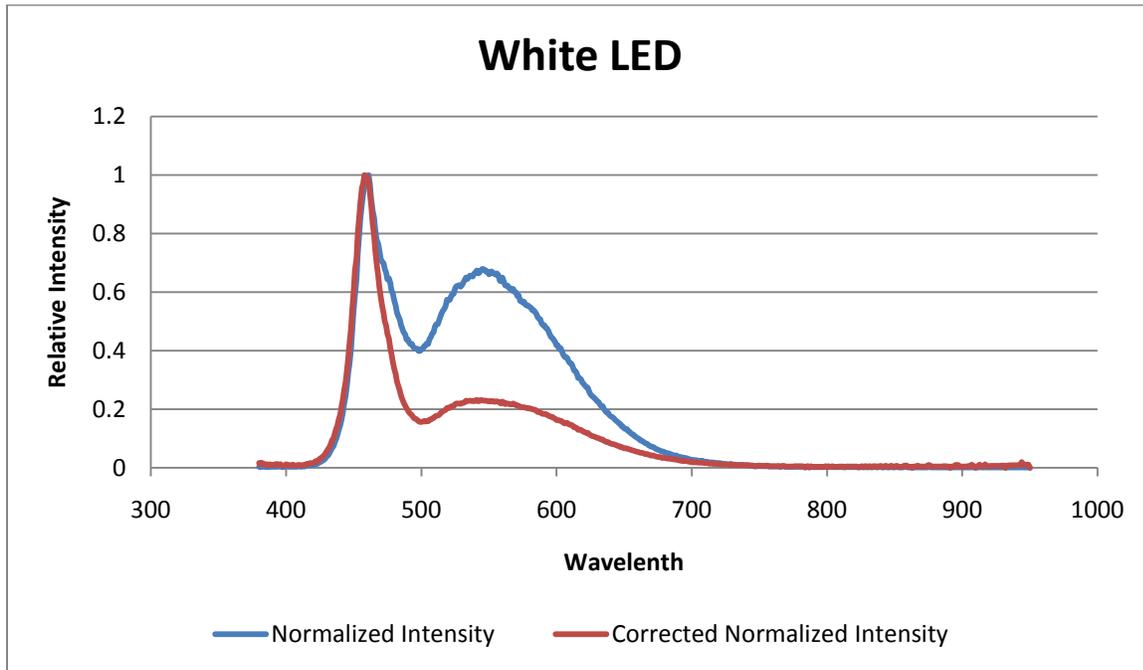


Figure 14: Spectrum from 380nm-950nm of a white LED.

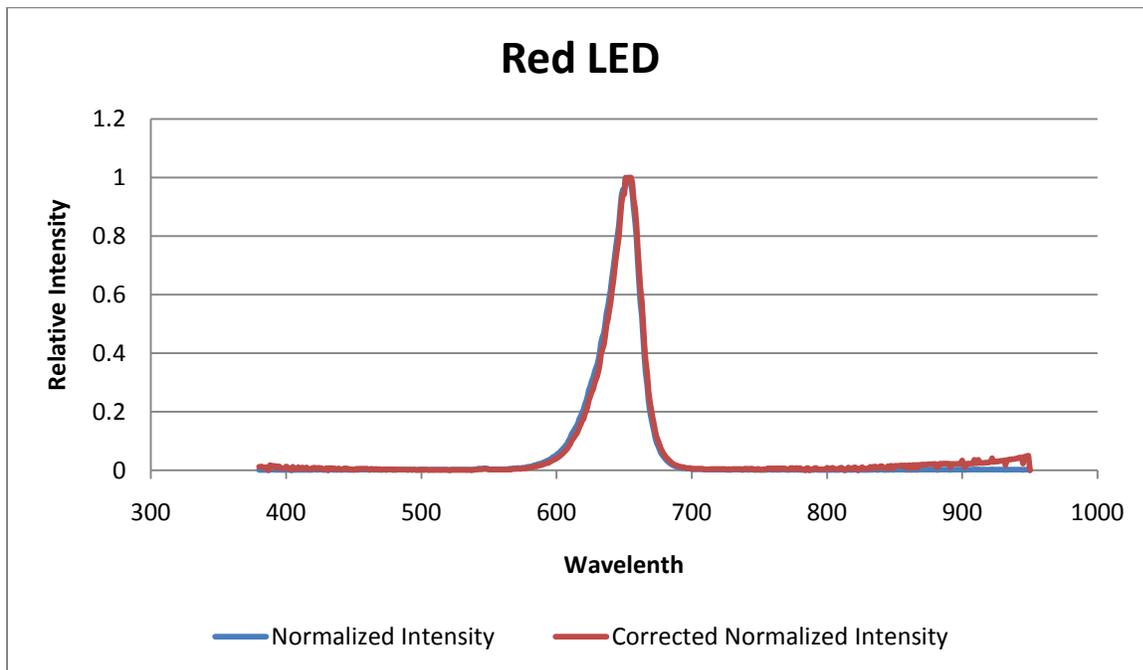


Figure 15: Spectrum from 380nm-950nm of a red LED.

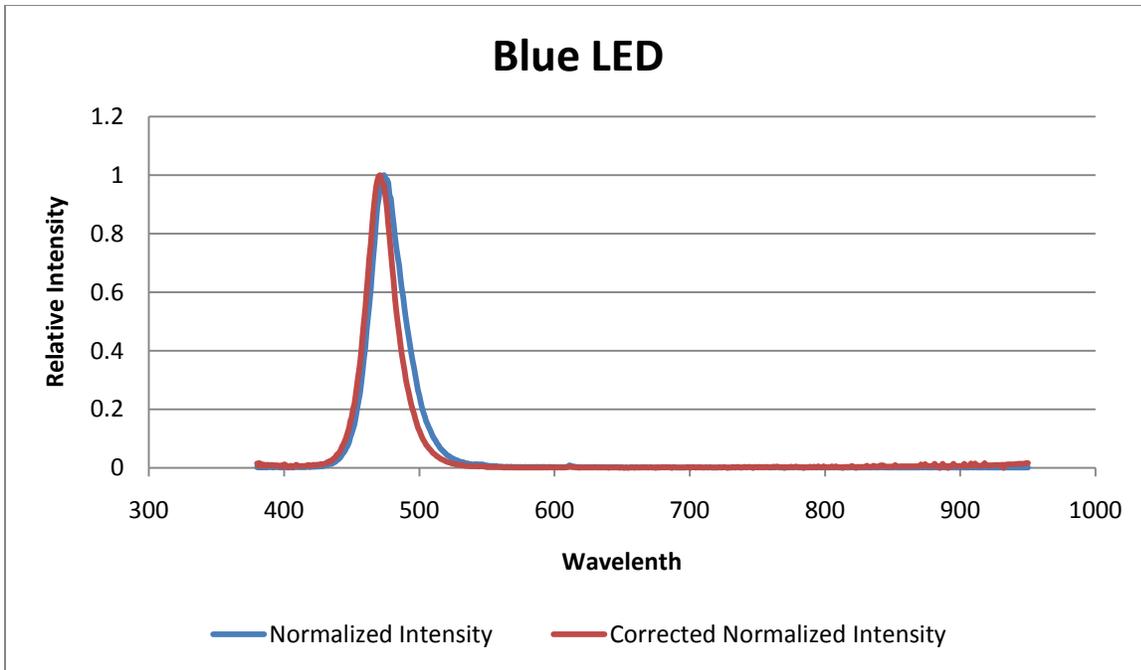


Figure 16: Spectrum from 380nm-950nm of a blue LED.

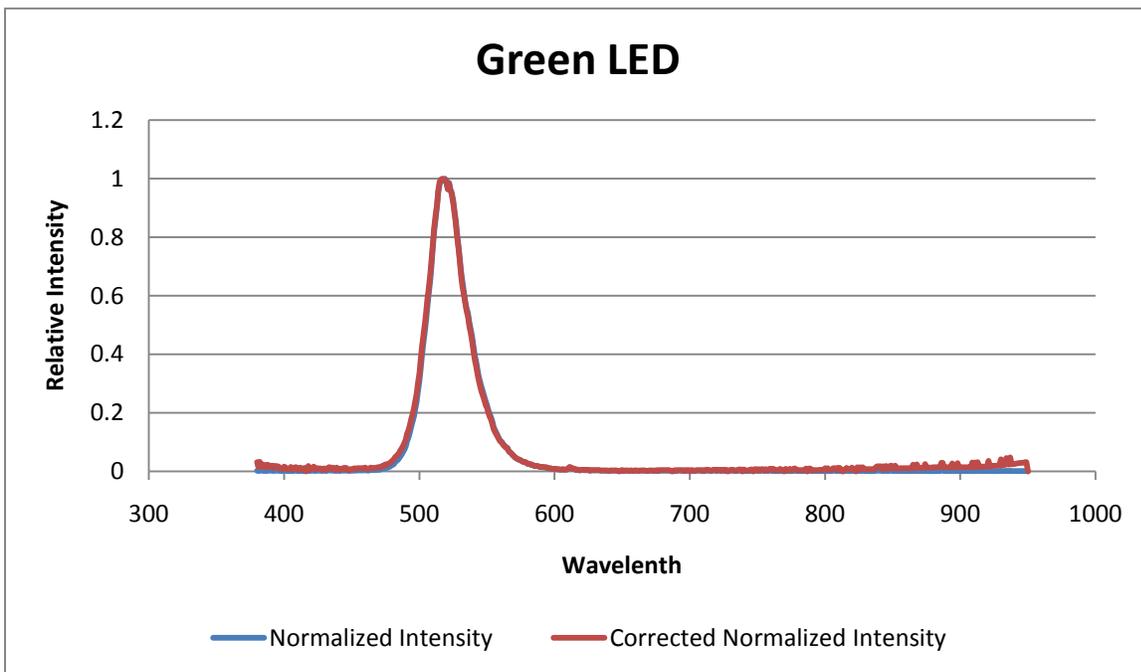


Figure 17: Spectrum from 380nm-950nm of a green LED.

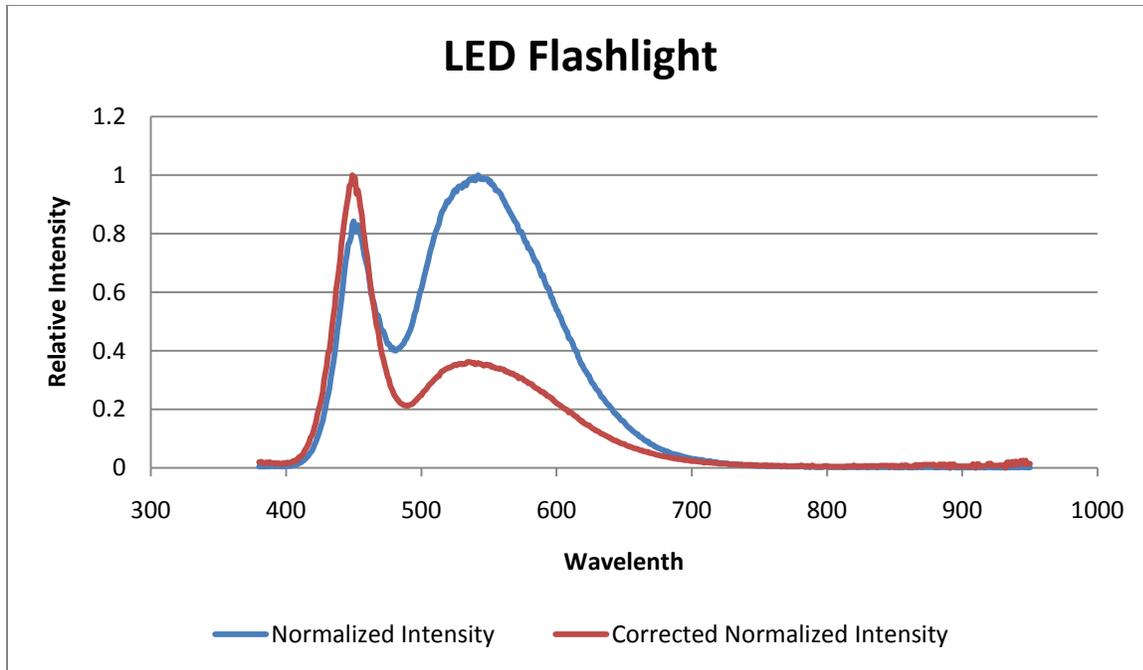


Figure 18: Spectrum from 380nm-950nm of an LED flashlight.

Figures 13-18 show the different types of LEDs I measured. Right away it is evident that the LEDs fall into two categories. The red, green, and blue LEDs all emit light of roughly a 100 nm range, peaking at 650nm for red, 515nm for green, and 470nm for blue. The red, green and blue LEDs all emit only wavelengths of light of their respective color. This makes LEDs very efficient.

The white LED and LED flashlight both have the same general shape, with peaks being slightly different sizes. There is a narrow peak centered in the blue, followed by a broad peak that covers the rest of the visible spectrum. Note that very little to none of the light emitted is non-visible. (Aside: compare this with the tungsten filaments, where the majority of the light emitted is infrared.) What is likely happening inside the LED is that the light that is being generated internally is the first narrow peak, very similar to the blue LED. This blue light is causing a material inside the LED housing to fluoresce, giving off the second broad peak. When all of this is added together, our eye sees white light. This type of LED is known as a phosphor-based white LED. An LED of a single color is coated in a phosphor which luminesces under the color of the LED.⁷

II. The Attenuation Coefficient of Water

Introduction and Setup

The basic idea is to send a laser through a vertically oriented tube in which water can be placed, with the transmitted laser directed to a photo detector. To accomplish this I used two turning mirrors with the laser pointing at the bottom one, turning the laser up through the tube. Then the top mirror turns the beam towards the photo detector, connected to a voltmeter and variable resistor in parallel. The purpose of these is to give a numerical value to the amount of light getting through the tube. I also discovered in the course of my experiments that the setup is very sensitive to vibrations; for example someone walking in the hallway would make the reading on the voltmeter change rapidly. It was useful to place a lens between the top turning mirror and the photo detector, shown at figure 19. This lens helps because any vibrations that deviate the beam slightly will not affect the beam's overall path to the photo detector, as the lens corrects for these vibrations by gathering light from a large area. Even if the beam moves several millimeters the lens still focuses it onto the photodetector.

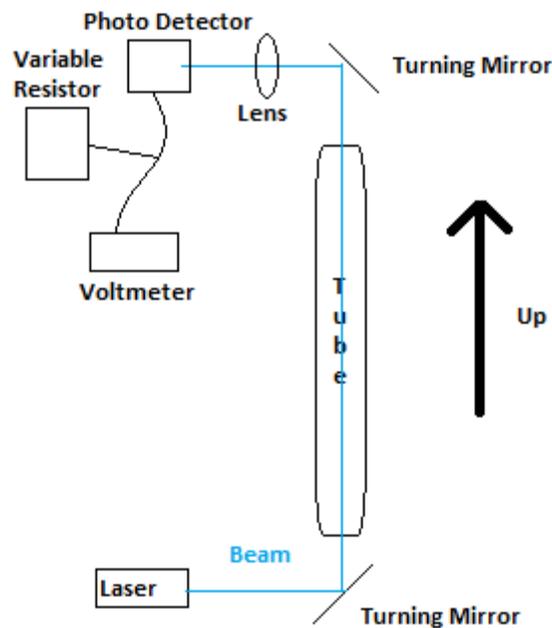


Figure 19: Setup for this experiment

The motivation for this set of experiments is to verify Beer's law, which says:

$$P_{out} = P_{in}e^{-\alpha L}$$

P_{in} is the amount of light that is reaching the photo detector with no water in the tube. P_{out} is the amount of light that is reaching the photo detector when the beam passes through water of depth L . With these parameters combined we can calculate α , which is the attenuation coefficient. There are many different measurements of α for the students to make. I discovered that water from different sources has different values of α . For this experiment three different sources were decided on: distilled water, water from the drinking fountain, and water from Prof. Quimby's lab sink, as well as food coloring added to the fountain water.

Blue food coloring was used because the other colors that were tried were blocking significantly more light, which required much more dilute concentrations that were more difficult to mix accurately. The concentration was measured in drops per liter of water. For example the red squares on figure 20 represent the data taken with water that has half of one drop of blue food coloring added per liter of fountain water. My method of achieving the various concentrations was slightly tedious. Using the beakers I had on hand, which were 200 mL each, I made a concentration of 5 drops/L by adding one drop into a full 200 mL beaker. Then using a graduated cylinder I mixed this higher concentration with clear fountain water in various ratios to end up with the five different concentrations I measured. Because of the necessity of having half-drop/L increments (anything at or above 3 drops/L is blocking too much of the light to get accurate measurements with the available photo detector), the only way to avoid this somewhat tedious ratio mixing would be to have a 2 liter container, adding 1 drop for 0.5 drop/L, etc. Having one batch of water at 5 drops/L then cutting it seems to be the easiest ratios to achieve the desired ratios. The concentrations of dye would likely be pre-mixed for the students.

