Lab 1: Refractive index and fluorescence of rare earth ions in borate glasses

Introduction

The optical properties of glasses are important in many wide ranging industrial as well as research applications, like windows, glass containers, camera lenses to lasers, waveguides and optical fibers for optical communications.

In this experiment we will prepare borate glasses by melt quench technique, measure refractive index by Brewster’s angle method and analyze fluorescence spectrum of samarium (rare earth) ion in these glasses. The spectrometer that you will be using to record fluorescence spectrum is a LEOI-101 Modular Multifunctional Grating Spectrometer.

A large variety of substances have disordered structures and the term “Non-crystalline solids” is employed generally to describe them. Although the atoms are close together as in crystals and liquids, the arrangement of atoms is not regular as in crystals but possess only the short range order of a liquid. These materials however, do not flow as liquids but retain their shape like crystals. An accurate definition of glass: “Glass is an inorganic product of fusion which cooled to a rigid condition without crystallization and exhibits glass transition temperature whose shear viscosity exceeds 10^{14.6} poise”.

The study of the interaction of electromagnetic radiation with glasses has proved to be of great significance especially in recent years, for the investigation of glass structure and the nature of the chemical bonds in glasses. For practical applications of glasses, the range of wavelengths studied is from 200 nm to 2400nm with the visible range lying between 400nm to 750 nm. All glasses that are good electrical insulators transmit radiation to some degree. Oxide glasses free from transition metal oxides, rare earth oxides, and certain other coloring agents are very transparent in the visible, near ultraviolet and near infra-red. Sulphide glasses and some other chalcogenide glasses are less transparent in the visible to significantly longer wavelengths in the infra-red.

The optical properties of rare earth ions and transition metal ions are decided by the structure of the host glass in which they are doped. These ions have absorption and fluorescence bands mainly in the visible and near IR regions and they are narrow for rare earth ions compared to those of transition metal ions. The absorption and fluorescence bands in rare earth ions are due to the electronic transitions that occur within 4f shell, which is well shielded by outer 5s and 5p shell. On the other hand, in transition metal ions the electronic transitions occur in the 3d shell which is the outermost shell. The strong/sharp absorption and fluorescence from rare earth doped glasses allow them to be used extensively as active media in optically pumped laser.
There are three main sections in this experiment
(1) Glass sample preparation - **50 points**
(2) Measurement of refractive index by Brewster’s Angle method -**75 points** *(This includes the questions given at the end of the manual)*
(3) Fluorescence of rare earth Sm$^{3+}$ (Samarium) ions in glasses -**75 points**

(1) **Glass sample preparation**

Each glass sample was weighed in a 30 gram batch. Strontium Bismuth borate glasses are prepared by taking appropriate amount of Bi$_2$O$_3$ of analar quality, H$_3$BO$_3$ of analytical grade, high purity Strontium carbonate and samarium oxide (Sm$_2$O$_3$).

**YOUR SAMPLE:**

i) xSrO : (69-x) B$_2$O$_3$: 30 Bi$_2$O$_3$: 1.0 Sm$_2$O$_3$ (x = 0) (Group 1)

ii) xSrO : (69-x) B$_2$O$_3$: 30 Bi$_2$O$_3$: 1.0 Sm$_2$O$_3$ (x = 5) (Group 2)

iii) xSrO : (69-x) B$_2$O$_3$: 30 Bi$_2$O$_3$: 1.0 Sm$_2$O$_3$ (x = 10) (Group 3)

iv) xSrO : (69-x) B$_2$O$_3$: 30 Bi$_2$O$_3$: 1.0 Sm$_2$O$_3$ (x = 15) (Group 4)

v) xSrO : (69-x) B$_2$O$_3$: 30 Bi$_2$O$_3$: 1.0 Sm$_2$O$_3$ (x = 20) (Group 5)

**YOU HAVE TO DO SAMPLE COMPOSITION CALCULATIONS FOR YOUR SAMPLE BY REFERRING THE EXAMPLE GIVEN BELOW. AFTER CHECKING WITH THE INSTRUCTOR YOU WILL BE ALLOWED TO MAKE THE GLASS SAMPLE.**

**Example:**

To prepare a typical 20 g sample of 69.5PbO : 30B$_2$O$_3$ : 0.5Er$_2$O$_3$, the following calculation was done. To find the necessary amount of each starting material, the molar mass was multiplied by the molar percentage and the stoichiometric constants of the reagents. The chemical reaction is given below.

