INVESTIGATIONS INTO ANOMALOUS SPECTROSCOPIC EFFECTS IN GE124 AND RECOMMENDATIONS FOR ALTERNATIVE MATERIALS

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I. Abstract

In examining Raman and photoluminescence spectra from GE124 fused quartz from multiple vendors, consistent luminescence peaks are observed at 1.7eV and around 1.37eV. These peaks have not been reported previously in the literature and are not due to compositional impurities. Rather, they are most likely due to some silica network defect or combination of defects that has not previously been recognized. The shape of the peak group around 1.37eV changes with different spots examined on samples slides; this observation suggests that the distribution of such a defect or defects is spatially heterogeneous. Large absorption bands at 2.22eV-2.38eV and at 1.68eV-1.82eV may be related to the observed photoluminescence anomalies. For applications requiring a high purity glass with essentially no spectral signature around 900nm (~1.37eV), Esco S1-UV Fused Silica is an ideal material.

II. Introduction

The choice of materials to be used in an experiment is nearly as important, perhaps even more important, than the physics and the questions behind the experiment itself, for the characteristics of all materials that comprise the experimental apparatus and setup play a critical role in determining the success or failure of the experiment. Specifically, unintended or unanticipated physical effects, whether spectroscopic or mechanical, have the potential to seriously disrupt the progress of the experiment. Such is the case with the biophysics experiments in the Kwok Lab; the glasses that have been used in the experimental setup have provided several problems that have temporarily impeded progress on the actual science. Most recently, the lab’s GE124 ‘fused quartz’ microscope slides, which have served as windows for the sample holders in which the biological materials being studied are deposited, have exhibited a very broad, anomalous, variable peak around 900nm that completely masks the expected spectroscopic response from the sample. In order to make progress on these biophysics experiments, a new material with a highly reproducible and spatially homogeneous Raman spectrum is necessary to replace the GE124 windows.

The first general goal of these biophysics experiments is to determine whether certain kinds of lipid molecules localize to form platforms that allow signaling proteins, which enable communication between the interior and exterior of a cell, to aggregate. The second goal of these experiments is to understand how lipid molecules are packed together at the molecular level.
(This work in part builds on [1, 2] and follows certain experimental design considerations from that research.) In order to investigate both of these questions, spatially resolved total-internal-reflection (TIR) Raman spectroscopy [3, 4] is implemented to examine the molecular structure of a single lipid bilayer that self-assembles within a sample holder, the windows for which have been made of GE124 in the Kwok Lab. Figure 1 schematically shows the configuration in which incident light is totally internally reflected within the sample holder window and evanescent light is then Raman scattered from the overlying biological material. With the TIR technique, evanescent waves only penetrate approximately 100 nm into the lipid bilayer (essentially only the thickness of the bilayer itself); this limited range of influence greatly reduces the unwanted signal that would otherwise be created by Raman scattering from the water in which the lipids must be kept at all times, including during the experiments. The expected measured signal from these experiments is a combination of Raman-scattered light from both the lipid bilayer and the glass (Figure 1). Because the part of the measured Raman spectrum that is of interest will essentially sit on top of the dominant Raman spectrum of the glass, a well behaved and reproducible glass signature is necessary to allow extraction of the lipid bilayer signature from the measured spectrum. Because these biophysics experiments also involve examining spatially variable characteristics of the lipid bilayers, a spatially homogeneous Raman spectrum for the window material is necessary and particularly important.

GE124 is a high purity silica glass (99.995% SiO₂ according to the vendor of the slides used in the Kwok Lab [5]) that is widely used across many fields of science for its excellent transmission properties and its (nominally) low OH content. This material is termed ‘fused quartz’; however, quartz is by definition a crystalline substance, different than the semi-amorphous material that is GE124 glass, so this term is used loosely. Tables 1 and 2 show the trace element compositions of GE124 from different vendors. Because the trace element compositions for this material are so low, the glass should not display any spectroscopic anomalies due to impurities, such as color-center luminescence effects. (For comparison, trace element concentrations on the order of tens to hundreds of parts-per-million by weight are necessary for color-center effects to become significant [6].) Figure 2 shows the nominal percent transmission plots for this material. Based on this plot, light in the range of interest for these biophysics experiments (~500-1000nm) should be transmitted almost perfectly with practically no interference from the material. Based on both the compositional data and the transmission
plot, no spectroscopic problems with GE124 in the operating wavelength bands in these experiments would be expected.

Figure 1: Schematic depiction of total-internal-reflection Raman spectroscopy. Laser light (in these biophysics experiments, 780 nm) approaches the lipid sample through the glass window and is totally internally reflected at the window-lipid interface. An evanescent wave is generated in the total internal reflection process that travels approximately 100 nm into the lipid bilayer, essentially just far enough to interact with the entire bilayer without Raman scattering off of the surrounding water in which the lipid must remain immersed. The incident laser light (red solid arrow), the reflected laser light (red solid arrow), and the evanescent wave (red dashed wave) will all Raman scatter off of the materials through which they propagate (black tightly dashed arrows indicate Raman-scattered light off of the lipid bilayer; black loosely dashed arrows indicate Raman-scattered light off of the glass). Some Raman-scattered light from both the window and the lipid bilayer will travel down through the rest of the experimental setup (see Figure 6) to the spectrograph to be registered.