Data and Analysis

The tube is 30 cm long. After taking a measurement at 5cm increments I decided that it looked like too few data points with the amount of scatter I had, so I upped the amount of data points to 11, taking a measurement every 3cm of water. The first step to each set of measurements was aligning the tube with the mirrors and photo detector. This proved to be frustrating sometimes, a few times even taking more time than the measurements. A few things I found to ease the process were to first align the laser and mirrors without the tube. Next to put a few drops of water in. The surface of the water, no matter the height, is slightly concave. This diverges the beam slightly. This means if the tube is aligned when it is dry, the beam will not be aligned once water is added to the tube. The procedure for taking the data was simple after the tube had been aligned. Using an "improvised water transfer device" (ok I used a turkey baster, it worked very well though!) I slowly added water while an assistant held a ruler beside the tube and told me when to

stop adding water. (aside: This is definitely not a single person job, which is good because the students in Quimby's lab work in pairs) After repeating the process for every 3cm of water, and again with each different liquid, the following data was obtained, plotted on a semi-log graph (figure 20):

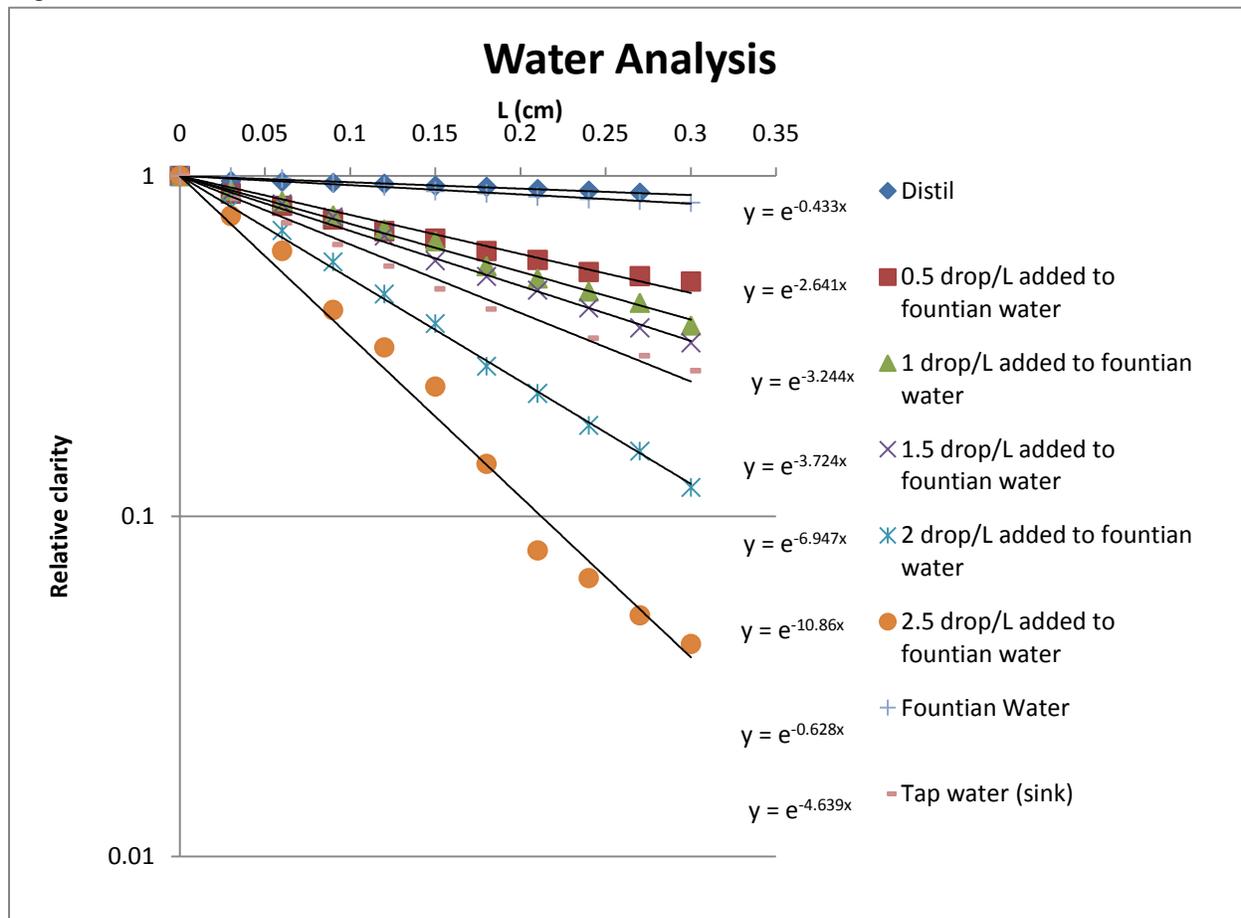


Figure 20: Relative clarity graphed on a semi-log slot with attenuation coefficients shown.

There are a few things that appear to be wrong with this data, the causes of which are emphasized in the student handout so they don't make the same mistakes. Looking at the top of figure 20 it is clear that the distilled water I used somehow got contaminated, as it should have yielded a much smaller attenuation coefficient than the fountain water. The attenuation coefficient of pure water⁸ should be on the order of 10^{-4} m^{-1} , whereas my measured coefficient for distilled water is 0.433 m^{-1} .

In addition the main discovery I had was the amount of bubbles in the water after I added some. Many tiny bubbles were diffusing the beam, which caused scatter in my data and could possibly account for other errors. This is another possible reason the distilled water showed higher attenuation than expected. One would expect that as the drops/L of food coloring varied linearly, so too should the attenuation coefficient, but this is clearly not the case (figure 21). It is unclear at

the moment whether this fits any trendline. It appears to vary linearly from 0 to 1.5 drops/L, and again from 1.5 to 2.5 drops/L with different values

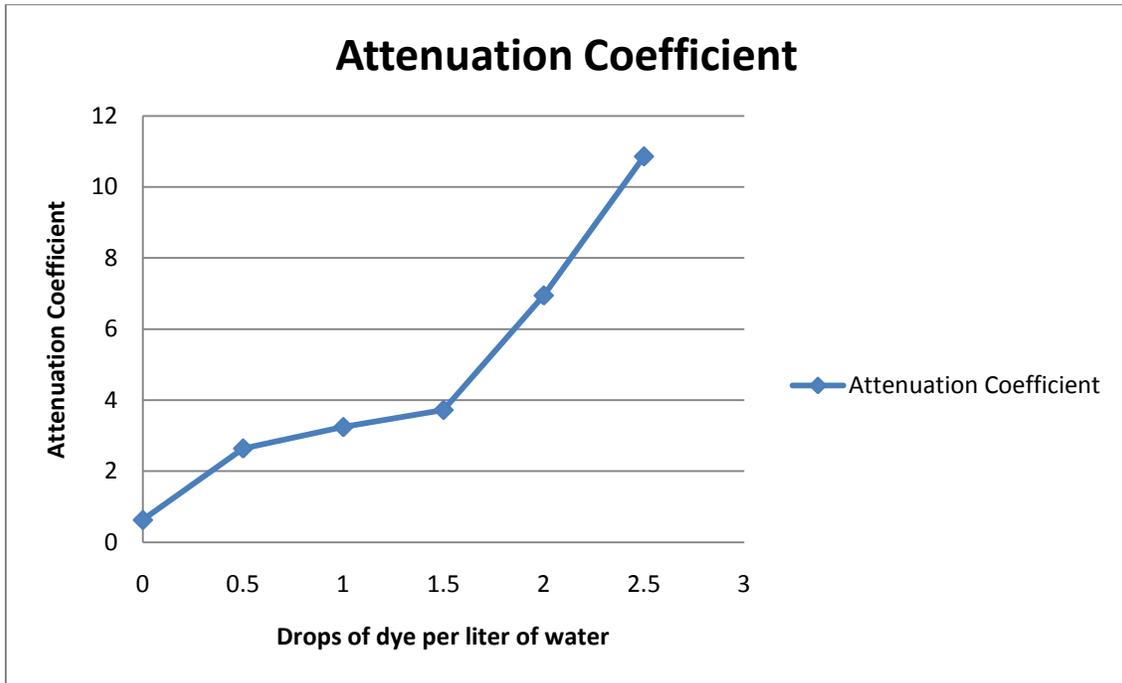


Figure 21: Attenuation coefficient as function of drops of dye per liter of water

It may be the dye was effecting the amount of bubbles that were able to form in the water.

I then ran two more trials, one with adding the water as carefully as possible, dribbling it down the side of the tube to try to create as little turbulence and bubbles as possible. The second trial I used the baster to gently take water out of the tube. I used the 2.5 drops/L water as this data has the most scatter in it. The results are shown in figure 22.

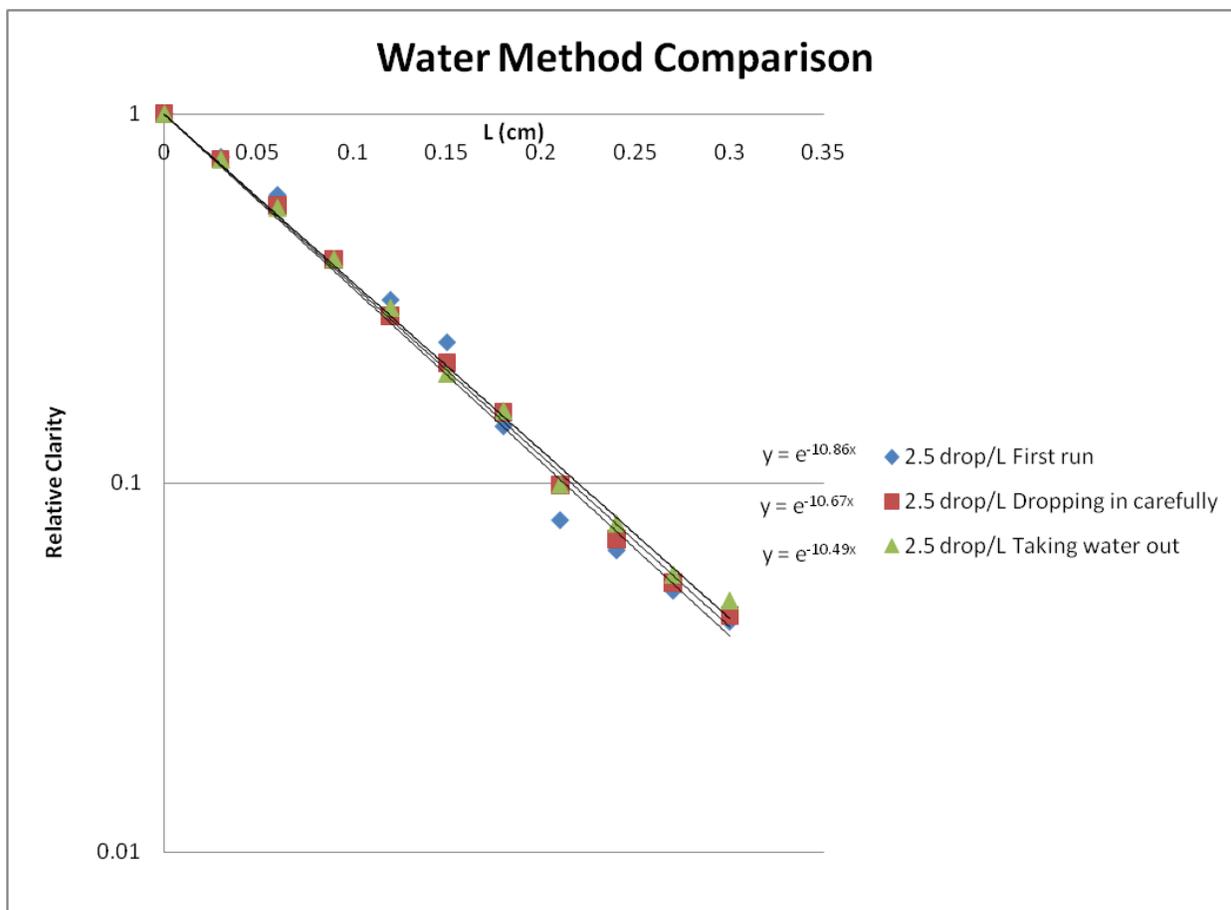


Figure 22: Relative clarity from the comparison of different water insertion methods.

Both new methods clearly showed a reduction in the scatter of the data, and also confirmed the attenuation coefficient to be close to the first measured. I am very confident there is little error in the y values on figure 22, as the measurements were taken after the voltmeter connected to the photodetector wasn't fluxuating out to several figures. However there is an error of a few millimeters either way on the L portion of the graph, as eyeballing the water to a ruler isn't exact. If there had been more time I would have liked to repeat all measurements using the carefully dropping in method to see if that fixed the error in my 0.5 - 1.5 drops/L data. However even without doing that this method of very gently putting water in the tube is clearly superior to thoughtlessly squeezing the baster's bulb and letting water rush into the tube, so this is the method I will stress to the students in the handout. I have chosen that method over taking water out of the tube as it is much easier and time effective to use.

III. Absorption and Emission of Impurity Ions in Glass

Introduction and Setup

The purpose of this set of experiments is to have students measure some of the energy levels of two different samples: Holmium (Ho) and Erbium (Er) doped glasses. They will achieve this by taking absorption and fluorescence spectra of both samples. Then the students will use the data they take to construct an energy level chart for both samples. My own chart is shown later on.

For the first part of the experiment, the students will be taking absorption measurements, as shown below (figure 23),

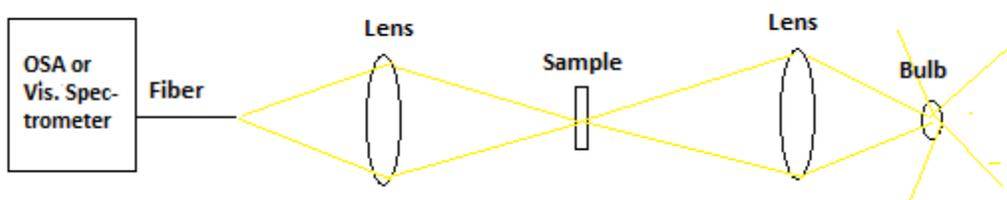


Figure 23: Setup for absorption measurements.

The setup for this is simple. A lens is placed between the sample and a tungsten filament bulb. This focuses the light from the bulb onto a small spot on the sample. The emerging light is then collected by another lens and focused onto the end of the spectrometer fiber. The measurement is done twice, once with the sample in and once with the sample removed, known as a "sample-in \ sample-out" measurement. Taking the ratio of these two spectra will give the percent of light that gets transmitted through the sample. As the broad spectrum of light from the bulb passes through the sample, most of it will go through and reach the input fiber. However there will be several narrow wavelength spikes where very little light will get through. This is caused by the material absorbing light at these wavelengths. This happens when the energy of a photon matches the energy difference between the ground state and one of the excited states of the material (see figure 24).

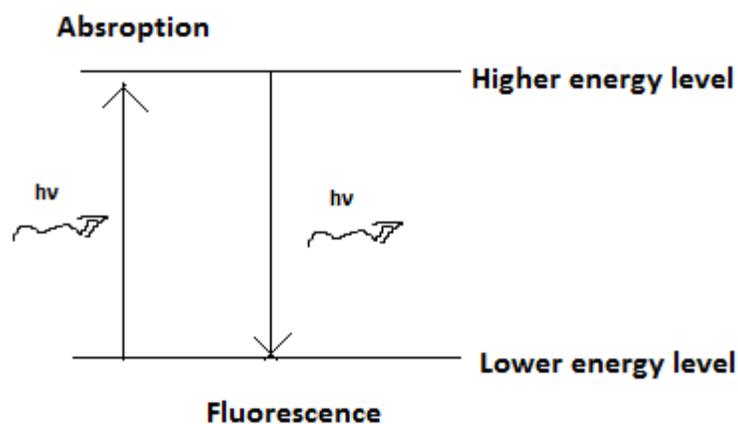


Figure 24: Simple diagram showing absorption and emission of a photon.

For the second part of the experiment, the students will be taking fluorescence measurements, as shown below in figure 25:

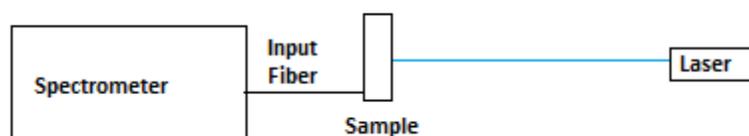


Figure 25: Setup for the fluorescence measurements.

The setup for this is also simple. A 410nm laser will be used to pump the sample. This excites the electrons in the sample. During their decay back to the ground state, some of the electrons go through a radiative decay (see figure 24). This gives off a photon of light with the energy of the difference between the two levels. These photons are then picked up by the spectrometer, and result in spikes on the spectrum. Through my experiments with this I found that the signal for this emission is weak, so it is important to line the fiber up as straight as possible on the brightest part of the sample. This may also involve rotating the sample so that the laser strikes at different angles to try to get the brightest fluorescence.