\[
PbO + 2H_3BO_3 + Er_2O_3 \rightarrow PbO:B_2O_3:Er_2O_3 + 3H_2O
\]

- PbO: \(223.2g/mol \times 69.5mol = 15512.4g\)
- H$_3$BO$_3$: \(61.83g/mol \times 2 \times 30mol = 3709.8g\)
- Er$_2$O$_3$: \(382.56g/mol \times 0.5mol = 191.28g\)

Two moles of boric acid (H$_3$BO$_3$) gives one mole of B$_2$O$_3$. The calculated mass values are then added and then converted to a ratio for each material. This ratio was multiplied by 20 grams yielding the necessary amount of each reagent.
\[
Total = 15512.4 \text{ g} + 3709.8 \text{ g} + 191.28 \text{ g} = 19413.48 \text{ g}
\]
\[
PbO: \frac{15512.4 \text{ g}}{Total} \times 20 \text{ g} = 15.98106 \text{ g}
\]
\[
H_3BO_3: \frac{3709.8 \text{ g}}{Total} \times 20 \text{ g} = 3.82188 \text{ g}
\]
\[
Er_2O_3: \frac{191.28 \text{ g}}{Total} \times 20 \text{ g} = 0.19706 \text{ g}
\]

**Weighing:** After the amount of each reagent was calculated, they were carefully weighed out using an ACCULAB digital balance. The ACCULAB digital balance has a precision of 0.1 mg and was used only for sample preparation weighing.

**Melting:** Once measured, each batch was mixed thoroughly in an agate mortar and then transferred to a porcelain crucible. CARBOLITE CWF 1300, a laboratory chamber furnace is turned on. The CWF 1300 can reach a maximum temperature of 1300 °C and has fully programmable cycles. The furnace was programmed to increase the temperature inside the furnace to 300 °C for 30 minutes, and increased at 200 °C/hour. The temperature of the furnace is held at 500 °C, 700 °C, and 900 °C for 30 minutes during the ramp up cycle. Once the furnace reaches 950 °C it is held at that temperature. The crucible was then placed into the furnace at this temperature for 20 minutes.

Each crucible was then stirred via agitation twice and checked to see if it had been fully melted. The melt was then poured onto a heated brass plate and quenched by another brass plate placed on top of it. A brass washer is used to retain a circular shape and give a uniform thickness. This quenching technique brings the melt close to room temperature in a matter of seconds and causes thermal strains to be generated in the glass. Care must be taken when moving the samples otherwise they shatter into many pieces and become unusable.

**Annealing:** Once all of the samples have been quenched they are placed in an alumina boat and put into the annealing oven, a CARBOLITE MTF 12/38/250 Wire Wound Single Zone Tube Furnace. The MTF has a maximum temperature of 1100°C and is also fully programmable. The annealing oven is heated at 200 °C/hour to 350 °C (just below the glass transition temperature) and held there for three hours. The temperature is then slowly decreased at a rate of 60 °C/hour until the samples reach room temperature.

**Polishing:** The samples were flattened with an Inland SwapTop™ 8” Flat Lap Machine (Figure 5) using a diamond lap with diamond coolant. Once flattened, the diamond lap was replaced with a wool felt polishing pad. Care had to be taken while flattening and polishing to keep the sample uniform in thickness, and to not break the samples.
(2) Measurement of refractive index by Brewster’s Angle method

INTRODUCTION

In this experiment, light is partially polarized when reflected off a nonconducting surface and Brewster's angle is measured.

Light from a diode laser is reflected off the flat side of an acrylic semi-circular lens. The reflected light passes through a polarizer and is detected by a light sensor. The angle of reflection is measured by a Rotary Motion Sensor mounted on the Spectrophotometer table. The intensity of the reflected polarized light versus reflected angle is graphed to determine the angle at which the light intensity is a minimum. This is Brewster's Angle, which is used to calculate the refractive index of acrylic and a Glass sample.

EQUIPMENT: Brewster’s Angle accessory, Educational Spectrophotometer System, Diode Laser and DataStudio Software

THEORY

Fresnel’s Equations and Brewster’s angle

Fresnel's equations describe the reflection and transmission of electromagnetic waves at an interface. That is, they give the reflection and transmission coefficients for waves parallel and perpendicular to the plane of incidence. For a dielectric medium where Snell’s Law can be used to relate the incident and transmitted angles, Fresnel's Equations gives amplitudes of the reflected and transmitted electric field.