Table 1: Elemental impurities in GE124 from Quartz Scientific, Inc., the vendor the slides used in the Kwok Lab. Data from [5]. Values in parts-per-million by weight; analysis via direct reading spectrometer.

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Table 2: Elemental impurities in GE124 from Ted Pella, Inc. Data from [7]. Values in parts-per-million by weight; analysis via direct reading spectrometer.

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The Kwok Lab has been using GE124 in microscope-slide form simply as windows for the sample holder setup. Aside from the known Raman scattering profile (see discussion in the Theory section), no other spectroscopic effects or problems were expected from this material. However, as Figure 3 shows, a very broad, highly variable, anomalous peak shattered expectations about the spectroscopic characteristics of this material. This peak is located exactly in the region in which the Raman scattered signal from the lipid bilayers should be observed, around 900 nm (or 1200 cm\(^{-1}\) Raman shift with 780 nm incident light). This anomalous signal will dominate and drown out the small Raman scattering signal from the lipid bilayers, thereby precluding the ability to make the desired measurements. This problem is made far more odious by the irregularity and spatial variability of the unexpected signature.
Because GE124 is such a commonly used glass in science, any potential problems with its use, even if only a side effect of the manufacturing process of one vendor, are important to note for the benefit of future researchers. Furthermore, this anomalous spectroscopic effect is stalling the continuation of science in the Kwok Lab, so a viable alternative that can be used in the biophysics experiments needs to be identified. The ideal sample holder window is one that displays a highly reproducible Raman spectrum and that shows a low intensity, flat spectrum between approximately 1200cm\(^{-1}\) and 2000cm\(^{-1}\). (The reason for this latter requirement is simply that it is far easier to measure a small signal from a low background than it is to measure a small signal from a large background.) This research attempts to answer the questions regarding the observed phenomena in the GE124 slides and to determine an appropriate alternative glass.

III. Theory

*Raman Scattering*

Raman scattering is the inelastic scattering of light incident off of some material. Rayleigh scattering, the more readily apparent scattering phenomenon that causes the sky and glacial tarns to appear blue, is elastic scattering. Essentially, Rayleigh scattering leads to light being dispersed in all directions at the same wavelength as that of the incident light, while Raman scattering causes light to be dispersed in all directions at longer (and sometimes shorter) wavelengths than that of the incident light. Physically, Rayleigh scattering occurs when the induced varying dipole only involves oscillation of electrons in the material [9]. This essentially does not cause loss of energy. Raman scattering occurs when the induced varying dipole involves oscillation of the nuclei in the material [9]. Energy is lost in displacing the nuclei; this energy goes into bond vibrations.

Raman spectroscopy is most effectively implemented to understand the bonding structure of matter. Because Raman-scattered light dominantly loses (or in some situations gains) energy to molecular and crystalline bonds, that is, to enabling transitions between vibrational energy levels of these bonds, the structure of the material of interest can be determined in part from interpretation of the characteristic spectrum of scattered light measured from the sample. (It is worth noting that, while Raman spectroscopy is most commonly implemented to examine vibrational transitions in a material, electronic transitions between ground states and low excited states can be observed with the technique [10].) Such bonds can of course be modeled as simple
harmonic oscillators. In reality, though, molecular and crystalline bonds are anharmonic [10],
and this anharmonicity leads to a modified version of the classic simple-harmonic-oscillator
solution to the Schrödinger Equation and to different selection rules for the vibrational energy
level transitions. The more important implication of anharmonicity for Raman spectroscopy is
this latter point. In the standard simple-harmonic-oscillator paradigm, only single-step transitions
are allowed (transitions that involve gaining or losing only one factor of $h\nu$); with an anharmonic
oscillator, transitions that step up or down two or three energy levels are weakly allowed
(transitions that involve gaining or losing two or three factors of $h\nu$) [10]. Therefore, overtones
can be observed in Raman spectra, although they are much weaker than fundamental transitions.

We can use classical electrodynamics to understand the cause of both Raman and
Rayleigh scattering. (The following derivation is from [10].) The electric field of an incident
laser beam is given by

$$E(t) = E_0 \cos 2\pi v_0 t$$

(Eqn. 1)

where $v_0$ is the laser frequency. When the laser light illuminates a sample of interest, this electric
field polarizes the material. The induced dipole moment is given by

$$p = \alpha E = \alpha E_0 \cos 2\pi v_0 t$$

(Eqn. 2)

where $\alpha$ is the atomic or molecular polarizability of the sample. Because the electric field is
oscillatory, the polarization of the material will also vary, although not necessarily at the same
frequency. The displacement of atoms in the material due to this varying polarization will excite
the normal modes of oscillation of the sample structure. The atomic displacements (specifically
those of the nuclei) in the sample are given by

$$q = q_0 \cos 2\pi v_m t$$

(Eqn. 3)

where $q$ is the displacement and $v_m$ is the frequency of a normal mode of oscillation. Because the
induced dipole moment, which depends on displacement of charges, is related to the
polarizability (eqn. 2), the polarizability is related to the nuclear displacement (eqn. 3). For
small-amplitude vibrations, we can make the approximation

$$\alpha \approx \alpha_0 + \left( \frac{\partial \alpha}{\partial q} \right)_0 q$$