The students will also be provided with a small side-project to do while the OSA is taking the absorption measurements, as that is a long process of waiting for the OSA to take the data. Prior to taking the fluorescence measurements for the Ho and Er samples, they will take a fluorescence spectrum of something most people are familiar with: white cloth fluorescing under a black light. This will be a simple measurement; just holding the end of the input fiber up to a piece of cloth under a black light. There isn't really any analysis for this part beyond looking at the spectrum. It serves the purpose of both giving the students something to do while the OSA runs,

and getting the students in the mindset thinking about fluorescence by giving them an example to measure that they've all seen before.

Data and Analysis

In order to construct an energy level diagram the only thing we need from the data is the center wavelength of each of the spikes (for fluorescence) and dips (absorbance). For this reason, even though there is much manipulation that could be done to the data, the only thing that needs to be done is to look at the initial graphs of % of light transmitted. Shown below in figures 26-30.

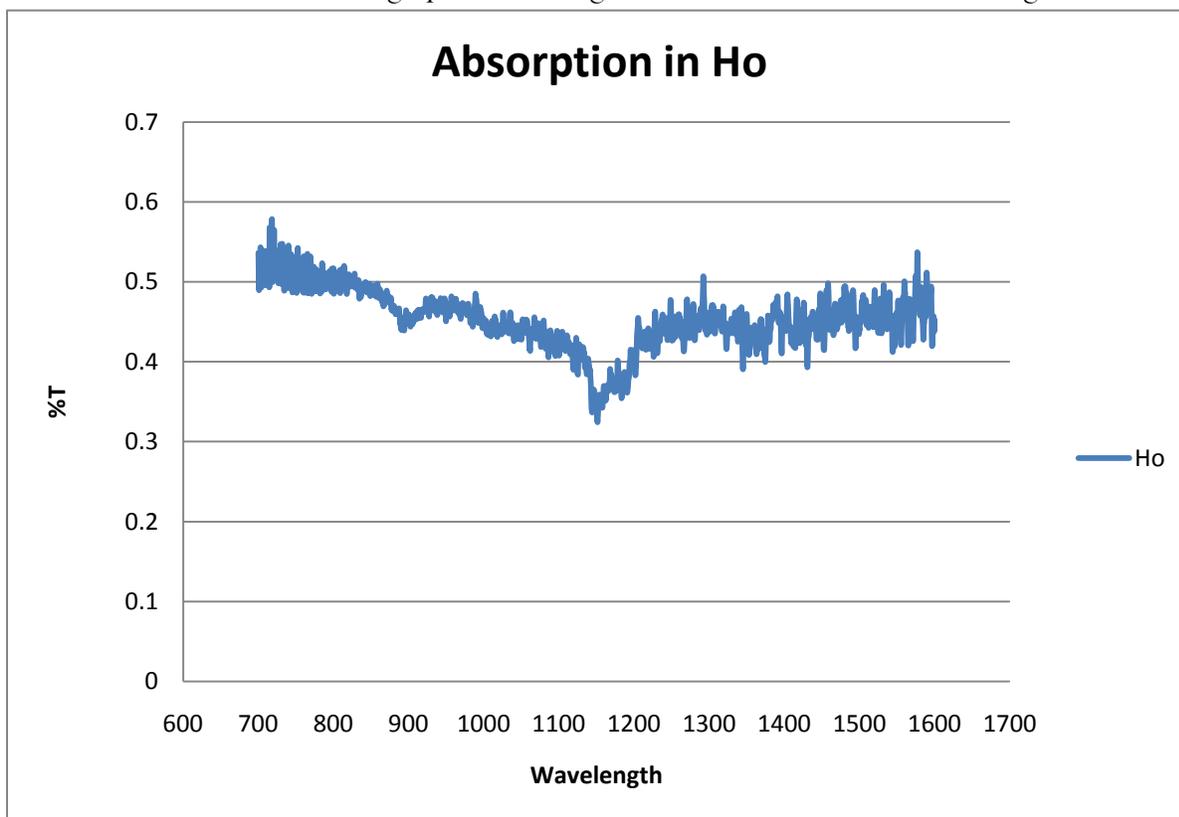


Figure 26: Absorption measurements for Ho from the OSA.

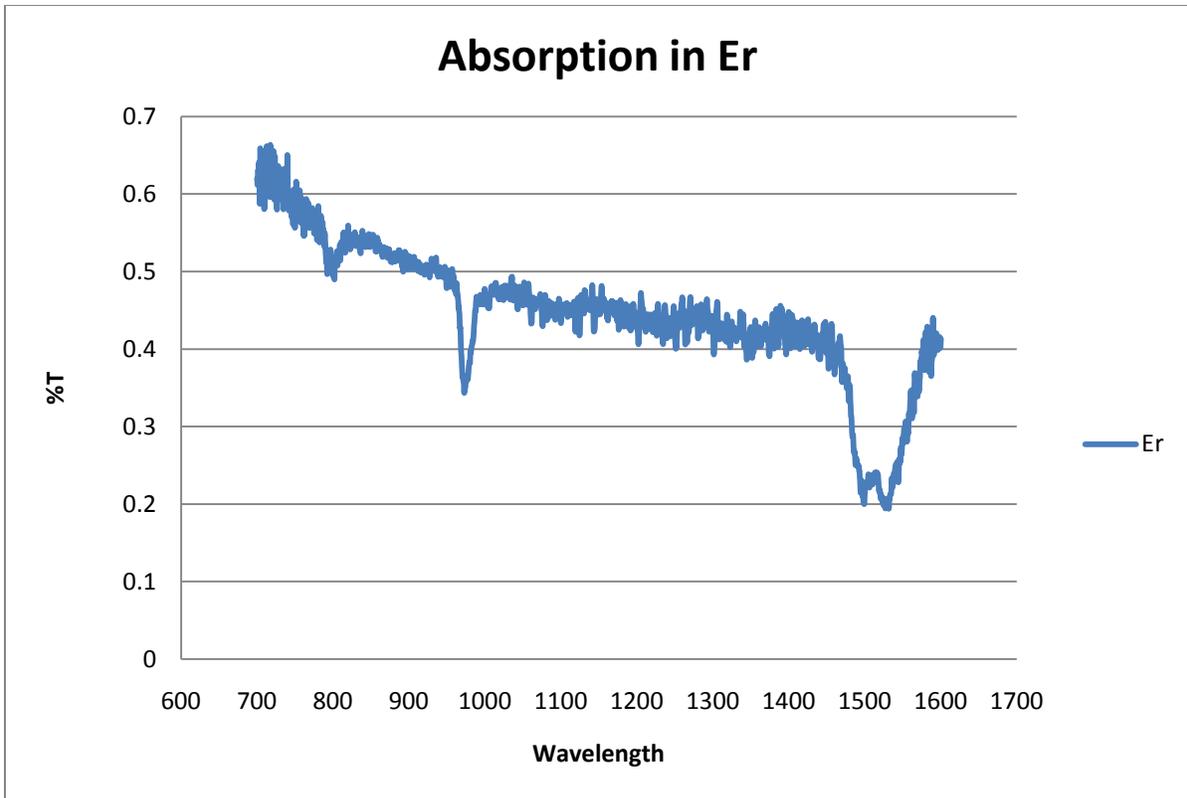


Figure 27: Absorption measurements for Er from the OSA.

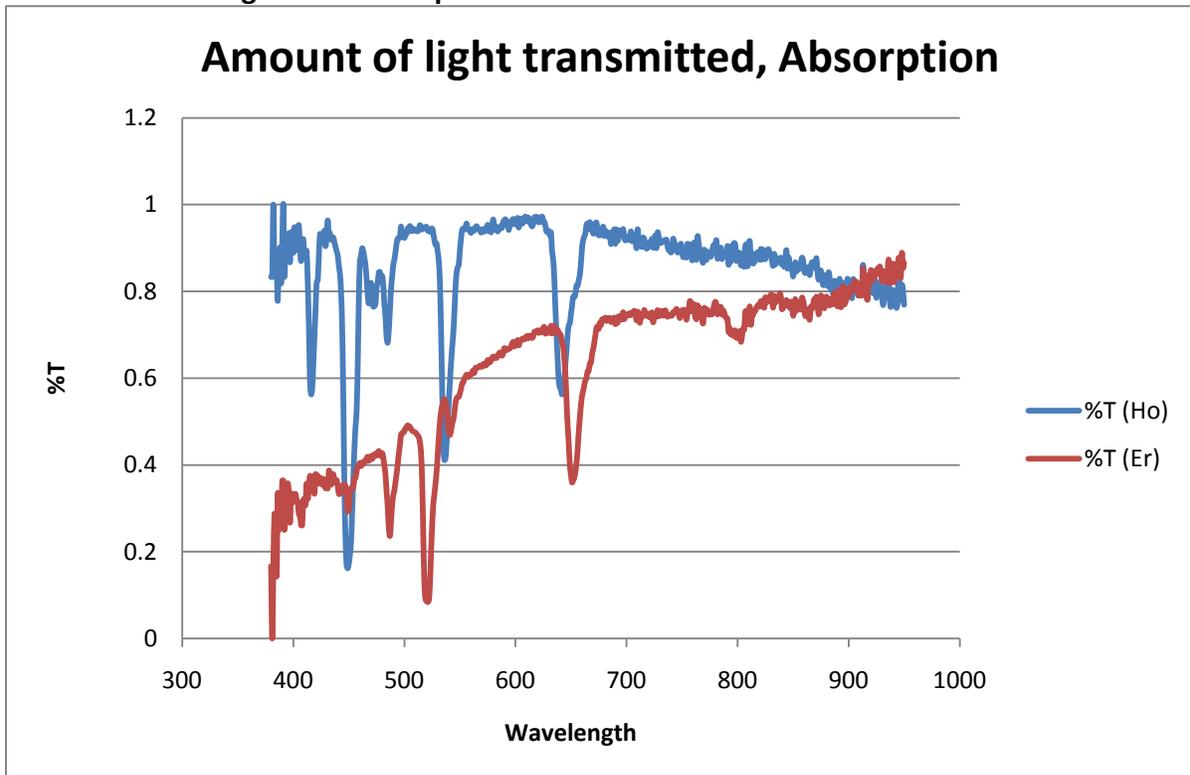


Figure 28: Absorption measurements from the visible spectrometer.

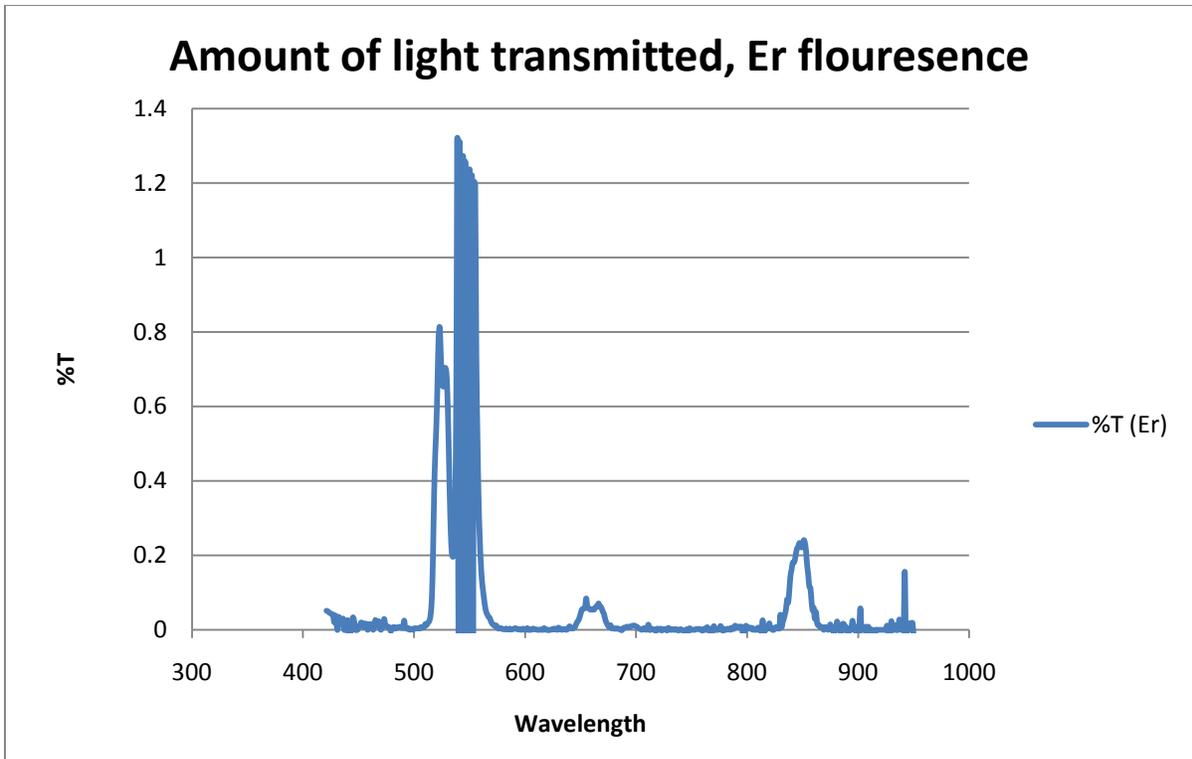


Figure 29: Er Fluorescence measurements from the visible spectrometer.

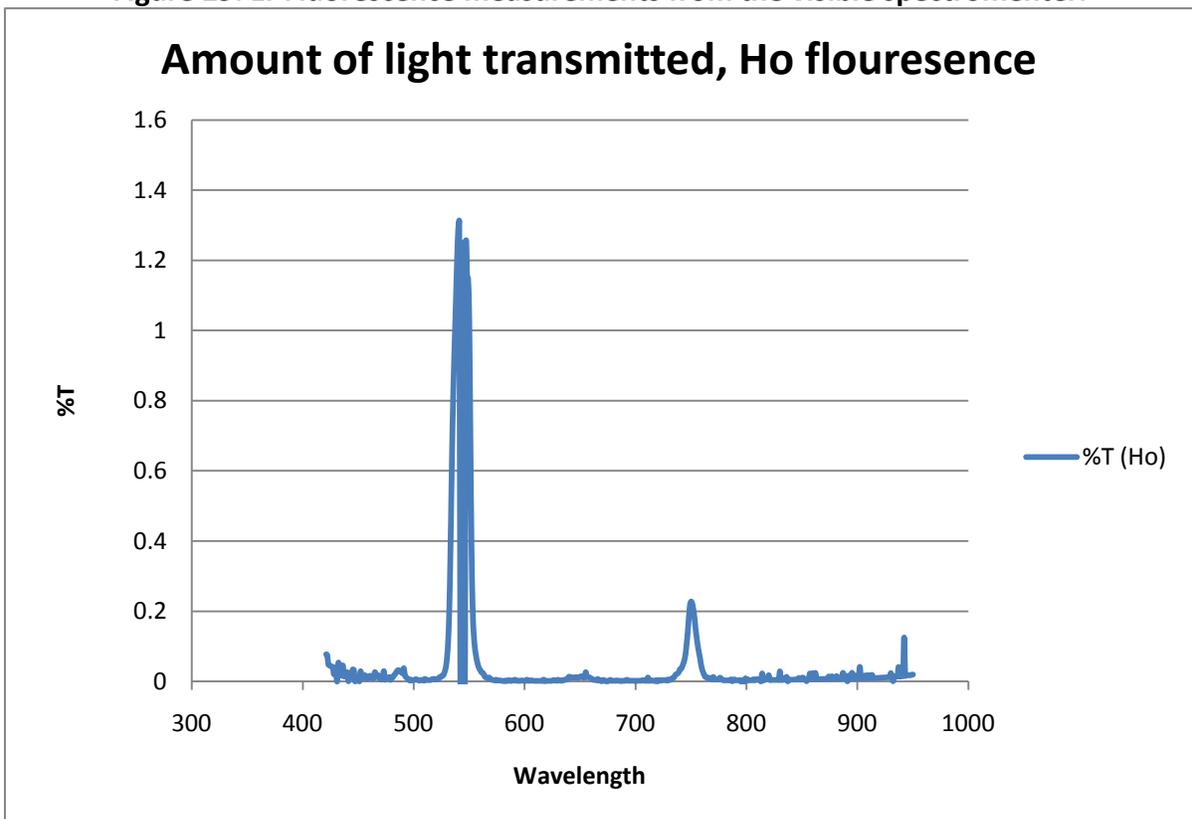


Figure 30: Ho Fluorescence measurements from the visible spectrometer.