Figure 1: Reflection and transmission of light at an interface
Amplitudes of reflected and transmitted polarized light

For p-polarized light (electric vector parallel to the plane of incidence)

\[
\begin{align*}
    r_\| &= \frac{E_{\text{refl}}}{E_{\text{in}}} = \frac{n_r \cos \theta_i - n_i \cos \theta_i}{n_r \cos \theta_i + n_i \cos \theta_i} = \frac{\tan(\theta_i - \theta_r)}{\tan(\theta_i + \theta_r)} \\
    t_\| &= \frac{E_{\text{trans}}}{E_{\text{in}}} = \frac{2n_i \cos \theta_i}{n_r \cos \theta_i + n_i \cos \theta_i}
\end{align*}
\]

Equation 1

For s-polarized light (electric vector perpendicular to the plane of incidence)

\[
\begin{align*}
    r_\bot &= \frac{E_{\text{refl}}}{E_{\text{in}}} = \frac{n_r \cos \theta_i - n_i \cos \theta_i}{n_r \cos \theta_i + n_i \cos \theta_i} = -\frac{\sin(\theta_i - \theta_r)}{\sin(\theta_i + \theta_r)} \\
    t_\bot &= \frac{E_{\text{trans}}}{E_{\text{in}}} = \frac{2n_i \cos \theta_i}{n_r \cos \theta_i + n_i \cos \theta_i}
\end{align*}
\]

Equation 2

The reflectance (intensity of reflection coefficients) is the square of the amplitude reflection coefficient

\[
R = r^2
\]

(s-polarized) \(R_\bot = \frac{\sin^2(\theta_i - \theta_r)}{\sin^2(\theta_i + \theta_r)}\) \hspace{1cm} (p-polarized) \(R_\| = \frac{\tan^2(\theta_i - \theta_r)}{\tan^2(\theta_i + \theta_r)}\)

Equation 3

Figure 2: This is the plot of reflectance with the angle of incidence given in equation 3
When partially polarized light (s-polarized and p-polarized – Figure 3) reflects off a nonconducting surface, it is completely polarized (s-polarized) perpendicular to the plane of reflection. This occurs at a specific angle of incidence called Brewster’s angle and the reflected ray and the refracted ray are 90 degrees apart ($\theta_i + \theta_t = 90^\circ$). In equation 3 only s-polarized is non-zero whereas p-polarized goes to zero.

According to Snell’s Law, 

$$ni \sin \theta_i = n_t \sin \theta_t$$

where $n$ is the index of refraction of the medium and $\theta$ is the angle of the ray from the normal.

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Figure 3: s-polarized (●) light and p-polarized light

When the angle of incidence is equal to Brewster's angle, $\theta_B$,

$$ni \sin \theta_B = n_t \sin \theta_t$$

and since $\theta_B + \theta_t = 90^\circ$, $\theta_t = 90^\circ - \theta_B$, and

$$\sin \theta_t = \sin(90^\circ - \theta_B) = \sin 90^\circ \cos \theta_B - \cos 90^\circ \sin \theta_B = \cos \theta_B$$

Substituting for $\sin \theta_t$ in Equation (2) gives

$$ni \sin \theta_B = n_t \cos \theta_B$$

Therefore, 

$$\frac{n_t}{ni} = \tan \theta_B.$$
SET UP (This part is ready, but read carefully before you proceed with the procedure part)

1. Attach the spectrophotometer table to the track. Put the diode laser, 2 polarizers and the collimating slits on the track as shown in Figure 4. Mount the Rotary Motion Sensor with the bigger diameter of spindle against the spectrophotometer table (see Figure 5). Attach the spectrophotometer table base to ground as instructed by your teacher.

![Complete Setup](image1)

Figure 4: Complete Setup

2. The spectrophotometer disk should be put on “backwards” with the 180 degree mark at the position where the zero mark is normally.

3. Two round polarizers are used on the holder. Rotate the second polarizer (second from laser) to 45 degrees and lock it in place by tightening the brass screw. The first polarizer (closest to the laser) is used throughout the experiment to adjust the light level. Since the ratio of reflected light to incident light is measured, better data will be obtained if the incident light level is kept above 50%.

![Large Spindle Is Used](image2)

Figure 5: Large Spindle Is Used

4. The square analyzing polarizer (in Figure 6) has its transmission axis marked, and for normal use the label should be on top with its axis horizontal and thus 90 degrees from the polarization axis of the reflected light. This is finding the variation in the “p” (parallel) component of the reflected light and is used to determine Brewster’s angle and to calculate the index of refraction. But by placing the analyzing polarizer with its transmission axis vertical, you can also look at the variation in the “s” (perpendicular component of the reflected light) as well.
5. The 45 degree polarizer is used to solve the problem that the laser light is already polarized. To make the relative intensities of the s and p components the same, the light is polarized at 45 degrees.