(Eqn. 4)

where $\alpha_0$ is the unperturbed polarizability and the derivative is evaluated at equilibrium (no
nuclear displacement, the relaxed state).
By substituting equation 4 into equation 2, we obtain

\[ p = \alpha_0 E_0 \cos 2\pi v_0 t + \left( \frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 \cos 2\pi v_0 t \]  

(Eqn. 5)

and then by substituting equation 3 into this equation, we obtain

\[ p = \alpha_0 E_0 \cos 2\pi v_0 t + \left( \frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 \cos 2\pi v_0 t \cos 2\pi v_m t \]  

(Eqn. 6)

Finally, by using a trigonometric identity, we arrive at a useful result:

\[ p = \alpha_0 E_0 \cos 2\pi v_0 t + \frac{1}{2} \left( \frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 \left[ \cos \{ 2\pi (v_0 + v_m) t \} + \cos \{ 2\pi (v_0 - v_m) t \} \right] \]  

(Eqn. 7)

The first term in this expression gives rise to Rayleigh scattering; the dipole radiation re-emitted from the induced dipole has the same frequency as the incident radiation \( v_0 \). The second term gives rise to Raman scattering; radiation of two distinct shifted frequencies is reradiated from the induced oscillating dipole. The re-emitted radiation in this case has frequencies that are shifted down (Stokes scattering) and up (anti-Stokes scattering) by a normal mode frequency.

An important feature of equation 7 is the partial derivative attached to the Raman scattering term. This factor indicates that for Raman scattering to occur, the polarizability of the material must change with small vibrational displacement from equilibrium. In effect, for a vibrational mode to be Raman active, the associated displacement must change the polarizability of the material around the bond \([9, 10]\). In contrast, for a bond to absorb infrared radiation (for it to be observable using infrared absorption spectroscopy), the dipole moment of the material around the bond must change during vibration \([9, 10]\). Figure 4 graphically illustrates these requirements in a physical sense. The polarizability and dipole moment do not have to vary together; they can change independently. In general, symmetric vibrational modes will be Raman-active and asymmetric vibrational modes will be IR-active \([9]\). Because bonds often are not active in both spectroscopic regimes, infrared absorption and Raman spectroscopies often gather different, complementary information (and for this reason are often used together).
Figure 4: IR/Raman activity of three CO₂ vibrational modes. In both asymmetric cases, the maximally stretched states are the same under 180° rotation; the polarizability at these extremes therefore must be the same. Furthermore, because all degrees of stretching will have rotational symmetry with the opposite stretching direction, the polarizability graph must be left-right symmetric. These conditions mean that at equilibrium the change in polarizability with small displacements is zero, so these asymmetric vibrational modes are Raman inactive. The 180° rotation symmetry is not true in the symmetric vibrational mode, so the change in polarizability with small displacements around equilibrium is non-zero and the mode is Raman active. Adapted from 1-16 from [10] and 1.6 and 1.7 from [9].

In order to better understand the fundamental physics behind Raman scattering, specifically with regard to Stokes and anti-Stokes scattering, we will consider a quantum mechanical model of the interaction between incident light and the sample. Figure 5 graphically shows the possible effects on vibrational states of a bond. If the energy of an incident photon
matches the energy required to excite the bond to a higher vibrational state, then the photon will be absorbed (this is known as the resonance condition and is the operating mechanism in infrared absorption spectroscopy). If the energy of the incident photon does not match the energy required to make a vibrational transition, then the photon will be scattered. This can happen in three separate ways; in all of these processes, the light causes an excitation to a virtual state (a state created when the laser light polarizes the material) [9]. In Rayleigh scattering, the laser light causes excitation from the original to a virtual state and the material then readmits light to drop down to the original state [9, 10]. In Stokes scattering, the laser light causes excitation to a virtual state and the material then re-emits light to attain a vibrational state that is higher than the original state [9, 10]. The re-emitted radiation has less energy than the incident light; the difference is equal to the energy required to raise the original bond vibrational state to the higher vibrational state. The radiation will have a lower frequency (longer wavelength) than the incident light. In anti-Stokes scattering, the laser light causes excitation to a virtual state and the material then re-emits light to attain a vibrational state that is lower than the original state [9, 10]. In this case, the re-emitted radiation has more energy than the incident light and the scattered light will have a greater frequency (shorter wavelength). The difference is equal to the energy lost in dropping from the original vibrational state to a lower state. For anti-Stokes scattering to occur, the bonds in the material must already be in an excited vibrational state; at room temperature, when the thermal energy of the system is much less than the energy required for an excited vibrational state in the sample, anti-Stokes scattering is much less probable than Stokes scattering.

Because the energy of Raman-scattered light is raised or lowered by an amount equal to the energy of an integer number of vibrational state transitions (most commonly one vibrational state transition), the observed shift yields information about the bonding structure of the material. It should be noted, however, that Raman scattering is a very weak process. Only one in every $10^6$-$10^8$ scattered photons will be Raman scattered; the vast majority are Rayleigh scattered [9].