As seen in figures 26-30, any sharp absorption dips or fluorescence peaks are clearly seen. The center wavelengths for those dips and peaks are shown in the following table, as well as the energy of photons at those using the equation:

$$E = \frac{hc}{\lambda}$$

where E is the energy of the photon, λ is it's wavelength, h is Planck's constant, and c is the speed of light. Also shown is a conversion into two popular energy units, electron volts and inverse centimeters. The latter of which is widely used in spectroscopy, so that's what I'll use (Table 1).

$$8065 \text{ cm}^{-1} = 1 \text{ eV} = 1.602 * 10^{-19} \text{ J}$$

Table 1: Calculated energy levels of Ho and Er

Peaks (Ho) (nm) Absorb	Energy (Ho) (J)	Energy (Ho) (eV)	Energy (Ho) (cm ⁻¹)
416	4.78E-19	2.98	24000
449	4.42E-19	2.76	22300
485	4.10E-19	2.56	20600
536	3.71E-19	2.31	18700
642	3.09E-19	1.93	15600
855	2.32E-19	1.45	11700
1150	1.73E-19	1.08	8700
Peaks (Ho) (nm) Emit	Energy (Ho) (J)	Energy (Ho) (eV)	Energy (Ho) (cm ⁻¹)
545	3.64E-19	2.27	18300
750	2.65E-19	1.65	13300
Peaks (Er) (nm) Absorb	Energy (Er) (J)	Energy (Er) (eV)	Energy (Er) (cm ⁻¹)
449	4.42E-19	2.76	22300
487	4.08E-19	2.55	20500
521	3.81E-19	2.38	19200
652	3.05E-19	1.90	15300
780	2.55E-19	1.59	12800
975	2.04E-19	1.27	10300
1540	1.29E-19	0.81	6500
Peaks (Er) (nm) Emit	Energy (Er) (J)	Energy (Er) (eV)	Energy (Er) (cm ⁻¹)
550	3.61E-19	2.25	18200
652	3.05E-19	1.90	15300
850	2.34E-19	1.46	11800

The only thing left to do is to make a simple chart of the last column in table 1, the column of energy levels in inverse centimeters (see figure 31)

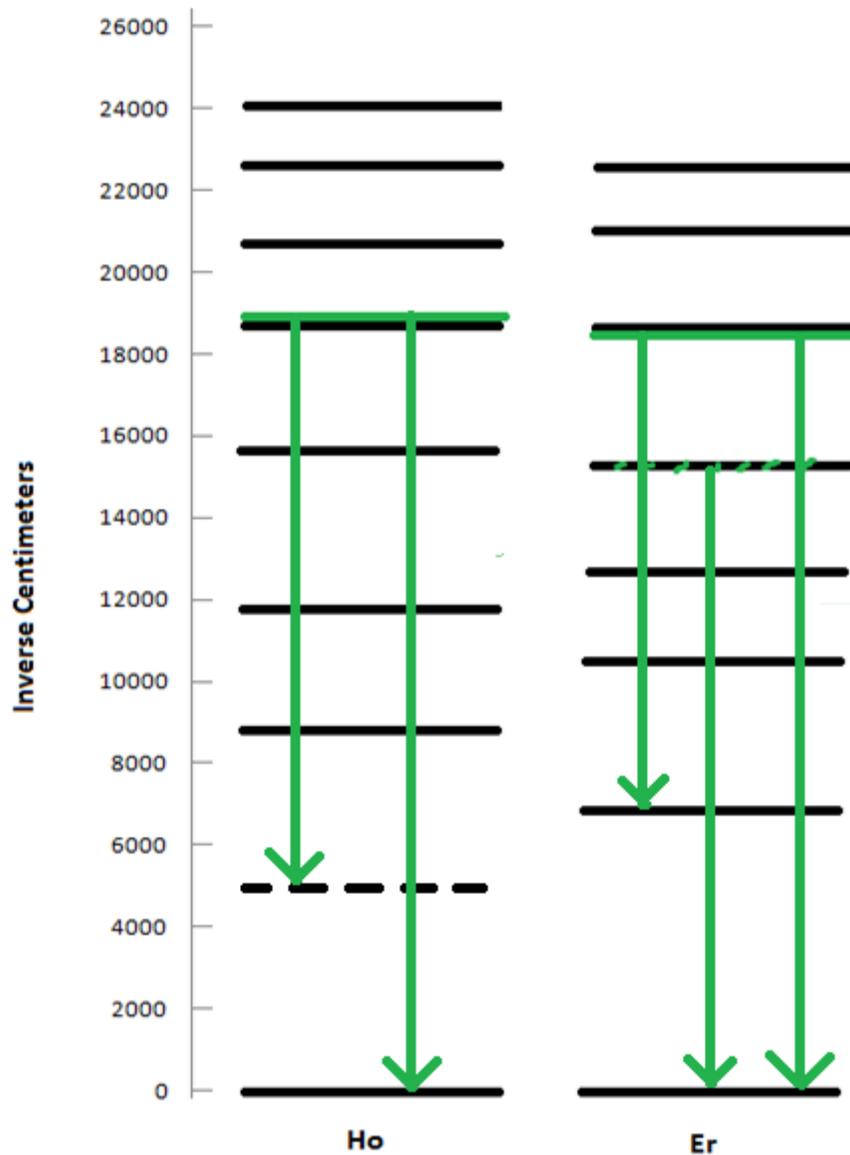


Figure 31: Energy level diagram for Ho and Er doped glasses. Green lines indicate fluorescence levels, black lines indicate absorbing levels. (Note: this graph assumes that fluorescence is due to a transition that ends at the ground state energy level)

Figure 31 shows my completed energy level graphs for both materials. The 0 energy level is taken to be the ground state. All other levels are the measured value above the ground state. This is necessarily true for the absorption levels because the electrons in the resting material are in their lowest energy, ground level state. For the fluorescence this is not necessarily true since the fluorescence could be coming from an energy transition between two excited states. The photon

energy measured from fluorescence is the difference in energy between two energy levels, the bottom of which does not need to be the ground state. The fluorescence around 18300 inverse centimeters for both of them is the primary fluorescence, with the light seen by the naked eye appearing blight green. The other fluorescing levels cannot be seen with the naked eye.

IV. Absorption and Emission in Semiconductors

Introduction and Setup

The purpose of this experiment is to have students measure the band gaps in three different materials. First we have two traditional semiconductors: silicon (Si) and indium phosphide (InP). The InP is a direct band gap semiconductor, meaning that in K space (momentum) the lowest energy of the conduction band is located at the same K value as the highest energy of the valence band (see figure 32). This leads to a very sharp transition wavelength. The InP sample we have available also has a very thin layer of InGaAs, leading to an interesting additional structure in spectrum I took. In contrast to the InP, the Si is an indirect band gap semiconductor, meaning that in K space the lowest energy of the conduction band is located at a different K value than the highest energy of the valence band.⁹ This leads to a more gradual transition.

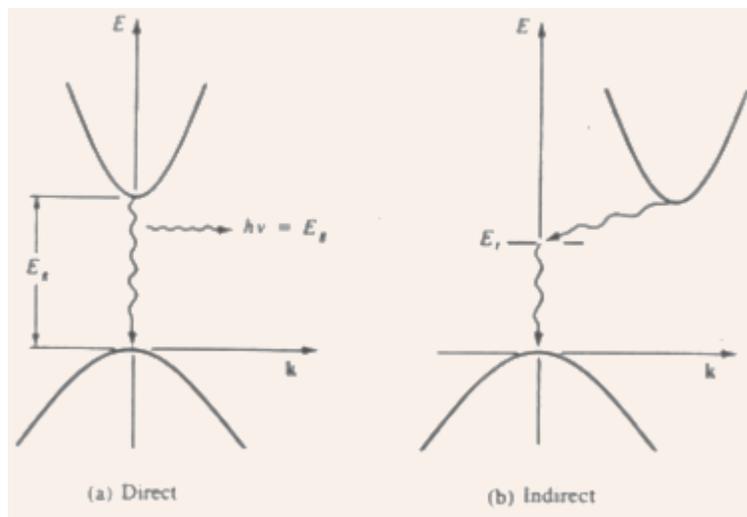


Figure 32: Comparison of direct and indirect bandgaps in K space.⁹

Lastly is a somewhat special case of a band gap in a glass semiconductor with arsenic tri-sulfide (As_2S_3). The band gap of As_2S_3 has a unique structure, which will be discussed later in the analysis section.

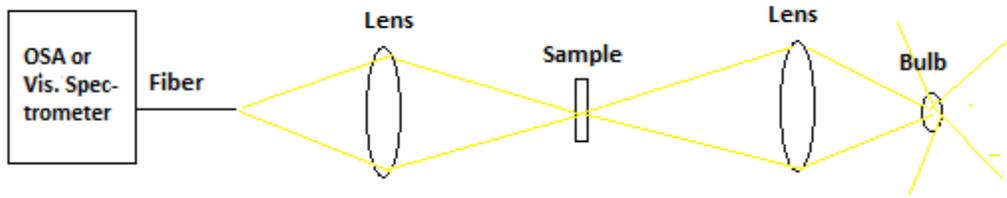


Figure 33: Setup for band gap measurements.

Shown in figure 33 is the same sample-in/sample-out setup as used in the Ho and Er doped glass experiment. A lens is placed between the sample and a tungsten filament bulb. This focuses the light from the bulb onto a small spot on the sample. The emerging light is then collected by another lens and focused onto the end of the fiber. The spectrum is measured twice, once with the sample in and once with the sample removed. Taking the ratio of these two spectra will give the percent of light that gets transmitted through the sample. In this case the percent transmitted data will exhibit broad spectral regions: a transparent region where almost all the light is let through, a transition region where some of the light is getting through, and a dark region where almost no light is getting through. Only the OSA is needed for the Si and InP, as the band gap is in the infrared. Both the OSA and visible spectrometer is needed for the As_2S_3 as its band gap is quite wide and starts in the red.

Data and Analysis

The first thing I did was to make graphs of the percent of light transmitted through the sample, shown in figures 34 and 35.

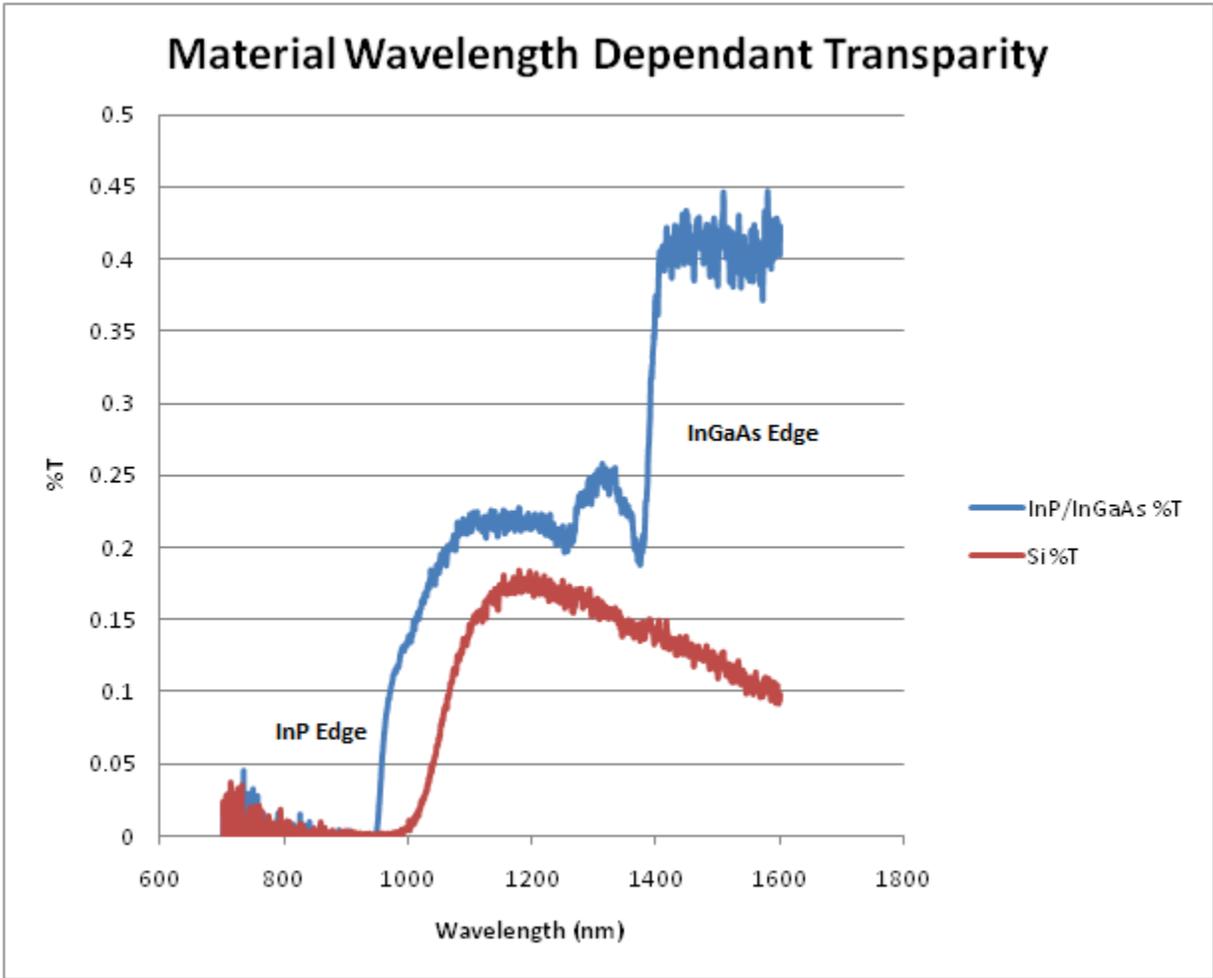


Figure 34: %T for InP and Si.

For the Si, we can see that it is an indirect bandgap material, having a broad transition range. This transition happens around 1100nm. A feature on this graph which has plagued my research through multiple attempts to fix, is the artifact at higher wavelengths. It should just level off to a constant value like the InP does, however after peaking at around 18%T, it starts getting dimmer again. I tried doubling the thickness of the silicon by using two samples, as well as making sure the light is coupled into the fiber as well as possible after the sample is moved in. I did this by using a device that allows me to move the end of the fiber 1/100th of a mm at a time in any direction, to no avail. This is the best data I have for Si so that is what I will show.

For the InP we see a very curious structure. This is caused by the thin layer of InGaAs on the InP. After the very sharp rise at around 970nm, the InP is transparent, but the InGaAs is not. If the InGaAs had been thick enough, we would not see any signal until the InGaAs's band gap at around 1400nm, where it spikes up to its final value. Note that both the transitions are very abrupt, confirming the direct band gap nature of Inp and InGaAs. There seem to be two regions between

1000nm and 1400nm, one is a steady area where I would say that the InGaAs is simply only blocking some of the light because it's so thin. Then there is a very curious bump between 1250 and 1400nm, which could be due to a number of things and is beyond the scope of my research, but is interesting nonetheless.

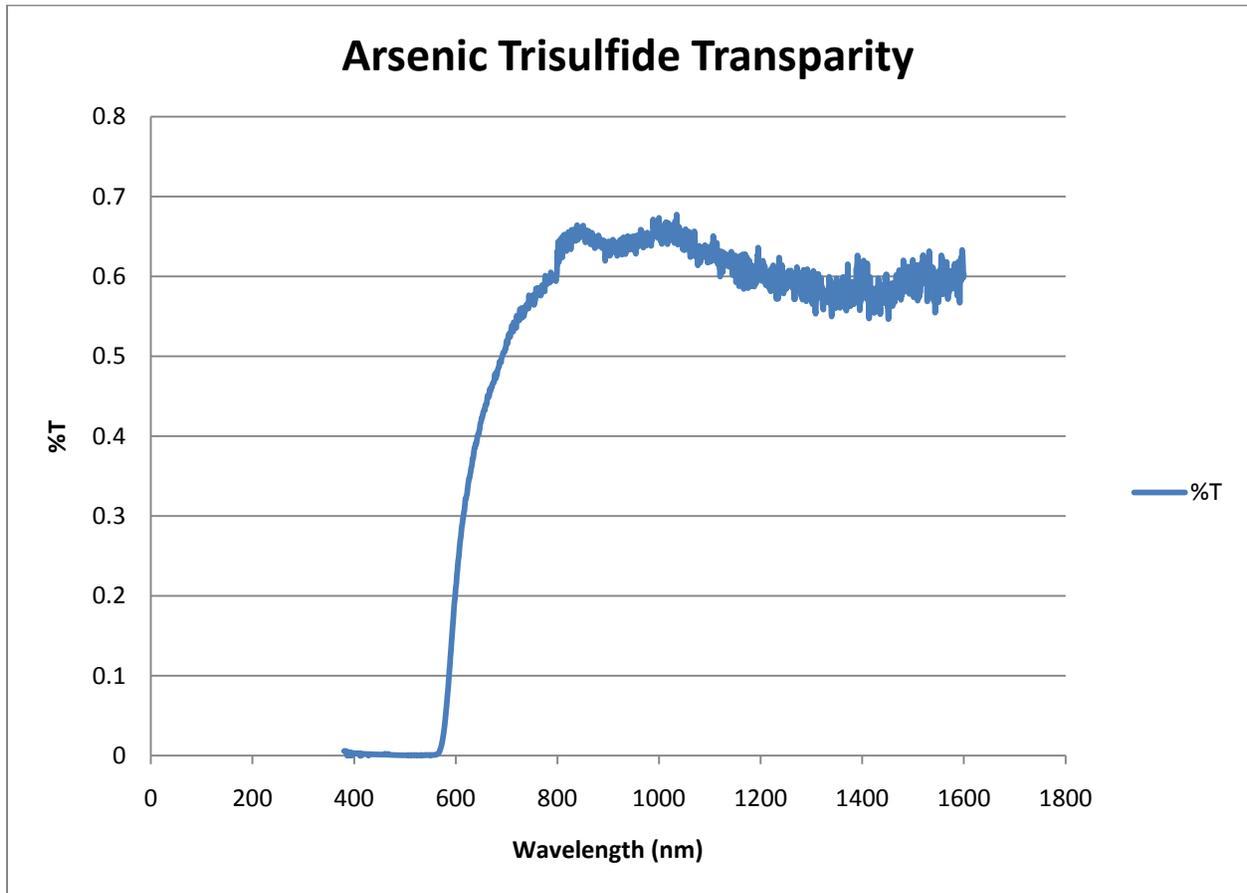


Figure 35: %T for As_2S_3 .