6. The small metal Brewster's angle base disk should be screwed in and zeroed so that the mark at the top of the label above the N in the word ANGLE is aligned with the zero angle mark on the spectrophotometer disk.

7. The plastic base has two zero marks. For reflected light, use the mark that is on the side with the higher step. The D lens is placed on the lower surface flush against the step when data is being collected. The other mark would be used for transmission, like for Snell’s Law.

8. To align the laser beam, remove all polarizers, collimating slits, and D lens. Set the spectrophotometer arm on 180 degrees. Use the x-y adjust on the laser to get the laser beam at the center of the Light Sensor slit. The Light Sensor bracket slit should be set on #4. Place the collimating slits on track and adjust the slit position so the laser beam passes through the #4 slit.

9. Plug the Rotary Motion Sensor into Channels 1 and 2 on the ScienceWorkshop 500 interface. Plug the Light Sensor into Channel A. Open the Capstone file called "Brewsters angle".

PROCEDURE

1. The program file capstone is already opened on the computer.

2. With the D lens removed, zero the angle for Rotary Motion Sensor: Rotate the spectrophotometer arm so the laser beam is centered on the Light Sensor slit. The spectrophotometer disk should be near 180 degrees but it doesn’t matter if it is slightly off. Click on START and move the arm back and forth in front of the laser, watching the intensity on the computer. Stop at the position that gives the maximum intensity. Click on STOP and do not move the arm until program is started to take the actual data run. This
insures that zero for Rotary Motion Sensor is at the center of the beam. Place the D lens on the platform against the step.

Note about angle measurement: The angle is computed by dividing the actual angle (recorded by the computer) by two. The best procedure is to move the spectrophotometer arm, reading the angle on the digits display, and then rotate the plastic Brewster's disk to match same angle. Thus the markings on Brewster's disk are only there for convenience (in this experiment) and are not used directly. But, to get the laser beam exactly on to the slit, you must make fine adjustments while watching the digits display for the maximum light intensity. You can adjust either the disk or the spectrophotometer arm until the intensity is maximized.

3. Turn out the room lights. A small light might be useful for seeing the computer keys to type in values and to put the analyzing polarizer on and off. Click on START. Do not click on STOP until all of the procedure steps are completed. Set angle to 85 degrees. The square analyzing polarizer should not be in place. Rotate the Brewster disk to about 85 and, while watching the digits display of light intensity, fine tune the position to get into the beam. It doesn’t have to be exact, just so that you get enough light. Rotate the first polarizer (nearest to the laser) to adjust the level to be as high as possible without exceeding 90%. The Light Sensor should be on gain of 1 or 10.

4. Create a table in your notebook and enter the angle into the table. Read the digits display of the light intensity and record the value under “Total Light” column. Place square analyzing polarizer (axis horizontal) on the arm just in front of slits. (Note: The square analyzing polarizer must sit level, flat on the arm.) Read the digits display of light intensity and record value under “Polarized Light” column. Calculate the ratio of polarized light to the total light and enter the value under “ratio” column. Find the percentage of the ratio by multiplying by 100.

5. Remove the analyzing polarizer and go to the next angle, in increments of 5 degrees. When the intensity is approaching the minimum, take data points every 1 degree near the minimum. (Approximately from 65 degrees to 55 degrees)

6. After finished recording the data, Plot ratio versus angle using PSI plot on the other computer. Choose the polynomial fit to get the value of angle at which the reflection is a minimum (Figure 7). (Hint: Differentiate the polynomial equation and equate it to zero) This is Brewster's angle. Find the refractive index from this angle.

7. Repeat steps 2-6 for a given glass sample.

8. Use significant figures for the data. Complete error analysis has to be done. Refer to the error analysis document.
(3) Fluorescence of rare earth Sm$^{3+}$ (Samarium) ions in borate glasses.

**Introduction:**

Luminescence is a general term used to describe the radiative emission which can be excited by a variety of methods. Photoluminescence depends on excitation by electromagnetic radiation of photons. Electroluminescence – by a voltage applied to the luminescent substance; Triboluminescence – by utilization of mechanical energy such as grinding; Cathodoluminescence – by energetic electrons or cathode rays; Chemiluminescence – by utilization of the energy of a chemical reaction. Thermoluminescence – light emitted upon heating.