Raman spectra are presented in Raman Shift, also referred to as relative wavenumber (cm$^{-1}$), to show the constant shift from the excitation wavelength.
Figure 5: Quantum mechanical energy level diagram depicting the transitions involved in infrared absorption, scattering, and fluorescence. The transition from $v$ states to $v'$ states represents an electronic transition. Virtual states are created by the interaction of the incident light with the material, which results in polarization of the latter. The transition between vibrational states in the excited electronic state is non-radiative. After Figure 1-8 from [10].

Luminescence

Luminescence effects can often cause problems in conducting Raman experiments [9, 10]. In this process, a vibronic (combined vibrational and electronic transition) or electronic transition takes the system from an original state or band to a higher energy state or band. The electron loses vibrational energy to the surrounding material lattice as phonons until it reaches the bottom of the energy band or well. It then can emit radiation to drop back into the original energy well or band. Figure 5 graphically shows this process. The emitted light is a lower energy (longer wavelength) than the incident light; the shift that occurs from the loss of energy to phonons is called the Stokes shift. The system can also return to the original electronic state through non-radiative transitions. The energy acquired during the excitation process can also be
transferred non-radiatively to another luminescence center, and that center can then emit radiation in a unique manner [11].

An important distinguishing characteristic between luminescence and Raman scattering is the stationary nature of fluorescence peaks. Raman peaks will always be observed at the same shifted position from the excitation laser wavelength; as laser wavelength is varied, the Raman peaks will therefore also vary. Because fluorescence involves a fixed electronic transition across a gap, the peak will remain stationary as excitation wavelength is varied.

Glass Structure

All glasses have some form of order, whether short-, intermediate-, or long-range, and are therefore not strictly amorphous on all scales [12]. (These forms of ordering are distinguished from global order, in which a crystal structure exists throughout a material.) GE124 displays short- and intermediate-range order and therefore displays the well-defined Raman spectrum shown in Figure 6. The silica tetrahedron, composed of four oxygen atoms arranged in a three-sided pyramid with a silicon atom at the center (Figure 6), forms the building block of all silicate materials, including almost all silica glasses. Such glasses exhibit short-range order, in which silica tetrahedra exist (although possibly with deformed and irregular bonds) but do not form a framework with other silica tetrahedra. This lack of a continuous framework of silica tetrahedra distinguishes GE124 ‘fused quartz’ from true quartz. Somewhat well established Si-O bonds within the discrete silica tetrahedra are responsible for the large, broad peaks at 450cm⁻¹, 800cm⁻¹, 1065cm⁻¹, and 1200cm⁻¹ in the Raman spectrum for GE124 glass (Figure 6). Silica glasses also may exhibit intermediate-range order, in which several silica tetrahedra (most importantly in groups of 3 and 4) bond in a ring [12, 13]. These rings are not regularly bonded with the surrounding amorphous lattice, but their internal bonding structures are regular enough to produce small, sharp peaks at 495cm⁻¹ and 606cm⁻¹ in the Raman spectrum for GE124 (Figure 6) [8, 12, 13]. Because the Raman scattering in GE124 is understood and well documented [8, 12, 13], the Raman spectrum in principle can easily be subtracted from the spectrographs obtained in the biophysics experiments.
Glass Structural Point Defects

As in crystalline materials, the short-range order of amorphous silica can be disrupted by defects within the system. Defects within high purity silica glasses have been studied extensively [14-34]; the most important types for this project are incorrect atomic coordination and missing species. These defect classes are to some extent related. In the former, an atom is not bonded to the correct number of neighbor atoms. Nominally, each oxygen atom should be bonded to two silicon atoms (coordination number is 2) and each silicon atom should be bonded to four oxygen atoms (coordination number is 4) [14]. However, if the glass is not perfectly stoichiometric [14], or if the glass structure is mechanically affected in some way that breaks bonds (possibly even during the manufacturing process) [15-18], then incorrect coordinations will occur. Figure 7 shows the structures of defects where the coordination number for oxygen is either 1 or 3 and the coordination number for silicon is either 3 or 5. The most important defects in the study of high purity silica glasses are due to under-coordination; these are also shown in Figure 7.
Figure 7: Models of silica point defects. In (A) through (D), black spheres represent silicon atoms and light gray spheres represent oxygen atoms. The dark gray sphere, which is also indicated with a blue arrow, is the improperly coordinated atom. (A) Under-coordinated oxygen. Coordination number = 1. This defect is the non-bridging oxygen hole center (NBOHC). (B) Over-coordinated oxygen. Coordination number = 3. (C) Over-coordinated silicon. Coordination number = 5. (D) Under-coordinated silicon. Coordination number = 3. This defect is an oxygen deficiency center. (E) Basic model of the E’ defect center. The silicon is bonded to three oxygen atoms, which are each bonded to another silicon atom. The fourth bond somehow is absent, so a free electron is instead present. (F) Basic model of the NBOHC. The silicon atom is surrounded by four oxygen atoms (properly coordinated), and three of the oxygen atoms are bonded to other silicon atoms, but one of the oxygen atoms is not bonded to another silicon atom (under-coordinated). The absence of a bond leaves a free electron attached to the oxygen. (A) - (D) from [14].
If the coordination number for silicon is only 3, then there will be an unbound electron attached to the silicon atom (Figure 7E). This defect is known as the $E'$ defect center ($\equiv Si \cdot$) [19], and it is part of the greater class of defects in which there is an apparent oxygen deficiency, at least on a local scale, in the glass [20]. In this defect center, an unpaired electron is localized in a single Si sp$^3$ orbital [21]. Oxygen deficiency can also lead to other bonding irregularities, such as silicon-silicon bonding. These defects can be caused either during the manufacturing process or by starting with a material that is lacking oxygen. In this case, the defect is fundamentally due to a missing species.