For the As_2S_3 , I had to take measurements with both the OSA and visible spectrometers, because the band gap is over a wide region between 600nm to around 850nm. The compound plot is shown in figure 35. The slight disconnect seen around 800nm is where the data was spliced together. This was the point where the two sets of data most closely matches, and is also where both sets of data were starting to get more noisy.

One thing to do is to calculate the index of refraction of each material using the %T of light in the transparency region. My first step was to make a graph that shows how much light of transmitted through the two surfaces of a sample (with no attenuation) due to its index of refraction. I have to be careful because there are two surfaces, and some of the light that makes it through the first surface will be reflected by the second surface, reflected again by the first surface, and then make it out of the sample, as shown in figure 36.

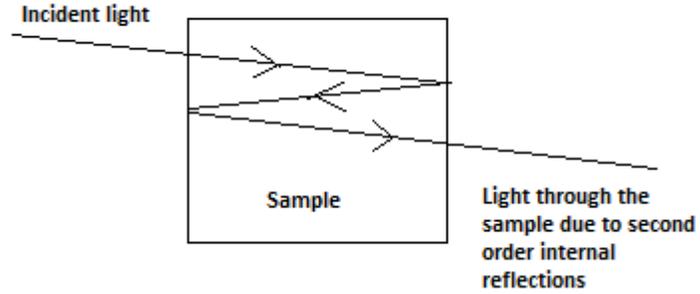


Figure 36: Second order reflections due to index of refraction.

The idea can be carried on to third order, fourth order, etc.

The governing equation for this work is:

$$R = \left(\frac{1 - n}{1 + n} \right)^2$$

Where R is the fraction of light reflected and n is the material's index of refraction (note that this equation assumes the material is in contact with air, with index of refraction = 1). So the amount of light that makes it through the first surface of the light T is:

$$T = 1 - R$$

The amount of light that makes it through the second surface then T_2 is:

$$T_2 = T(1 - R)$$

The variation of T_2 with index n is shown in figure 37.

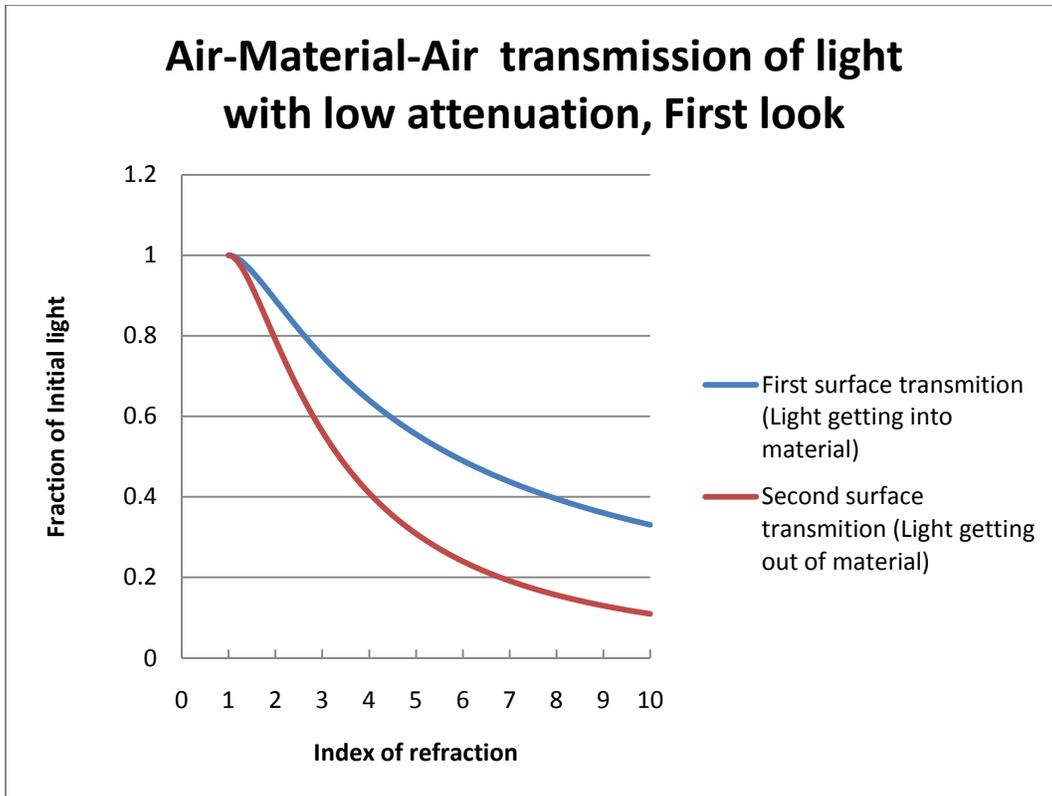


Figure 37: Transmission of light through first and second surfaces of a material in air.

The top line in figure 37 shows how much light gets through the first surface, into the material. The bottom line shows the second surface transmission (SST). The difference of these two lines is therefore the fraction of light that is reflected from the second surface, back into the sample. This is a very non-ignorable amount of light, especially at higher indices of refraction. So second order effects must be taken into account. There is light that will again be reflected from the first surface into the sample, and again meet the second surface. The light that gets through this time is:

$$SST_2 = (T_2 - T)(1 - R)^2$$

With the 1-R term being squared because the light is interacting with two surfaces.

This idea can be continued with:

$$SST_3 = (SST_2)(1 - R)^2$$

etc. in this recursive way.

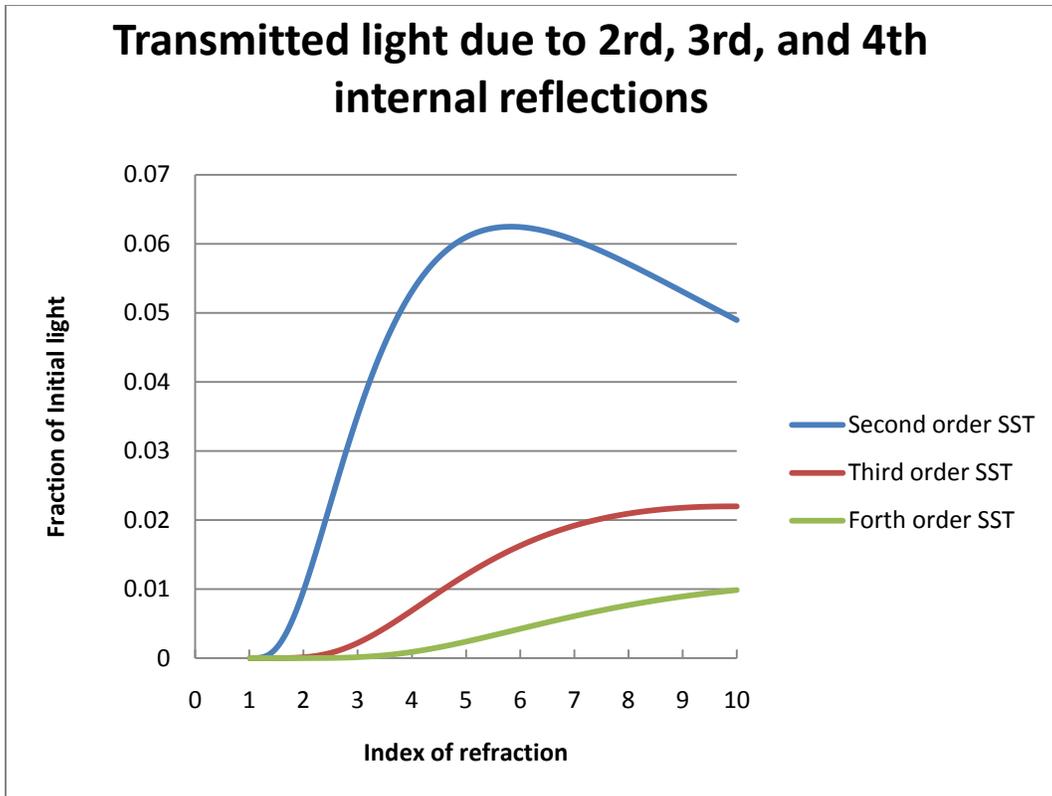


Figure 38: Second, third, and fourth order SST.

The graph in figure 38 shows the fraction of light getting through the second surface for the second, third, and fourth times the light is hitting it. For example for the bottom line, that light has gone through the first surface, then reflected off the second surface and first surface 3 consecutive times each, to finally make it out of the material on the fourth time. As long as the index of refraction isn't very high, after the second time the rest are negligible.

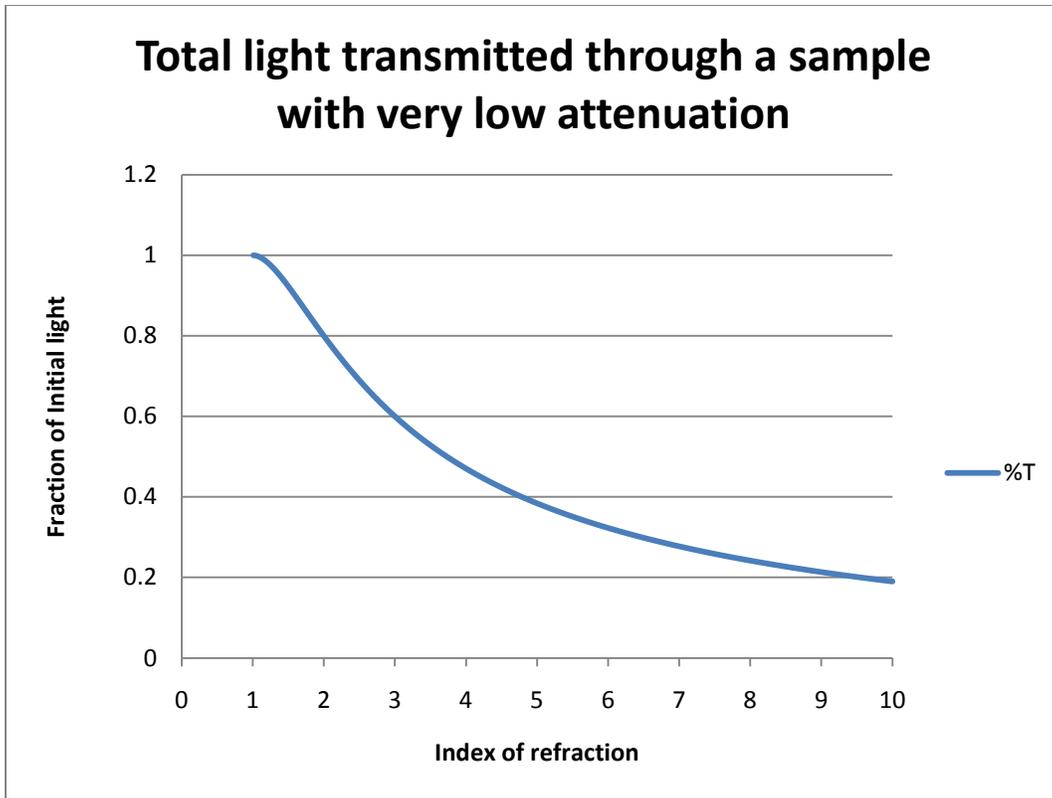


Figure 39: Total light transmitted through a sample.

On this final graph, figure 39, I show the amount of light that is finally transmitted through the material. I have added in each of the high order effects that I calculated, after deciding that the fourth order effect was small enough not to warrant going any further. From this graph I can check to see what index of refraction the materials have.

Material	% of transmitted light in constant region	Measured index of refraction	Actual index of refraction
Si	0.18 (peak)	10	3.42
InP	0.42	4.5	3.1
AsSo3	0.6	3	2.5

As you can see, my measured values are much higher than the known values, however measured these values are consistent for me through multiple measurements for each sample. The measured values remain consistent even with moving the fiber with an x,y,z fine tuner with a photo detector to be certain that for each measurement both with sample in and sample out that I am at the peak intensity point of the focused light. There is an unknown effect that is throwing all of the data off. Somehow there is less light getting into the fiber than is expected.

The last thing to determine is the absorption coefficient for these different materials as a function of wavelength. I did this using:

$$T = e^{-\alpha L}(1 - R)^2$$

Where T is the fraction of transmitted light, $(1 - R)^2$ is the factor of light that doesn't get to the fiber due to reflections, and $e^{-\alpha L}$ is Beer's law: the amount of light that doesn't get to the fiber due to absorption, with α being the absorption coefficient and L being the thickness of the material.

Solving this for α :

$$\alpha = -\frac{1}{L} * \ln \frac{T}{(1 - R)^2}$$

Where the value of T, shown earlier in figures 34 and 35, is used. These are plotted on a semi-log graph, so the noise looks much worse at the bottom of the graph, just because of the way it is structured.

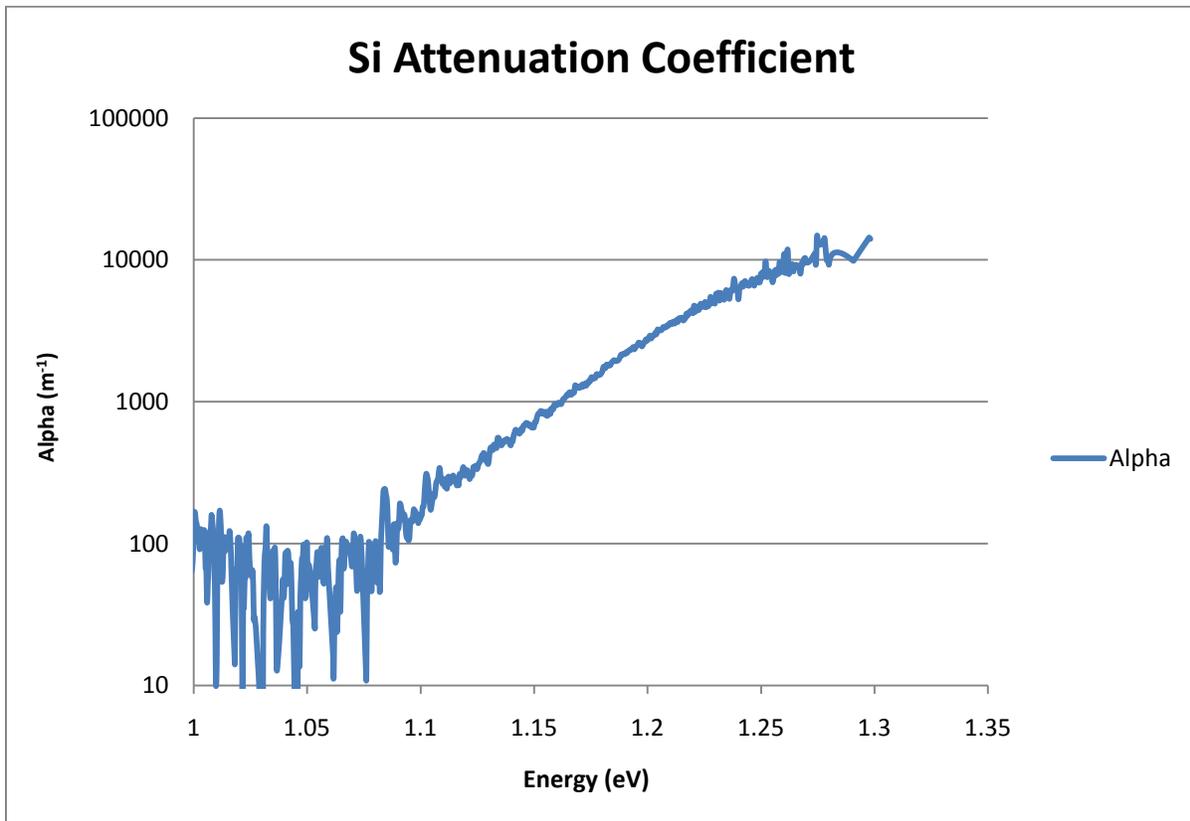


Figure 40: Attenuation coefficient for silicon.