Photoluminescence has been classified, as fluorescence and phosphorescence according to the nature and duration of the emission following the removal of excitation. Schematically it is shown in Figure 8. For fluorescence, when excitation is removed, there is an exponential afterglow, whose rate is independent of excitation intensity and temperature. In Phosphorescence, there is an additional component of the afterglow, which decays more slowly and with more complex kinetics. Phosphorescence has a lifetime longer than $10^{-4}$ sec, whereas the lifetime of fluorescence is generally of the order of $10^{10}$ to $10^{-1}$ sec. The emitted photon energy is different (generally lower) than the energy of the excitation for both fluorescence and phosphorescence.
Fluorescent emission involves optical transitions between electronic states characteristic of the radiating substance. These electronic states may be localized as in the fluorescence of some rare earth compounds or they are bands, as in the radiative recombinations of conduction electrons with valence holes in semiconductors. Fluorescent emission can be distinguished from the Raman effect, Compton and Rayleigh scattering and Cherenkov emission by the time delay between excitation and fluorescent emission, which is long compared to the period $\lambda/c$ of the radiation, where $\lambda$ is the wavelength and $c$ is the velocity of light. The radiative lifetimes of the excited electronic states which are responsible for the time constants for fluorescence vary from $10^{-10}$ to $10^{-1}$ sec depending on the type of fluorescing ion. The most striking feature of fluorescent emission is that it occurs in the spectral region where the crystal or glass is non-absorbing. Thus, the fluorescence of solids is distinguished from incandescence, whose emissivity by Kirchoff’s law is strong only in the spectral region where absorptivity is strong. Unlike incandescence, fluorescent emission is not a high temperature phenomenon. In fact with increasing temperature the competing non-radiative de-excitation processes become more probable and the intensity of the fluorescent emission decreases. If the non-radiative de-excitation is from the same excited electronic state as the radiative de-excitation, the time constant for fluorescence decreases.

When an electron is excited from ground state to an excited state, it relaxes back to ground state either radiatively or non-radiatively. The radiative de-excitation (fluorescence) is affected by the asymmetry of the surrounding binding forces. In a glass matrix these binding forces are determined by the immediate neighborhood of the fluorescing ion. Glasses lack the lattice periodicity in the atomic arrangement. Therefore, potential fluorescent centers may find themselves in different environments within a given glass. In general, this leads to broadening of the fluorescence bands as compared to the bands of similar centers in crystals or in vapors. Position, intensity and full width at half maximum of the fluorescence line and the fluorescence decay time are the parameters that are affected by the structure of the glass matrix. Hence, it is of interest to study the fluorescence of a given center as a function of composition of the host glass.

Rare earth ions are more important than transition metal ions as fluorescent species because glasses doped with rare earth ions have a greater potential as laser materials. In lanthanides, the intraionic electronic transitions of interest are f-f transitions and they are influenced by the local crystal field. Fluorescent transitions of rare earth ion like samarium in glasses are shown in Figure 9.
The optical line spectra of triply ionized rare earth ions originate from intra-ionic electronic transitions. They exhibit very sharp absorption and fluorescence lines compared to transition metal ions, as the 4f shell are well shielded by the outermost electrons. These transitions occur between the levels of $4f^N$ (N is the number of electrons in 4f shell) which is shielded by two 5s and six 5p electrons. The position of these levels arises from a combination of the coulomb interaction among the electrons, the spin-orbit coupling and the crystalline electric field. The resultant splitting of the $4f^N$ configuration is shown in Figure 10.

Figure 9. Electronic energy levels of Samarium ion and fluorescence spectrum of samarium ion.

Figure 10. Schematic representation and order of magnitude of the effects of ionic and ligand field interactions acting on a $4f^N$ configuration.
The Hamiltonian, $H_{\text{FI}}$, for the rare earth free ion is composed by one part due to the central field, $H_0$, and by several other interactions, which are generally treated as perturbations. Among these interactions the inter-electronic repulsion (Coulomb interaction), $H_c$, and the spin-orbit interaction, $H_{\text{SO}}$, are the most relevant.

$$H_{\text{FI}} = H_0 + H_C + H_{\text{SO}} + H_{\text{LF}}$$

The magnitudes of these interactions follow the order $H_0 > H_C > H_{\text{SO}}$. Although the ligand field (crystal field) Hamiltonian is weak, the interaction between 4f electrons and the chemical environment is responsible for the most interesting spectroscopic features of rare earth ions.