If the coordination number for oxygen is only 1, then there will be an unbound electron attached to the oxygen atom (Figure 7F). This defect is the iconic non-bridging oxygen hole center (NBOHC, $\equiv Si - O \cdot$) [22]. In this case, the unpaired electron is localized in a $p\pi$ orbital of a monovalent oxygen and it therefore does not ‘bridge’ between the oxygen and a silicon atom [21]. This defect can be caused by having an excess of oxygen in the system or by mechanically affecting the melt in some way during the glass manufacturing process [14-16].

Incorrect bonding can also occur within the glass structure. The peroxy linkage is formed when two oxygen atoms bond (POL, $O_3 \equiv Si - O - O - Si \equiv O_3$) so that each is bonded to one silicon atom and one oxygen atom instead of to two silicon atoms [23].

While photoluminescence apparently does not occur in $E'$ centers [24], other oxygen deficiency structures, NBOHCs, and POLs will display unique photoluminescence patterns if the excitation laser wavelength is within an absorption band. The exact nature of the photoluminescence observed in GE124 will be discussed in the Results section below.

IV. Experimental Methods

Sample Preparation

In general, samples were cleaned with ethanol and a pressurized de-dusting agent (canned air) prior to collecting Raman spectra. For most samples, a small piece of adhesive paper was attached to a corner of the sample to provide a convenient scattering surface on which to focus the collecting microscope objective. With several Quartz Scientific GE124 samples, the same slide preparation procedure as that implemented for the actual biophysics experiments had already been utilized. The samples are placed in a Teflon slide holder that is immersed in piranha solution, which is a mixture of 80 mL hydrogen peroxide and 240 mL sulfuric acid. The beaker
that holds the slides within the solution is initially lightly agitated, and the slides are left in the piranha solution for 45 minutes. The slides are then removed from solution and thoroughly rinsed with deionized water. This method is a standard procedure for cleaning materials to ensure no contamination by unwanted compounds. A comparison between samples that were and that were not prepared in this way will not be considered in this study because previous tests have shown that this cleaning method does not affect the observed spectroscopic anomalies.

*Raman Spectroscopy*

To collect the Raman spectrum for a sample, laser light is directed at the sample and the Raman-scattered light is collected through a microscope and measured using a grating spectrograph and CCD. The complete experimental setup is shown in Figure 8.

The sample is illuminated with light from one of three lasers. The Spectra-Physics Model 3900S tunable Ti:Sapphire laser (labeled A in Figure 8) emits laser light between 750 nm and 900 nm. This laser is pumped by a diode-laser-pumped intracavity frequency-doubled 532 nm Nd:Vanadate Spectra-Physics Millennia Xs laser. The Millennia Xs pumping laser is run at 5-6W, which yields a Ti:Sapphire laser power output of ~0.6W at 800 nm. The light from this pumping laser is also diverted for use in the Raman experiments. The green laser is run between 0.2W and 2W when used for Raman experiments. A dichroic mirror (labeled C in Figure 8) combines the light paths of the main Ti:Sapphire laser and an auxiliary laser, a blue Melles Griot 43 Series 488 nm Argon Ion Laser (labeled B in Figure 8), that is also used in the Raman experiments. These multiple illumination sources are useful in distinguishing between true Raman peaks and luminescence peaks. The light from any one of these lasers is then directed through a 50cm focal length lens that focuses the laser beam onto the sample, which is placed on the stage of a Nikon Eclipse TE2000U microscope (labeled D in Figure 8).

Because the biophysics experiments for which this experimental setup was originally designed rely on the generation of evanescent waves in the sample (see the *Introduction* section), the laser light is directed at the sample stage at 65° (Figure 8). (In the actual biophysics experiments, light is passed through a prism, which has been removed from the current setup, to cause total internal reflection in the manner discussed in the *Introduction*.) The path of the incident laser light for the present study is left in this configuration since the angle of incidence with the sample is not expected to have any effect on the measured Raman spectrum.
Figure 8: Schematic diagram and pictures of the Raman spectroscopy experimental setup. (A) Tunable Ti:Sapphire laser (750-900 nm) that is used as the primary light source for the Raman spectroscopy experiments. (B) Argon Ion Laser (488 nm) that is used as a secondary light source. (C) Dichroic beam-path combiner. (D) Microscope, where the sample is placed for the Raman experiments. (E) Microscope objective that collects scattered light and Raman Steep Edge Filter that cuts out Rayleigh scattered light and that only passes Raman scattered light (i.e. light of longer wavelengths than that of the illuminating source). (F) Grating spectrograph. (G) CCD camera, connected to computer running WinSpec spectroscopy software.