For the indirect bandgap silicon (figure 40) we see the attenuation coefficient rises much more gradually than the direct bandgap for InP (figure 41). The data for Si showed a rising pattern below 1 eV which has been omitted as it is clearly not from attenuation.

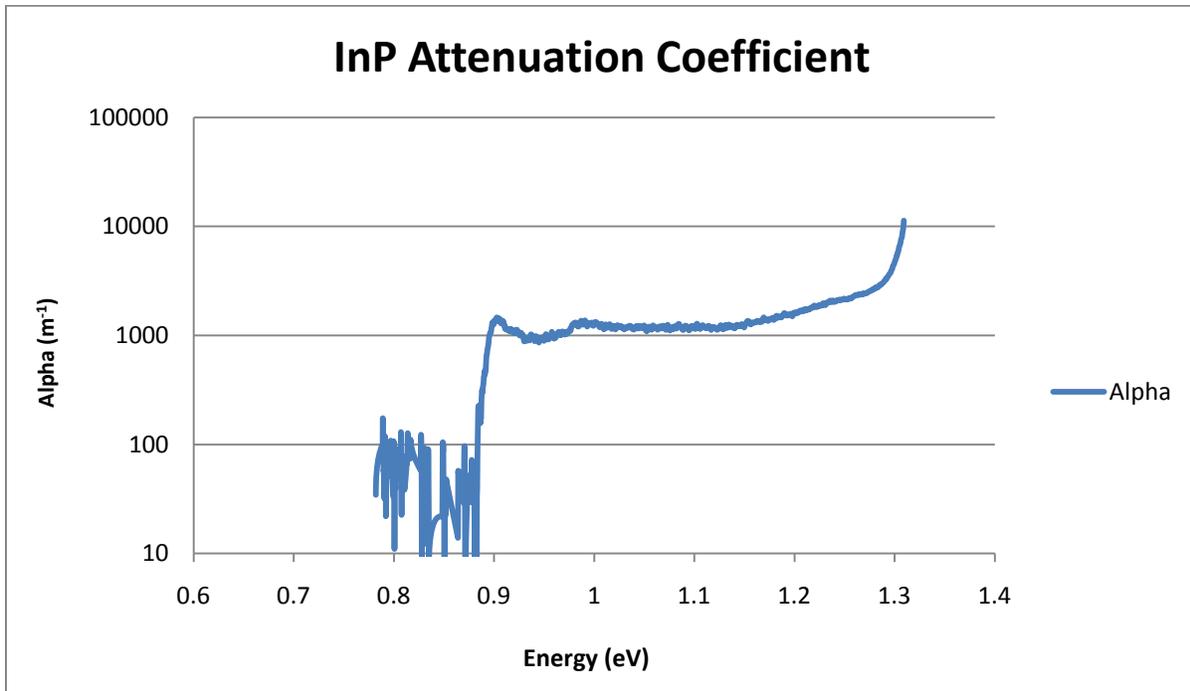


Figure 41: Attenuation coefficient for InP.

For the InP we see a sharp drop at around 1.3 eV, after which the InP is transparent. However there is also a strange leveling off and dip produced by the InGaAs layer, with a sharp drop around 0.9 eV to very low alpha. From this I can conclude that both InP and InGaAs are direct band gap materials.

InP Quantum Dots

I was also able to study four different sizes of quantum dots made from InP. These quantum dots fluoresce under laser light of 410nm. The four different types fluoresce green, red, orange, and yellow. I took a spectrum of each of these and noted the center wavelength of each peak. Using the equation for the energy of a photon I calculated the energy for photons at each wavelength.

$$E = h\nu = \frac{hc}{\lambda}$$

The known value for the bandgap of bulk InP is 1.344 electronvolts (eV), which is close to my measured value of 1.3. I then subtracted the known band gap energy from the photon energy.

Table 2: Peak wavelength from fluorescing quantum dots.

Vial	Peak (nm)	Photon energy (eV)	Energy difference from bulk gap (eV)
Red	625	1.98	0.64
Orange	594	2.09	0.74
Yellow	564	2.20	0.85
Green	541	2.29	0.95

This energy difference is a quantum effect, an effect known as quantum confinement. The particles are so small that they are forcing the "bandgap" of the InP higher. The smaller the particles are, the larger the effect is. This means that I can calculate the diameter of the quantum dots from the energy of the light they give off (note that this equation is for a thin planar layer, and doesn't exactly apply to spherical geometries):¹⁰

$$h\nu - E_g = \frac{h^2}{8m_e^*d^2} + \frac{h^2}{8m_h^*d^2}$$

E_g is the bandgap energy of bulk InP, 1.344 eV. h is Planck's constant. The other two terms, m_e^* and m_h^* are mass terms. They are the effective masses of electrons and holes in InP. For InP¹¹: $m_e^* = 0.077m_e$ and $m_h^* = 0.64m_e$, where m_e is standard electron mass. d is the diameter of the quantum dots. Rearranging this equation:

$$d = \sqrt{\frac{h^2}{8(h\nu - E_g)} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right)}$$

From this equation we can calculate the diameters of the quantum dots, shown in table 3 in angstroms (10^{-10} m).

Table 3: Diameters of quantum dots.

Vial	Diameter of Qdot (Å)
Red	27.6
Orange	25.6
Yellow	23.9
Green	22.7

As seen in tables 2 and 3, smaller quantum dots exhibit larger confinement effect, resulting in shorter wavelength light.

Arsenic Trisulfide and the Urbach Edge

The absorption coefficient vs. photon energy for the glassy semiconductor As_2S_3 is shown in figure 42.

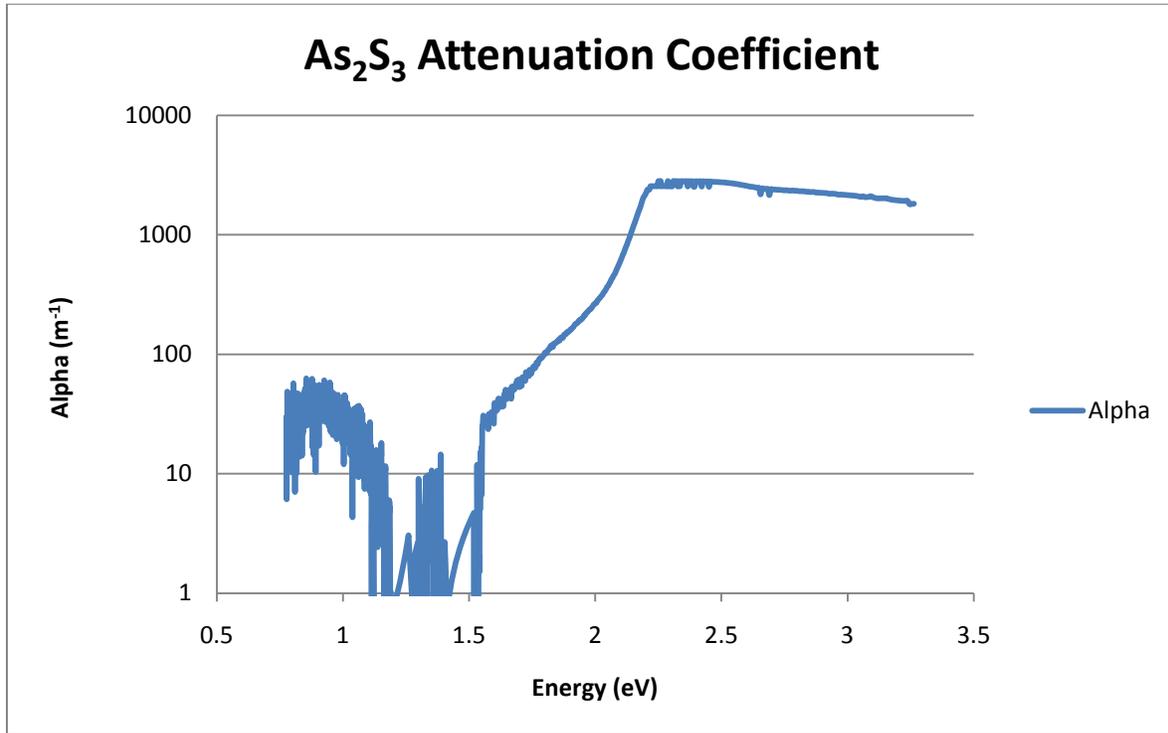


Figure 42: Attenuation coefficient for As_2S_3 .

For the As_2S_3 we have an artifact below 1.2 eV where the graph raises slightly. This is clearly not due to attenuation. The interesting region is the band gap, which is between 1.5 eV and 2.2 eV. It appears it can be broken into two different parts, both of which look like relatively straight lines on our semi-log graph. This means they can be fitted to an exponential function.

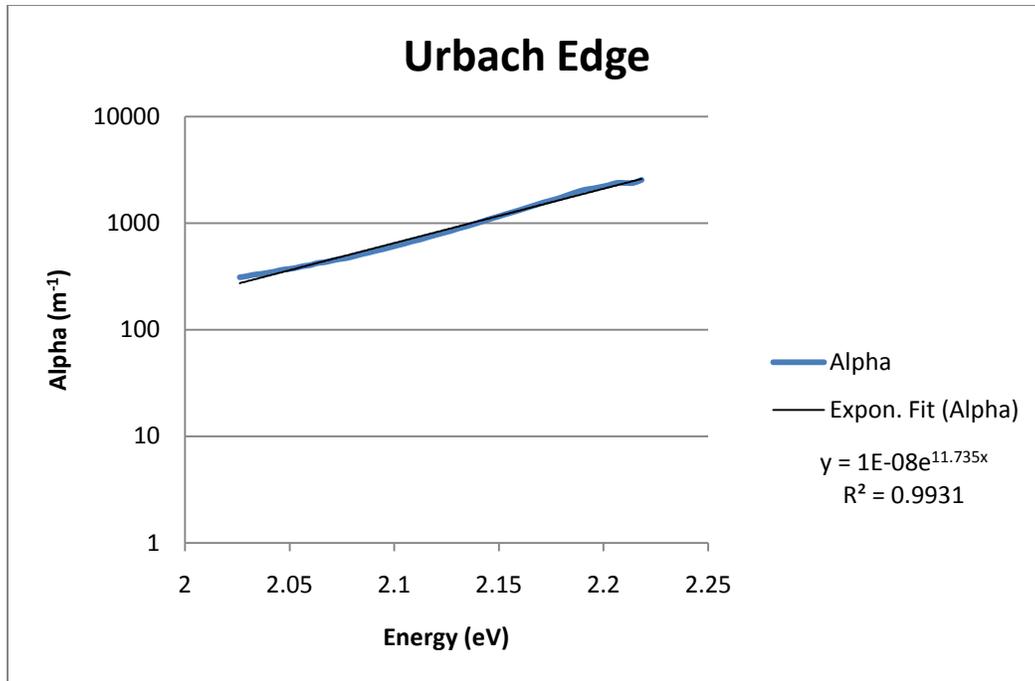


Figure 43: The Urbach edge in As_2S_3 .

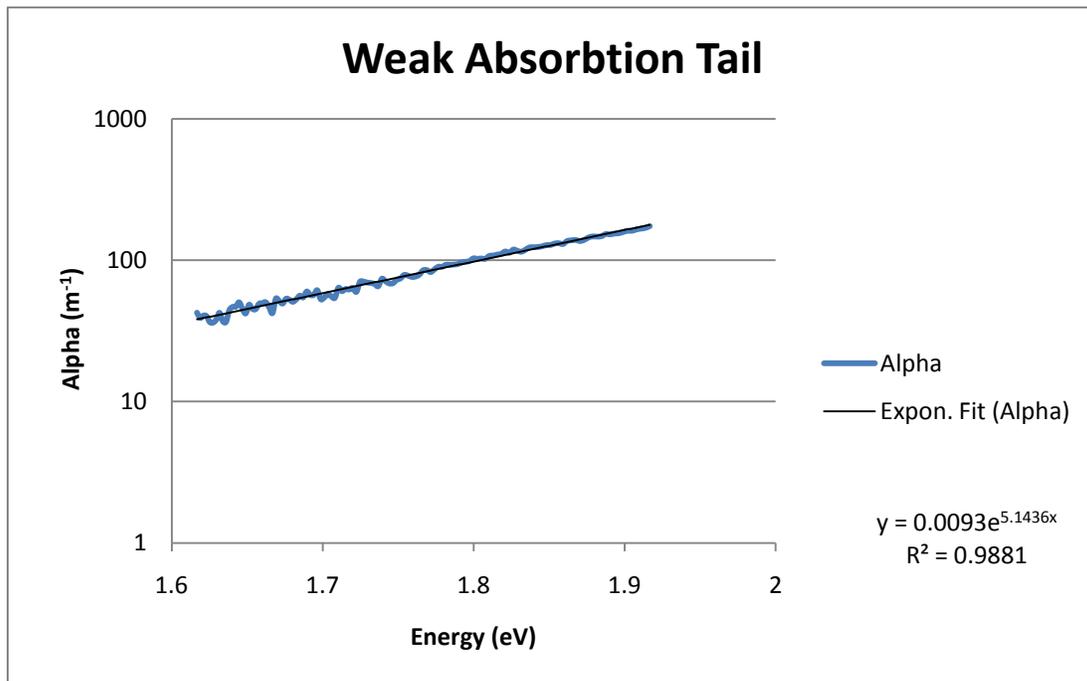


Figure 44: The weak absorption tail in As_2S_3 .

These two parts are called the Urbach edge, and the weak absorption tail.¹² As you can see in these two regions the value of alpha fits exponential functions very well. This is very different from both the indirect and direct band gap materials which lack this type of structure in the transition

reign. The weak absorption edge is only seen in amorphous (glass) semiconductors. The Urbach edge is seen in crystalline semiconductors as well, for example silicon (figure 45)

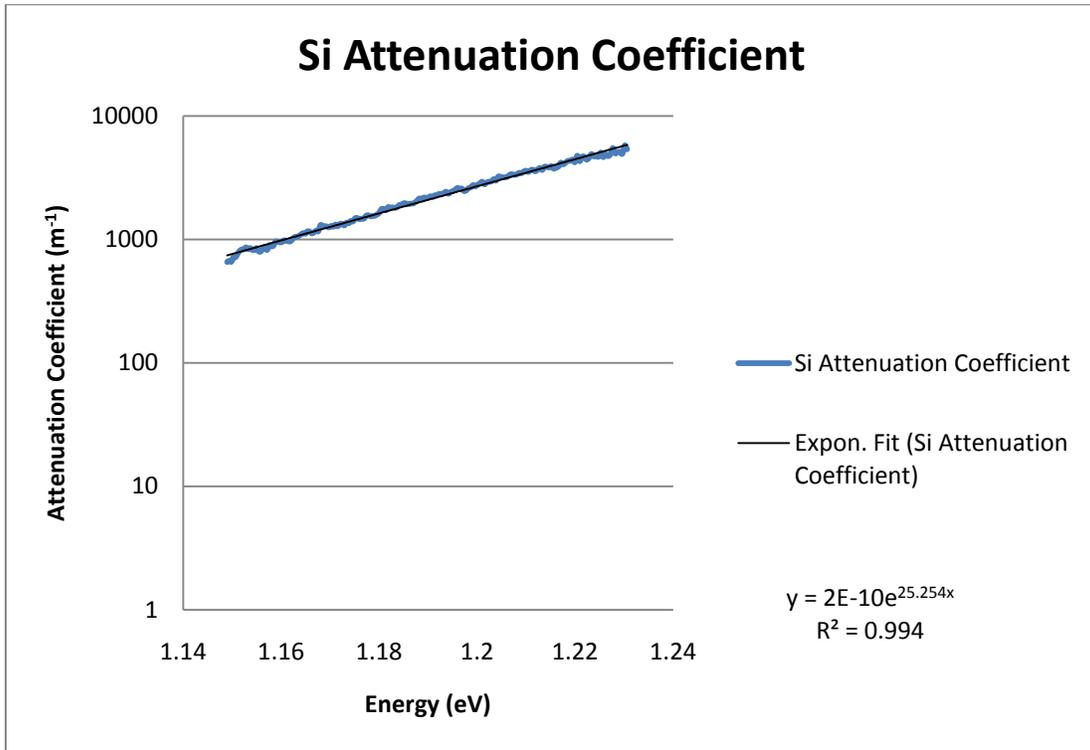


Figure 45: Urbach edge in Si

The silicon also exhibits an area that is linear on a semi-log plot, that fits to an exponential function very well. The slope is much steeper than the Urbach edge of As₂S₃.