The inter-electronic repulsion or coulomb interaction ($C$) yields terms $2S+1L$ with separations of the order of $10^4$ cm$^{-1}$. The spin-orbit interaction (SO) then splits these terms into $J$ states with a typical splitting of $10^3$ cm$^{-1}$. Finally, the J degeneracy of the free ion states is partially or fully removed by the crystalline electric field (Ligand field). The width of the crystal field splitting usually extends over several hundred cm$^{-1}$.

The electronic configuration of rare earth elements are given in Table 1. The electronic energy levels of Samarium ion (Sm$^{3+}$) is given in Figure 11.

<table>
<thead>
<tr>
<th>Number</th>
<th>Element</th>
<th>Symbol</th>
<th>Electronic configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>54</td>
<td>Xenon</td>
<td>Xe</td>
<td>1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$ 4s$^2$ 3d$^{10}$ 4p$^6$ 5s$^2$ 4d$^{10}$ 5p$^6$</td>
</tr>
<tr>
<td>58</td>
<td>Cerium</td>
<td>Ce</td>
<td>1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$ 4s$^2$ 3d$^{10}$ 4p$^6$ 5s$^2$ 4d$^{10}$ 5p$^6$ 6s$^2$ 4f$^1$ 5d$^1$</td>
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<tr>
<td>59</td>
<td>Praseodymium</td>
<td>Pr</td>
<td>1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$ 4s$^2$ 3d$^{10}$ 4p$^6$ 5s$^2$ 4d$^{10}$ 5p$^6$ 6s$^2$ 4f$^1$</td>
</tr>
<tr>
<td>60</td>
<td>Neodymium</td>
<td>Nd</td>
<td>1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$ 4s$^2$ 3d$^{10}$ 4p$^6$ 5s$^2$ 4d$^{10}$ 5p$^6$ 6s$^2$ 4f$^1$</td>
</tr>
<tr>
<td>61</td>
<td>Promethium</td>
<td>Pm</td>
<td>1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$ 4s$^2$ 3d$^{10}$ 4p$^6$ 5s$^2$ 4d$^{10}$ 5p$^6$ 6s$^2$ 4f$^1$</td>
</tr>
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<td>62</td>
<td>Samarium</td>
<td>Sm</td>
<td>1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$ 4s$^2$ 3d$^{10}$ 4p$^6$ 5s$^2$ 4d$^{10}$ 5p$^6$ 6s$^2$ 4f$^1$</td>
</tr>
<tr>
<td>63</td>
<td>Europium</td>
<td>Eu</td>
<td>1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$ 4s$^2$ 3d$^{10}$ 4p$^6$ 5s$^2$ 4d$^{10}$ 5p$^6$ 6s$^2$ 4f$^1$</td>
</tr>
<tr>
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<td>Gadolinium</td>
<td>Gd</td>
<td>1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$ 4s$^2$ 3d$^{10}$ 4p$^6$ 5s$^2$ 4d$^{10}$ 5p$^6$ 6s$^2$ 4f$^1$ 5d$^1$</td>
</tr>
<tr>
<td>65</td>
<td>Terbium</td>
<td>Tb</td>
<td>1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$ 4s$^2$ 3d$^{10}$ 4p$^6$ 5s$^2$ 4d$^{10}$ 5p$^6$ 6s$^2$ 4f$^1$</td>
</tr>
<tr>
<td>66</td>
<td>Dysprosium</td>
<td>Dy</td>
<td>1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$ 4s$^2$ 3d$^{10}$ 4p$^6$ 5s$^2$ 4d$^{10}$ 5p$^6$ 6s$^2$ 4f$^{10}$</td>
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<tr>
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<td>Holmium</td>
<td>Ho</td>
<td>1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$ 4s$^2$ 3d$^{10}$ 4p$^6$ 5s$^2$ 4d$^{10}$ 5p$^6$ 6s$^2$ 4f$^{11}$</td>
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<tr>
<td>68</td>
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<td>Er</td>
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</tr>
<tr>
<td>69</td>
<td>Thulium</td>
<td>Tm</td>
<td>1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$ 4s$^2$ 3d$^{10}$ 4p$^6$ 5s$^2$ 4d$^{10}$ 5p$^6$ 6s$^2$ 4f$^{13}$</td>
</tr>
<tr>
<td>70</td>
<td>Ytterbium</td>
<td>Yb</td>
<td>1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$ 4s$^2$ 3d$^{10}$ 4p$^6$ 5s$^2$ 4d$^{10}$ 5p$^6$ 6s$^2$ 4f$^{14}$</td>
</tr>
<tr>
<td>71</td>
<td>Lutetium</td>
<td>Lu</td>
<td>1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$ 4s$^2$ 3d$^{10}$ 4p$^6$ 5s$^2$ 4d$^{10}$ 5p$^6$ 6s$^2$ 4f$^{14}$ 5d$^1$</td>
</tr>
</tbody>
</table>
For triply ionized rare earth ion you have to remove three electrons from the outermost orbit configuration. For example for Nd$^{3+}$ ion the electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 4f^3$. Two electrons from 6s and one electron from 4f are removed.