At the sample stage, the incident laser spot size for the Nd:Vanadate laser is 34µm, the spot size for the Ti:Sapphire laser is 77µm, and the spot size for the Ar+ laser is 58µm. Scattered light from the sample is collected through a 10x magnification water immersion microscope objective (labeled E in Figure 8). This light passes through a high-pass Raman filter that attenuates any light with wavelength shorter than the cutoff wavelength by 6 orders of magnitude. For the Ti:Sapphire laser, a Williams Advanced Materials 785nm Raman Steep Edge Filter is used. For the Nd:Vanadate laser, a Semrock 532nm Edge Basic LWP Filter is used. For the Ar+ laser, a Chroma Technology HQ500LP (500nm cutoff) is used. These filters are used to cut out any incident laser light that is Rayleigh scattered into the objective; the light that is allowed to pass is therefore only the Raman scattered signal. The light is then sent to an Acton Research Corporation 300i grating spectrograph (labeled F in Figure 8), which has a focal length of 300 mm and an adjustable entrance slit width of 30 - 100 µm. The frequency-separated signal is then registered by a Roper Scientific Spec-10 camera (labeled G in Figure 8) with a 100 pixel by 1340 pixel EEV chip. Each pixel is 20 µm x 20 µm. WinSpec spectroscopy software is used to collect the spectra. Exposure time and spectrograph entrance slit are varied as appropriate.
Spectra Processing

No filtering was applied to the acquired spectra. Where necessary, cosmic ray spikes were removed by manually applying a linear interpolation in order to produce values that follow the local data trend to replace the values from the affected pixels. Spectra were plotted in WaveMetrics IgorPro.

Chemical Analysis

Chemical composition is determined using the Pomona College Geology Department x-ray fluorescence (XRF) spectrometer. The XRF excites the innermost core electrons within individual atoms in the sample with X-ray radiation and then measures the x-ray spectrum re-emitted from the sample. Because each element emits a distinct, characteristic set of x-ray wavelengths, elemental composition of can be determined from the measured spectrum. (Determining the abundances of certain elements through this technique is much more difficult than it is for most elements because of inconveniences that arise with the characteristic x-rays for those certain elements. The Pomona College Geology Department XRF measures those elements listed in the tables in Appendix A.)

Samples of slides and bulk glass were placed directly into the XRF for analysis. Both the standard measurement routine, which reports major and trace element concentrations, and the ProTrace routine, which only reports trace element composition, were utilized.

Structural Analysis

Analysis of crystalline structure is conducted using the Pomona College Geology Department’s x-ray diffractometer (XRD). The XRD measures diffracted x-ray intensities over a range of incident x-ray angles; diffraction maxima can be used to determine the orientation and frequency of occurrence of atomic planes. The full-width at half-maximum (FWHM) of the diffraction peaks can be used as an indication of disorder within the crystalline structure. Broader peaks indicate a less ordered structural feature within the crystalline lattice.

The powder-diffraction method is used to examine the samples in this study. Samples are ground to a powder by hand using a mortar and pestle. Diffraction data was collected in Bragg Brentano (BB) Mode with a nickel filter and no monochromator. Table 3 summarizes the XRD settings.
### Table 3: Operating conditions for XRD structural analysis of GE124.

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### V. Results

**Raman Spectroscopy: Material Assessment**

Samples of six viable window materials were examined for spectral suitability. These include GE124 supplied by Quartz Scientific, Inc.; GE124 supplied by Ted Pella, Inc.; Fused Quartz supplied by Pyromatics Corp.; S1-UV Fused Silica supplied by Esco Optics; Pyrex® (Corning 7740) supplied by Esco Optics; Corning 7980 supplied by Esco Optics; and Corning 7979 supplied by Esco Optics. Glass samples were rectangular or circular and were between ~1mm and 5mm thick. Generic soda lime glass and a sample of custom-produced Corning 7980 from Quartz Scientific were also analyzed for comparison.

Figure 9 shows spectra of inelastically scattered light from Quartz Scientific GE124. Data were collected using each of the three lasers. The 780nm excitation data is much noisier than the 488nm excitation data because the intensity of Raman scattering scales with the frequency of the incident light to the fourth power [9]. Figure 10 also shows the Raman spectrum for Quartz Scientific GE124, but the data were collected on a Raman apparatus at the University of California Riverside. Though very noisy due to low signal strength, the general outline of the broad peak that appears at approximately 1700cm⁻¹ in Figure 3 is still visible. This anomalous spectroscopic signature is therefore reproducible on other experimental apparatuses. Figure 11 shows spectra of inelastically scattered light from Ted Pella GE124. Again, Raman and photoluminescence data were collected using each of the three lasers. The features of the GE124 spectra are discussed further below.
Figure 9: Spectra for Quartz Scientific GE124. Data were collected using the Ti:Sapphire red laser (upper left), the Nd:Vanadate green laser (upper right), and the Argon Ion blue laser (bottom two). The details of these spectra are examined further below.