Conclusion

We have 4 completed lab modules that are ready for students to try them. I have no doubt there will be hitches that professor Quimby will need to work out as the students do these labs, but I feel that a strong foundation has been laid. The students in future PH2601 classes will have the option to learn how to take a spectrum and analyze it, as well as have the opportunity to learn about Planck's law (black body spectra), Beer's law (attenuation), fluorescence, absorbance, and energy levels. An idea for future work would be to work with my sample of silicon in much more detail and try to figure out what was causing the strange behavior of diminishing signal as wavelength increased after the bandgap.

Appendix A: Student Handout for Introduction to Spectroscopy lab.

Introduction to Spectroscopy

The purpose of this set of experiments is to give you an introduction to the process of spectroscopy. Along the way you will see firsthand the composition of light from many different familiar sources. Spectroscopy is the measurement of the intensity of light over different wavelengths, a power per wavelength interval. These wavelength intervals are small, ranging from 2nm to 0.2nm or smaller. The resulting graph from plotting all these wavelength intervals looks something like figure A1:

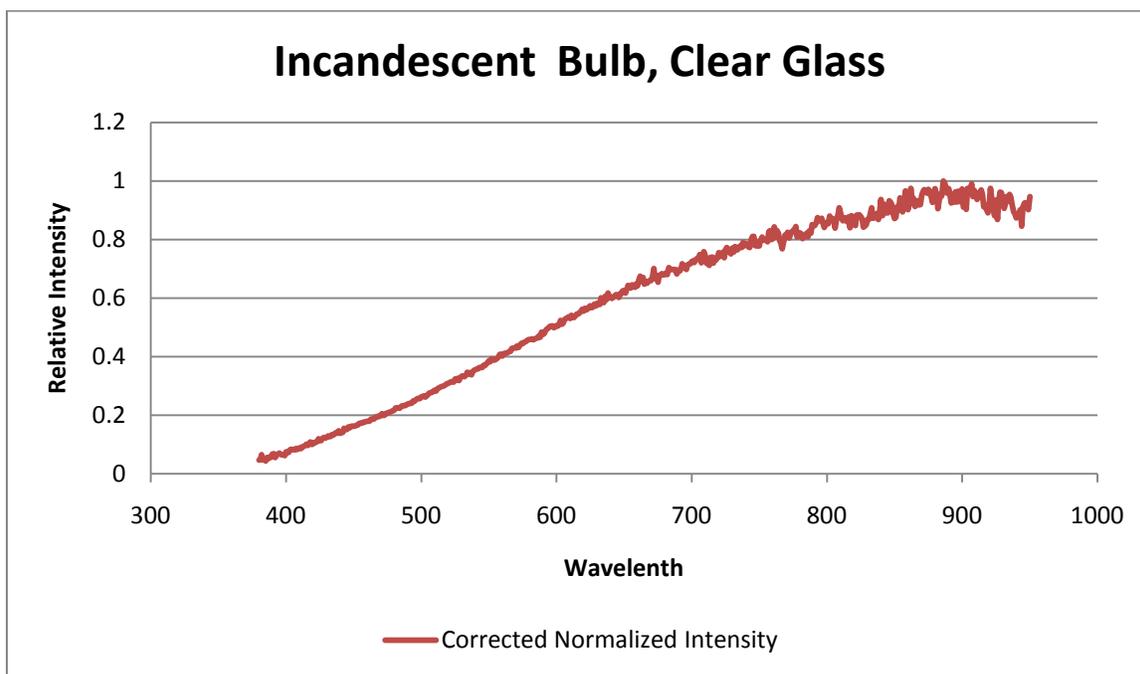


Figure A1: Spectrum from 380nm-950nm of an incandescent bulb, clear glass exterior.

This graph is the spectrum of an incandescent bulb, normalized to 1. It is important to note that this graph is only a relative intensity. For example the bulb is giving off twice as much power at 750nm than it is at 550nm. We cannot say anything about the actual amount of power, only the power's relative values.

A variety of different sources to take spectra of will be provided. You will be using two different spectrometers to look at their light. The first one is a small USB spectrometer which accepts light from an input fiber, scans across the different wavelengths, then outputs the data to a computer. The program that will be used to process this data is called Logger Pro. Start up Logger Pro now. There are a few settings in logger pro that need to be set before taking your first spectrum.

1) Under Experiment go to Change Units and click on Intensity. This sets the spectrometer to take the spectrum as described above.

2) Under Experiment, go to Setup Sensors, and click on the spectrometer. This should open up a window. Make sure the range of the spectrometer is set from 380nm to 950 nm. The other two settings are the integration time and samples to average. In simple terms, the integration time tells the spectrometer how long to look at the light and the samples to average tells the spectrometer how many times to look at the light. The bigger the integration time is, the higher the signal you will get. If the integration time is too big however the spectrometer will flood. Higher samples to average reduces noise and smooth's the data; coming at the cost of a long time to take the spectrum. As a rule of thumb keep the samples to average set at 5 or higher, unless you are looking at something very dim and need a very long integration time.

3) With the end cap still on the end of the input fiber, click collect. You will see that the signal isn't zero, even though there is no light getting into the fiber. This is called the background signal. You will need to subtract this background signal from all spectra you take with this spectrometer. Now click stop. You now need to export this data to a file so that you can later work with it in a spreadsheet program. Click File, go to Export As... and then select GIS format. Be sure to make a note in your lab notebook of the name of your file and what it is.

4) Now take the cap off the end of the fiber. **Be sure not to touch the end of the fiber with anything.** The first thing you will be taking a spectrum of is the fluorescent room lights. These lights have several characteristic peaks which you will need to become familiar with, as these peaks will show up any time some of the room light is getting into the fiber. Being able to recognize these fluorescent light peaks will be important later on when you only want light from other sources. Click collect and point the fiber directly at one of the room lights. Experiment with the Integration time. Try setting it to 5, 50, 500. As a general rule you want an integration time that will give you the biggest signal possible without causing the spectrometer to flood. Once you are happy with the spectrum, click stop and again export as a GIS format.

5) The next spectrum will be that of a tungsten filament bulb. Turn the bulb's power supply on and slowly increase the voltage on the power supply to 6. This bulb is very bright, try not to look at it directly, much the same way you do not want to look directly at the sun. This is going to be a reference measurement for your analysis of all other spectra later on. Again point the end of the fiber directly at the bulb. Change the integration time around, you should find that a relatively low integration time is needed, depending on how close the fiber is to the bulb. Click stop once you are satisfied with the spectrum and save as GIS format.

6) Repeat this process to take spectra of the other sources

The other spectrometer you will be using is called an Optical Spectrum Analyzer. This OSA is a finely tuned and powerful machine, do not let its use of a floppy drive fool you. Like the USB spectrometer the OSA also uses an input fiber. There are many settings and computations that can be done on the OSA, however you are only concerned with a few of them.

1) Under setup make sure the resolution is set to 2.0nm. Set the sensitivity to medium, and the average times to 3. This will ensure the OSA produces a spectrum in a short time, albeit somewhat noisy. Also in setup make sure to set the scan range to 700nm to 1600nm.

2) Your first sample will be the tungsten bulb. Turn it on if it isn't already, and position it in front of the input fiber. Push Sweep and select single. The OSA should make a humming sound and produce a spectrum. You may or may not be able to see the spectrum on the OSA's current settings. If you cannot see it well go into Level and change the top value up or down until the spectrum can be viewed nicely. The intensity of different sources you will be looking at will vary greatly, so you may need to change the Level often.

3) To save the spectrum insert a black floppy and push the floppy button. Select "Trace RD\WRT". In the next screen make sure the box that says BIN/TXT has TXT selected, and push execute.

4) Repeat steps 2 and 3 for all infrared sources.

Analysis

The first step when working with any data from the visible spectrometer is background subtraction. Simply subtract the background signal (the spectrum you took with the cap on the input fiber) from all data. The other thing that needs to be done is a calibration correction. To do this you need to come up with a correction function. The spectrum you took of the tungsten bulb will be assumed to be a black body, and needs to be compared to a theoretical black body.

The following is Planck's Law, which states that the power that is given off by a black body as a function of wavelength is:

$$I(\lambda, T) = \frac{2\pi hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda kT}} - 1}$$

Where λ is the frequency of interest, T is the absolute temperature of the source, c is the speed of light, h is Planck's constant, and k is Boltzmann's constant. The temperature T can be assumed to be 2900K. The first time you plot this you will notice that the scale is very different from your measured black body spectrum. Remember that the data you have taken is only a relative intensity.

Scale the theoretical black body spectrum down to the same scale by dividing it by the theoretical black body spectrum's value at the wavelength that is the peak value of your measured spectrum. For example, suppose your tungsten bulb's spectrum has a maximum value at 580nm. To scale your theoretical black body spectrum you would divide each value by that 580nm value, such that the 580nm value is 1, the lower wavelengths are less than 1, and the higher wavelengths are more than one. Your two spectra should look something like figure A2:

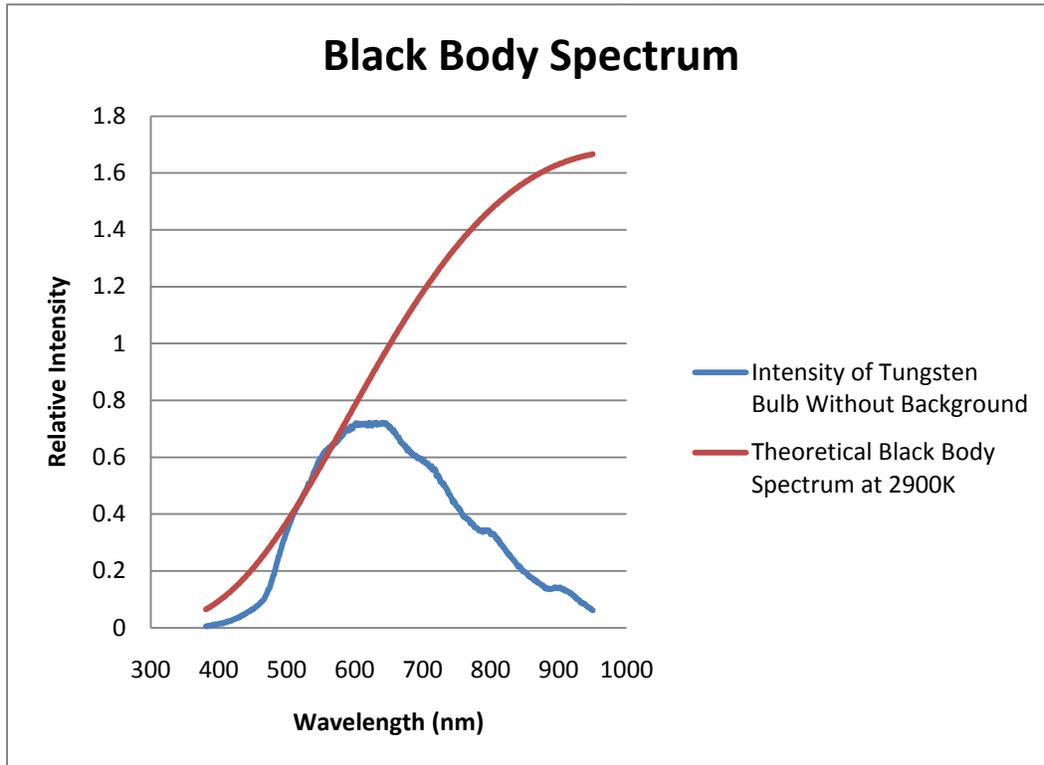


Figure A2: Comparison of measured black body spectrum to theoretical black body spectrum.

The final step is to divide your theoretical black body spectrum by the measured spectrum, producing a correction function. This correction function needs to be multiplied by all data taken by the visible spectrometer, effectively calibrating it.

Once you have the correction function, graph the rest of your data by first subtracting the background signal then multiplying it by the correction function. Be sure to normalize all graphs. To do this divide every value by the set's maximum. This makes the maximum of the graph 1 and scales everything else. Remark on anything interesting and compare similar spectra.

The OSA, in contrast to the visible spectrometer, is already calibrated and has no background signal that is indistinguishable from noise. Simply normalize the spectra and graph. You may need to truncate some spectra if they are too noisy below 700nm or 800nm in order to see detail above those values (i.e. if you have a noise spike that is 10's of times higher than your

meaningful data, get rid of it!). The OSA tends to be very noisy towards the lower end of its detection range.

Appendix B: Student handout for The Attenuation Coefficient of Water lab.

The Attenuation Coefficient of Water

For this experiment you will be measuring the attenuation coefficient of water and verifying Beer's law. Beer's law states:

$$P_{out} = P_{in}e^{-\alpha L}$$

P_{in} is the power of a source of light before that light passes through a material. P_{out} is the power of a source of light after that light passes through a material. The two terms in the exponential are L , the length of the material, and the attenuation coefficient α , which is an intrinsic property of the material. The material you will be working with is several different types of water. By knowing P_{in} and measuring P_{out} while varying L you will be able to calculate the attenuation coefficient.

The setup is as follows in figure B1:

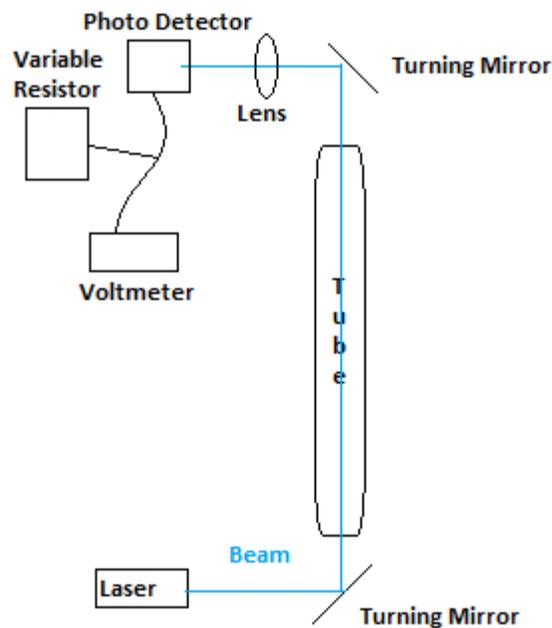


Figure B1: Setup for this experiment

The basic idea is to send a laser through a tube in which water can be placed, with the laser ending up on a photo detector. To accomplish this you will use two turning mirrors with the laser pointing at the bottom one, turning the laser up through the tube. Then the top mirror turns the beam towards the photo detector, connected to a voltmeter and variable resistor in parallel. The purpose of these is to give a numerical value to the amount of light getting through the tube. The setup is

very sensitive to vibrations; for example someone walking in the hallway will make the reading on the voltmeter change rapidly. The lens helps reduce the movement of the beam on the detector caused by vibrations that deviate the beam.

The value of the variable resistor effects the reading on the voltmeter. The higher the resistance the larger the signal. To ensure the operation of the photodetector in the linear regime, make sure the voltage is not more than about 50 mV. In the linear regime, doubling the resistance will double the voltage.

The types of water you will be experimenting with are: tap water, fountain water, distilled water, as well as several concentrations of dyed tap water.

1) Begin by putting a small amount of tap water in the tube before lining everything up. This is important because of the concave surface that forms on top of the water. If the tube is lined up dry it will be off-alignment after the first water is poured in.

2) With everything lined up flip the variable resistor to 10 ohms. Write down the reading on the voltmeter. This is your P_{in} .

3) Add 3cm of tap water to the tube by **carefully** dribbling the water down the side of the tube. Your goal is to disturb the water as little as possible. Lots of bubbles form in water when it is agitated, and these bubbles will scatter the laser light. The scattering effect of these bubbles has the capacity to overwhelm the attenuation coefficient you are trying to measure.

4) Let the water settle for several seconds to one minute. Once the voltmeter is reading a fairly steady number (steady to at least 0.1 mV) take note of the voltage.

5) If the reading on the voltmeter drops below 2 mV, double the current resistance. The reading on the voltmeter should double. Your goal is to keep the voltmeter above 2 mV.

6) Repeat steps 3-5 until you reach a total length of 30cm. This will give you 11 data points including the "0" value with only a small amount of water.

7) Repeat measurements for different kinds of water.

Analysis

One important thing to realize when you're entering your data is the resistance value for each of your voltage values. You need to convert all your voltages that were not measured at 10 ohms into an effective voltage at 10 ohms. To do this simply divide the higher resistance values by

the factor that it is higher than 10. For example a value taken at 20 ohms will need to be divided by 2, 40 ohm values divided by 4, etc. Below is a sample table for this process:

L (cm)	R(ohm)	V(mV) Measured	V(mV) Effective
0	10	8.4	8.4
3	10	4.5	4.5
6	20	6.5	$6.5/2 = 3.25$
9	40	7.6	$7.6/4 = 1.9$

Figure B2: Sample data for showing how to incorporate the resistor value.