Figure 11: Energy level diagram of Sm$^{3+}$ with absorption lines in the low energy and high energy regions, and the emission (Fluorescence) lines. (William Heidorn’s Thesis)

The electronic configuration and the effects of the environment determine the electronic energy levels of rare earth ions. For instance, the two 4f electrons of Praseodymium (Pr) ions in the central field interact electrostatically (coulomb interaction) and as a result their energy levels splits into seven levels with different energies such as $^1S$, $^3P$, $^1D$, $^3F$, $^1G$, $^3H$ and $^1I$. Then due to spin-orbit coupling, the triplet levels $^3P$, $^3F$, $^3H$ which show the total spin of $S=1$. The $^3H$ level split into three levels such as $^3H_6$, $^3H_5$, $^3H_4$. Whereas singlet levels $^1S$, $^1D$, $^1G$, $^1I$ do not split.

The expressions such as $^3H_6$, $^3H_5$, $^3H_4$ are called term symbols which provide three pieces of information.

- The letter “H” indicates the total orbital angular momentum L. The letters S,P,D,F,G,H,I corresponds to L=0,1,2,3,4,5,6 respectively.
- The left superscript in the term symbol shows the multiplicity of the term. This is given by the total spin S and the multiplicity $2S+1$.
- The right subscript in the term symbol is the value of the total angular momentum quantum number J and is given by $J = L+S, L+S-1,\ldots,L-S$. 
Russel-Saunders coupling (LS coupling) is most often used to describe the states of lanthanides, and the states are therefore expressed as $^{2S+1}L_J$. For samarium ion there are 5 electrons in the 4f shell. This results in large number of spectral terms.

**Procedure:**

PROCEDURE HAS TO BE WRITTEN BY YOU USING THE INFORMATION GIVEN BELOW AND DOING EXPERIMENT IN THE LAB

- Sm$^{3+}$ fluorescence spectrum will be observed by exciting the glass samples by 403 nm excitation wavelength and viewing the light emitted by the excited atoms with LEOI-101 Modular Multifunctional Grating Spectrometer.

![Schematic diagram](image)

**Schematic diagram**

S1: Entrance slit  
M1: Plane mirror  
M2 and M3: Spherical mirrors  
G: Grating  
S2: PMT  
M4: Folding mirror  
S3: CCD
### Specifications of the spectrometer

<table>
<thead>
<tr>
<th>Description</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Focal Length</td>
<td>500 mm</td>
</tr>
<tr>
<td>Wavelength Range</td>
<td>Grating B: 200 ~ 800 nm</td>
</tr>
<tr>
<td>Slit Width</td>
<td>0~2 mm adjustable with a reading resolution of 0.01 mm</td>
</tr>
<tr>
<td>Relative Aperture</td>
<td>D/F=1/7</td>
</tr>
<tr>
<td>Grating</td>
<td>Grating B:1200 lines/mm</td>
</tr>
<tr>
<td>Blazed Wavelength</td>
<td>250 nm</td>
</tr>
<tr>
<td>Wavelength Accuracy</td>
<td>Grating B: ± 0.4 nm</td>
</tr>
<tr>
<td>Wavelength Repeatability</td>
<td>Grating B: ≤ 0.2 nm</td>
</tr>
<tr>
<td>Stray Light</td>
<td>≤ 10⁻³</td>
</tr>
<tr>
<td>Resolution</td>
<td>Grating B: ≤ 0.1 nm</td>
</tr>
<tr>
<td>Photomultiplier Tube (PMT)</td>
<td></td>
</tr>
<tr>
<td>Wavelength Range</td>
<td>Grating B: 200 ~ 800 nm</td>
</tr>
<tr>
<td>CCD</td>
<td></td>
</tr>
<tr>
<td>Receiving Unit</td>
<td>2048 cells</td>
</tr>
<tr>
<td>Spectral Response Range</td>
<td>Grating B: 300 ~ 800 nm</td>
</tr>
<tr>
<td>Integration Time</td>
<td>88 steps (each step: approximately 25 ms)</td>
</tr>
<tr>
<td>Filter</td>
<td>White filter: 320~ 500 nm; yellow filter: 500~ 660 nm</td>
</tr>
<tr>
<td>Dimensions</td>
<td>560×380×230 mm</td>
</tr>
<tr>
<td>Weight</td>
<td>30 kg</td>
</tr>
</tbody>
</table>
**Data Analysis:**