Figure 10: Spectrum for Quartz Scientific GE124 collected at UC Riverside. The low intensity and low signal-to-noise ratio is due to the low power output of the laser used in this Raman experiment. Despite the noisy spectrum, the outline of the broad peak centered at approximately 1700 cm$^{-1}$ is still apparent.
Figure 11: Spectra for Ted Pella GE124. Data were collected using the Ti:Sapphire red laser (top), the Nd:Vanadate green laser (middle), and the Argon Ion blue laser (bottom). The details of these spectra are discussed below.
Figure 12: Spectra for Esco Optics S1-UV Fused Silica. Data were collected with the Ti:Sapphire red laser (top), the Nd:Vanadate green laser (middle), and the Argon Ion blue laser (bottom). Note the flat signal to the right of the 1200 cm\(^{-1}\) silica Raman peak in the red and the green spectra. All acquired Esco Fused Silica spectra displayed this low, flat signal in the region in which the Raman signature from the lipid bilayers is expected to appear. The blue spectra, however, does show an anomalous large bump centered around approximately 3000 cm\(^{-1}\). The suitability of Esco Fused Silica for use in the biophysics experiments is discussed further below (see Recommendation for Alternative Experimental Materials in the Discussion section).
Figure 12 shows the inelastic spectra for Esco Optics S1-UV Fused Silica. Because the spectroscopic signature in the region in which the lipid bilayer Raman signature is expected to appear (approximately 1400-1800cm\(^{-1}\)) is due almost solely to the background signal, this material is an excellent choice for use in the biophysics experiments. The suitability of Esco Fused Silica for use in this capacity is discussed further below. Figure 13 shows spectra for Esco Optics Pyrex. Because the spectroscopic signal was consistently poor in terms of reproducibility and unexpected features, data were only collected with the Nd:Vanadate 532nm laser and the Argon Ion 488nm laser.
Figure 14: Spectra for Corning 7980 (top) and Corning 7979 (bottom) supplied by Esco Optics. Data were collected using the Nd:Vanadate green laser. Because these spectra are not featureless and do not display low intensity in the region in which the lipid bilayer Raman signature is expected, these materials are not suitable for use in the biophysics experiments.
Figure 14 shows the Raman signatures for Corning 7980 and Corning 7979 supplied by Esco Optics. The irregular and intense signals make both of these materials unsuitable for use in the biophysics experiments. Figure 15 shows the Raman signature for generic soda lime glass. This type of glass contains large amounts of alkali and alkaline earth metals (compositionally 20-25%), specifically sodium and calcium. The massive spectroscopic signature from this material makes it extremely useless for the biophysics experiments.

![Raman spectrum for generic soda lime glass.](image)

*Figure 15: Raman spectrum for generic soda lime glass. This spectrum is presented for comparison with the (relatively) more regular Raman signatures from higher purity silica materials.*

Figure 16 shows spectra for Corning 7980 supplied by Quartz Scientific. The measured spectra closely resemble those of the Esco Optics S1-UV slides (Figure 12). That the signal in the spectroscopic region of interest under red-laser illumination is due almost exclusively to background noise makes this a suitable material as well.
Figure 16: Spectra for Corning 7980 provided by Quartz Scientific. The flat signal in the spectroscopic region in which the lipid bilayer Raman signatures should appear would make this material a suitable choice in the biophysics experiments.
Raman and Photoluminescence Spectroscopy: GE124

Both the well defined Raman signature of high purity silica and a distinct but partially unexpected luminescence spectrum were observed in multiple samples of GE124 from multiple suppliers. Figure 17 shows both the Raman and the luminescence spectra together for Quartz Scientific GE124. The three spectra that comprise this figure were collected using the three different laser excitation sources and were all measured at the same point on the slide. These spectra are generally representative of the observed spectra from all examined GE124 samples.

The Raman signature for GE124 includes large peaks at 450cm⁻¹, 800cm⁻¹, 1065cm⁻¹, and 1200cm⁻¹ that are due to short-range order [8, 12] and smaller peaks at 495cm⁻¹ and 606cm⁻¹ that are due to intermediate-range order [13] (see Theory section). An additional Raman peak at approximately 1600cm⁻¹ is also observed in these data; this peak is inferred to be due to OH content on the order of 10³ ppm [25]. The peak is certainly due to Raman scattering because it has the same Raman shift in both the green-excitation data and the blue-excitation data. The peak is not observed in the red-excitation data; this apparent absence is most likely due to the large, broad, anomalous luminescence peak, which in this case has probably masked that Raman band.

The luminescence spectra for GE124 are readily apparent in Figure 17 as the peaks that do not maintain a constant Raman shift with changes in excitation wavelength. Figure 18 shows just the luminescence spectra for the same point on a sample of Quartz Scientific GE124 with the three different excitation wavelengths. The peak that appears at approximately 1.9eV is due to direct excitation of the non-bridging oxygen hole center (NBOHC) [26]. (In keeping with the standard language for photoluminescence studies in amorphous materials, all luminescence peaks will be identified based on their energy in electron volts.) While the absorption band for this luminescence is centered at 2.0eV, reference [27] reports observing the peak with 2.33eV (532nm) excitation wavelength. The absorption band for the NBOHC does extend to include both 2.33eV (532nm) and 2.54eV (488nm), although the strength of absorption decreases through those energies [28]. The peak at approximately 1.82eV is due to an oxygen deficiency [28]. Reference [28] does report observing the peak with 2.33eV (532nm) excitation. The 1.82eV peak could conceivably be due to excess oxygen since reference [29] reports observing a 1.85eV in high purity silica glass that is due to oxygenation of the material during manufacturing. However, this excess-oxygen peak was not observed with a 2.33eV (532nm) excitation source [29], so the 1.82eV peak observed in GE124 is due to oxygen deficiency.
Figure 17: Raman signature and luminescence spectra for Quartz Scientific GE124. The data in each plot were collected at different excitation wavelengths. All three were collected from the same spot on the GE124 sample slide. These spectra are generally representative of all GE124 samples examined in this study.
Figure 18: Luminescence spectra for Quartz Scientific GE124. The data in each plot were collected at different excitation wavelengths. All three were collected from the same spot on the sample slide. NBOHC = Non-Bridging Oxygen Hole Center. ODC = Oxygen Deficiency Center.
Occasionally, a small peak at 1.53eV is observed in samples of GE124 from multiple vendors. (The Ted Pella 532nm excitation plot in Figure 19 shows this peak.) No cause for this uncommon feature could be identified.