So for these made-up values the data you would work with would be 8.4, 4.5, 3.25, and 1.9. You might ask yourself why go through this trouble when you could just measure the 1.9 and 3.25 values at 10 ohms? The reason is that the noise begins to overwhelm the signal below 2 mV. The resistor is a way to combat this.

For each type of water you have a P_{in} and values for P_{out} for different L. From here it is an exercise in data manipulation. Construct semi-log graphs for each water source and fit an exponential function to each. Remark on the different attenuation coefficients. It may also be useful to make a graph of α vs. number of drops/L of dye.

Appendix C: Student handout for Absorption and Emission of Impurity Ions in Glass lab.

Absorption and Emission of Impurity Ions in Glass

The two samples you will be working with in this experiment are rare earth ions doped in glass, Holmium and Erbium. In contrast to the broad spectral absorption and emission typically observed in solid materials, the Ho and Er atoms have rather discrete energy levels, similar to isolated atoms. Transitions are possible between these energy levels using a photon emitted or absorbed in the process. This is shown in figure C1.

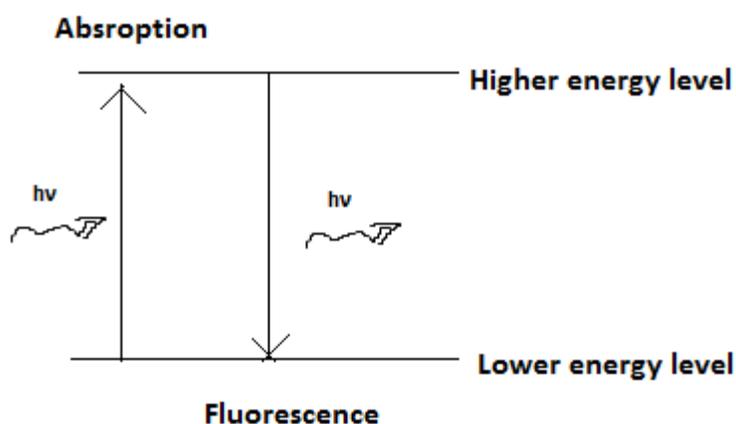


Figure C1: Simple diagram showing absorption and emission of a photon.

These two processes are called absorption and fluorescence. A photon has an energy $h\nu$, Planck's constant times the frequency of the photon. If this energy matches the difference in energy between an atom's ground state and one of its excited states the process of absorption may occur. The atom will absorb the photon's energy and jump to the corresponding excited state. During the atom's decay back to the ground state, some of the energy levels can have a radiative decay. This is called fluorescence and gives off a photon of light with an energy equal to the difference between the energies of the two levels.

Your goal is to construct an energy level diagram of the rare earth ions Ho and Er by taking spectra and seeing at which wavelengths they absorb and fluoresce.

Absorption Measurements

The measurements for absorption will be using the sample-in/sample-out method.

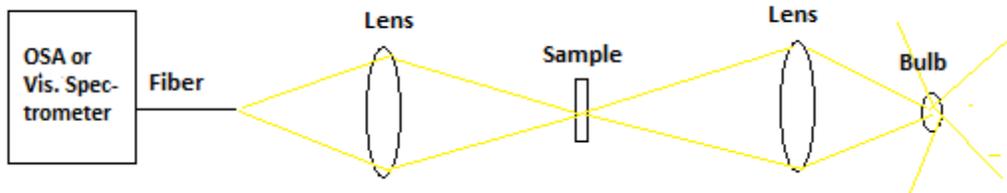


Figure C2: Setup for absorption measurements.

- 1) Begin with the Holmium sample. Focus the light from a bulb that gives off black body radiation onto the sample, using a lens. The spot that is being illuminated on the sample is then focused onto the input fiber with a second lens.
- 2) Take the spectrum using the visible spectrometer. A copy of the handout for the introduction to spectroscopy lab is available for reminders on how to do this
- 3) Now remove the sample and take a spectrum again. Do not move the lenses.
- 4) Repeat for the Erbium.
- 5) Take the same three measurements (no sample, Ho, and Er) using the OSA. It is important that you use the High 3 sensitivity when using the OSA for these samples.
- 6) The OSA will take quite some time to produce the spectrum when running on High 3. Take this time to start the analysis of your spectra from the visible spectrometer.

The other measurement you need to take is a fluorescence measurement.

Fluorescence Measurements

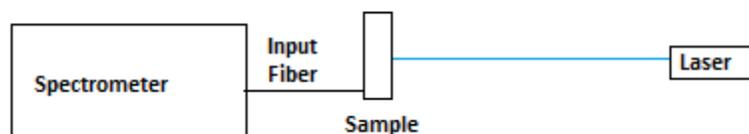


Figure C3: Setup for the fluorescence measurements.

The 410nm laser pumps the atoms into an excited state. As they decay back to the ground state some of the transitions result in a radiative decay. The signal for this emission is relatively weak, so it is important to line the fiber up as straight as possible on the brightest part of the sample. This may also involve rotating the sample so that the laser strikes at different angles to try to get the brightest fluorescence. You will only be looking at the fluorescence with the visible spectrometer, so it may be a good idea to take these fluorescence measurements with one sample while making absorption measurements on the other sample using the OSA.

Analysis

Graph the absorbance by dividing sample out spectrum by the sample in spectrum. Be sure you remember to first subtract the background spectrum and multiply both graphs by your correction function before dividing them if (and only if) they came from the visible spectrometer. This will give you a fraction of light transmitted spectrum. There will be several clear dips on these graphs. Take note of the center wavelength for each of the dips.

Graph the fluorescence simply by subtracting the background and multiplying it by your correction function. Take note of which wavelengths the peaks occur at.

Now you can use the equation which gives the energy of a photon:

$$E = h\nu = \frac{hc}{\lambda}$$

to find out the energy levels, with λ being the wavelengths you took note of. Using SI units for h (Planck's constant), c (the speed of light) and λ , the energies are currently in Joules. It is customary in spectroscopy to use a unit of energy called inverse centimeters.

$$8065 \text{ cm}^{-1} = 1 \text{ eV} = 1.602 * 10^{-19} \text{ J}$$

After conversion your energies should come out in the 1000's of inverse centimeters.

The energies from your absorbance measurements are always from the ground level up to an excited level. However the energies from your fluorescence are only an energy difference between two levels, the bottom of which may or may not be the ground level.

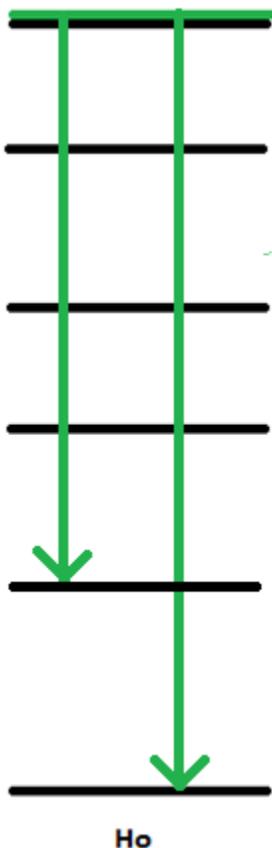


Figure C4: Sample energy level diagram.

Shown in figure C4 is an energy level diagram for holmium the lowest levels of Ho^{3+} , without the energy values of the levels. Two fluorescence energies match up with the energy difference between the top level and the two bottom levels. The black lines include the energy levels that you calculated from the absorbance measurements. Your final goal is to make one of these diagrams for both samples, with the levels labeled with their energy in units of cm^{-1} (taken with respect to the ground state, which can be taken as 0).

Appendix D: Student handout for the Absorption and Emission in Semiconductors lab.

Absorption and Emission in Semiconductors

For this experiment you will be given three pieces of semiconducting material, silicone (Si), indium phosphide (InP), and arsenic trisulfide (As_2S_3). Your task is going to be to characterize the bandgaps of these materials as either direct or indirect.

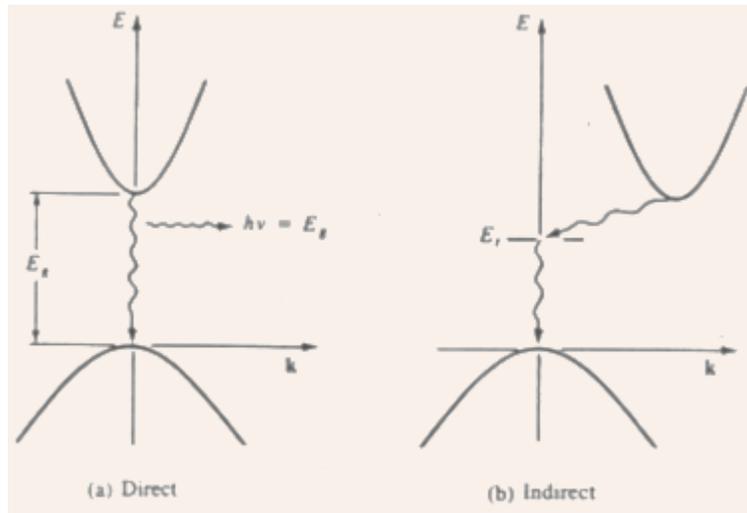


Figure D1: Comparison of direct and indirect bandgaps of semiconductors in K space.⁹

Figure D1 shows the bandgap structure for two different types of semiconductors. The top band is the empty conduction band, and the bottom one is the filled valence band. A photon has an energy $h\nu$, Planck's constant times the frequency of the photon. If this energy matches or exceeds the difference in energy between these two bands in a direct semiconductor, the light will be blocked as the semiconductor is absorbing that light. This change is very abrupt. Any photon below the cutoff energy will pass through, and any photon above the cutoff energy will be blocked. For the indirect bandgap semiconductor, the lowest energy in the conduction band and the highest energy in the valence band are at different k space values (they have different momentum). Photons have very little momentum, and in order to conserve momentum, a phonon (lattice vibration) is involved in this type of transition. This leads to a more gradual change from transparency to blocking light

You will be taking absorption measurements to look at the band gap structure of these materials. Measurements for absorption will be using the sample-in/sample-out method.

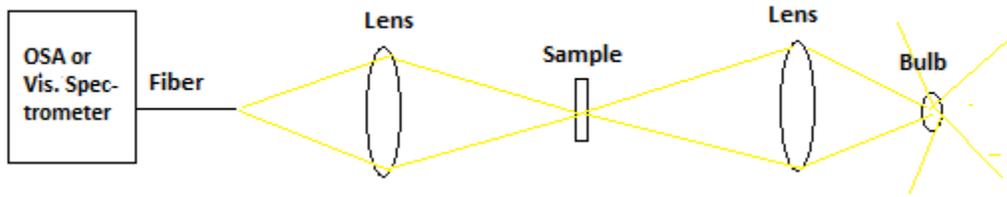


Figure D2: Setup for absorption measurements.

- 1) Using the OSA, Begin with the As_2S_3 . Focus the light from a bulb giving off black body radiation onto the sample with a lens. Then image the focused spot on the sample onto the input fiber using a second lens.
- 2) Take the spectrum on High 3 sensitivity. A copy of the handout for the introduction to spectroscopy lab is available for reminders on how to do this. This will take several minutes.
- 3) Now remove the As_2S_3 and take a spectrum again. Do not move the lenses.
- 4) Repeat for the Si and InP samples. Note that because these samples block all visible light you will need to make sure everything is lined up before you put the sample in.
- 5) While absorption data for the Si and/or InP are being acquired by the OSA, take both sample in and sample out spectra for the As_2S_3 sample using the visible spectrometer. This is the only sample which lets some visible light through, so you do not need to do this step for InP nor Si.
- 6) Before completing the lab make sure to carefully measure the thickness of each sample. This will be important for your analysis.
- 7) There is also a side project to do while you are waiting for the OSA to scan. You should also have a set of quantum dots. Shine a laser into the bottom of the vials and move the end of the input fiber for the visible spectrometer up to the side of the vial. Take a spectrum for the four different colors. In the analysis section you will see how to calculate the size of the quantum dots from these spectra.
- 8) If you are done with the quantum dots, and you are still waiting for the OSA to run, you may find this time useful to start your analysis with the next section on index of refraction.

Index of Refraction Exercise

When light enters a material from air, the amount of light that is reflected, R , is

$$R = \left(\frac{1 - n}{1 + n} \right)^2$$

where n is the materials index of refraction. This is an intrinsic property of the material. It follows then that the amount of light transmitted, T , is

$$T = 1 - R$$

This same reflection also happens when light is exiting a material. Some of the light is reflected from the interface back into the material. Some of that light is then reflected yet again and meets the second interface again. This process theoretically continues ad infinum. Figure D3 shows the resulting light beam that exits the sample after reflecting internally twice, let's call that T_2 .

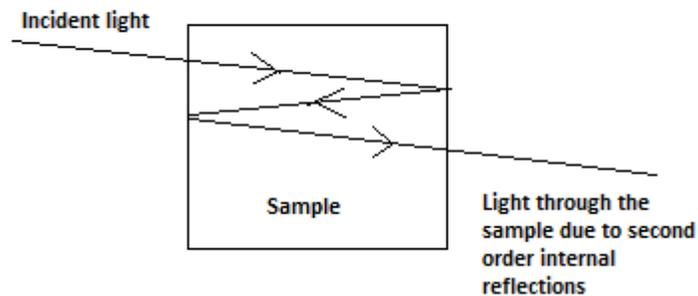


Figure D3: Second order reflections due to index of refraction.

Each time the light is reflected twice to again make it back to the exit interface the amount of light is drastically reduced. For low indices of refraction only the first few reflections matter. Work with the equations for R and T to come up with an expression and graph for the total light that is transmitted through the sample. You do not have to go beyond the fourth time light hits the exit interface.

Analysis

Start off by making a graph of the fraction of transmitted light through each sample. Divide each sample's spectrum by the spectrum you took with no sample in place. You will need to splice the two spectra for As_2S_3 together. From here there are two things you can calculate about the sample. The first is its index of refraction.

There should be a relatively flat region for each of the materials after a certain wavelength. Take the value of this region, and find the corresponding index of refraction on your graph. Compare this value with the known values and comment.

The other part of analysis you can do is to come up with an attenuation coefficient for each semiconductor as a function of wavelength. Beer's law states the power of light exiting a material is the power of light entering a material multiplied by an exponential.

$$P_{out} = P_{in}e^{-\alpha L}$$

With the two values in the exponential being L , the length or thickness of the material, and α the material's attenuation coefficient. $\frac{P_{out}}{P_{in}}$ in the context of your experiment is the fraction of transmitted light that you have graphed. This also needs to be multiplied by a factor of $(1 - R)^2$ to account for the reflections from the index of refraction of the material.

$$T = e^{-\alpha L}(1 - R)^2$$

Note: Please use the known value of each sample's index of refraction if your measured n is different.

With a bit of rearranging and spreadsheet work you can calculate the materials attenuation coefficient, knowing L , R , and T . Graph for each semiconductor on a semi-log plot (linear wavelength axis and logarithmic α axis) and comment on it's shape. For each material is it a direct or indirect bandgap? Why?

Hint 1: Look at the structure of the InP's attenuation coefficient. Is this what you would expect? Is this sample pure InP?

Hint 2: Take a close look at the transition region of the As_2S_3 . There should be a slight bend in it, with the regions to either side of the bend appearing linear on a semi-log plot. Make two separate

graphs for these linear regions and do an exponential fit. Available from the professor is a paper detailing this structure and exponential behavior.

Quantum Dots

Graph each spectrum for the different color quantum dots, remembering to subtract the background and multiply by your correction function. Find the center wavelength for each peak and make note of it. Using the equation for the energy of a photon to calculate each energy.

$$E = h\nu = \frac{hc}{\lambda}$$

The known value for the bandgap of bulk InP is 1.344 electronvolts (eV). An eV is a unit of energy that is commonly used when dealing with energies that atoms possess.

$$1 \text{ eV} = 1.602 * 10^{-19} \text{ J}$$

Put your energies into eV and you will see that each value is higher than 1.344. This means that the InP is giving off photons that are more energetic than its band gap. This is a quantum effect! Section 10 (p175-176) in professor Quimby's book has a good discussion of this effect for thin layered semiconductors. What you are seeing is an effect known as quantum confinement. The particles are so small that they are forcing the "bandgap" of the InP higher. The smaller the particles are, the larger the effect is. This means that you can calculate the diameter of the quantum dots from the energy of the light they give off!

$$\frac{hc}{\lambda} - E_g = \frac{h^2}{8m_e^*d^2} + \frac{h^2}{8m_h^*d^2}$$

E_g is the bandgap energy of bulk InP. Please use the known value of 1.344 eV if this differs from your measured value. h is Planck's constant. The other two terms, m_e^* and m_h^* are mass terms. They are the effective masses of electrons and holes in InP. $m_e^* = 0.077m_e$ and $m_h^* = 0.64m_e$, where m_e is standard free electron mass. d is the diameter of the quantum dots. Using this equation you should be able to calculate d and report the diameter of each color of quantum dot.

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