The fluorescence spectrum you obtain for your sample will look very similar to figure 9. Plot Intensity Vs wavelength. The fluorescence spectrum exhibit four emission peaks which are assigned to $^4G_{5/2} \rightarrow ^6H_{5/2}$ (565 nm), $^4G_{5/2} \rightarrow ^6H_{7/2}$, (598 nm), $^4G_{5/2} \rightarrow ^6H_{9/2}$ (646 nm), $^4G_{5/2} \rightarrow ^6H_{11/2}$ (707 nm) transitions, respectively. Among the four observed bands, the $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition is more intense and $^4G_{5/2} \rightarrow ^6H_{11/2}$ transition is found to be weak in intensity. The $^4G_{5/2} \rightarrow ^6H_{7/2}$ and $^4G_{5/2} \rightarrow ^6H_{9/2}$ transitions correspond to the orange and red luminescence respectively. The $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition is magnetic dipole allowed but electric dipole dominated with the selection rule $\Delta J = \pm 1$ and $^4G_{5/2} \rightarrow ^6H_{9/2}$ band is purely electric dipole (ED) transition. $^4G_{5/2} \rightarrow ^6H_{5/2}$ is magnetic dipole transition (MD). The area ratio of ED/MD tells the symmetry of the rare earth site in the glass matrix. The Higher intensity of the electric dipole transition exhibit less symmetric nature of the rare earth ion environment.

To find area ratio we need to find the area under each transition. For this we will be using Origin 9.1 software in Lab 109. We can clearly see that all four transitions are stark split transitions (The splitting of atomic spectral lines as a result of an external electric field was discovered by Stark, and is called the Stark effect). In glass materials, the external electric field comes from the electrostatic interaction between the rare earth ions and the lattice. Now to find total area under each transition, the peaks are deconvoluted by fitting with two Gaussian curves. From this fit a sum of the two curves was utilized to find the maximum peak values, and the effective bandwidth of the total Stark split transitions.

The procedure for Gaussian fitting will be explained by the instructor during the time of fitting. **YOU HAVE TO WRITE THE DATA ANALYSIS PROCEDURE IN YOUR OWN WORDS.**

Once the area, height and FWHM (Full Width at Half Maximum) are obtained for each transition you tabulate them. Then you find area ratio of ED/MD.
Error analysis:

Error analysis has to be carried out for refractive index data and fluorescence data. This part will be explained in the lab. The error analysis file is available online.

Questions

1. Derive Fresnel’s equations 1 and 2 for reflectance of s-polarized light and p-polarized light. 8 points (Include this in the theory part – derive the derivation with hand – NO TYPING)

2. Using the index of refraction for the glass sample and acrylic that you have obtained in this lab, find \( \theta_i \) from Snell’s Law. Then use equation 3 and make a plot of the reflectance (intensity of reflection coefficients) Vs incident angle (0 to 90\(^0\) in steps of 0.1) similar to figure 2. 8 points

3. Would Brewster's angle be more or less for light in air reflecting off water? Why? 2 points

4. A parallel beam of unpolarized light in air is incident at an angle of 54.5\(^0\) (with respect to the normal) on a plane glass surface. The reflected beam is completely linearly polarized. (a) What is the refractive index of the glass? (b) What is the angle of refraction of the transmitted beam? 3 points

5. Light travelling in water strikes a glass plate at an angle of incidence of 53.0\(^0\). Part of the beam is reflected and part is refracted. If the reflected and refracted portions make an angle of 90\(^0\) with each other, what is the index of refraction of the glass? 3 points

6. Find the ground state of Sm\(^{3+}\) ion and Dy\(^{3+}\) ions. Write all the term symbols for Samarium ion (Refer ppt slides- example 28-29) 8 points

7. What is electric dipole radiation? 2 points

8. What is magnetic dipole radiation? 2 points