The peaks observed at 1.7eV and 1.37eV could not be correlated to known peaks in the literature. A peak at 1.3eV has been reported as due to decomposition of Cl₂ gas trapped within the amorphous structure [23]; however, the energy required for this dissociation is greater than the excitation energies used in this study [30]. A peak complex that extends to around 1.37eV and that is due to Cl₂ has also been reported [23], but its structure is incorrect. Further study will be necessary to understand the cause of these parts of the GE124 luminescence spectrum.

The 1.37eV peak observed here is specifically the problem that makes GE124 unsuitable for the biophysics experiments because it will dominate the lipid bilayer Raman signature under red excitation. This signal is indeed coming from the GE124 material, both as Figure 10 confirms and as was determined through simple tests in the Kwok lab. The peak does not show up when laser light is not incident on the sample, so the observed signal is not due to background from the surrounding environment. Two heat filters, which block light in the near-infrared and infrared, were placed in the red laser beam path to test if the photons associated with this peak were coming from the laser (even though the 1.37eV peak is observed with all three lasers). If the anomalous photons were coming from the red laser, they should have been blocked along the beam path; however, the 1.37eV peak was still observed. Finally, the heat filters were placed between the slide and the spectrograph, along the path that collected light follows, to test if the signal could be due to spectrograph problems. In this case, the heat filters completely cut out the peak so that it was not observed in the acquired spectrum. Based on these observations, the 1.37eV peak is an unidentified luminescence effect from GE124.

Figure 19 shows blue and green luminescence spectra from three different samples of GE124 from three different suppliers. Several important observations can be drawn from this figure. First, under green laser light, a sharper 1.37eV peak consistently appears on top of a broader base (also visible in Figures 18 and 20) while under blue laser light the broader base is the only feature that consistently appears at that energy. Under red excitation, the sharper 1.37eV peak is common but does not always appear (Figures 20 and 21). This suggests that two processes are at work in creation of the anomalous luminescence: one process causes the broader base centered at approximately 1.37eV that appears with all three excitation wavelength used in
this study, and another process causes the sharper peak at 1.37eV that appears consistently under green excitation, commonly but inconsistently under red excitation, and not at all under blue excitation. While these processes are most likely different and distinct, the common center energy suggests that they are also related in some way. Figure 20 further demonstrates this point.

Figure 19: Luminescence spectra from blue and green excitation for three different samples of GE124 from three different vendors. Note that the 1.37eV peak includes both a broad base and a sharp upper peak in all three samples under green excitation while the peak includes only the broad base under blue excitation. The sharper peak overlying the broad base is common but not consistently present under red excitation (see Figure 20). These patterns are inferred to indicate that two distinct but most likely related processes are responsible for the 1.37eV peak. Also note that the 1.9eV NBOHC peak shifts to higher energy with increased excitation energy.
Another important observation from Figure 19 is that the ~1.9eV NBOHC peak shifts from 1.88eV under green excitation to 1.91eV under blue excitation. Such a shift with changing excitation energy has been reported for amorphous high purity silica, but it can only be observed with purely electronic transitions (zero-phonon lines, ZPL) because the spectroscopic line width must be small enough to observe the change [27]. This phenomenon also relates to the significant difference in full widths at half maximum (FWHMs) seen in these spectra versus those reported in the literature. Reports of the noted peaks (~1.9eV NBOHC, ~1.8eV ODC) indicate FWHMs of 0.2-0.4eV [26, 28]; the FWHMs for those peaks in the spectra presented here are 0.02-0.04eV, a full order of magnitude smaller. These features are discussed further below.

As Figure 21 demonstrates, the GE124 spectroscopic signature varies greatly across a single slide and in different slides. The general form of the luminescence is consistent (Figures 18-20), but the exact shape of the peaks change significantly in different locations. This diversity in the spectra indicates that the distribution of the phenomenon causing the anomalous 1.37eV luminescence is highly heterogeneous.

Figure 20: Examples of spatial variations in spectroscopic signature. Each spectrum in a row was collected on the same spot on the indicated slide. Note the changes in the shape of the 1.37eV peak in the red-excitation data. Also note that the smaller peak on top of the broad base at 1.37eV is not present under blue excitation.
Figure 21: Variations in the nature of the 1.37eV peak at different points on different slides under red excitation. Such variations suggest that the distribution of the defect or impurity that is causing this luminescence is highly spatially heterogeneous.
At select points on the Quartz Scientific GE124 slides, the special features shown in Figures 22 and 23 are observed. The most important features in these spectra are the large, very pronounced dips in the blue excitation spectra and in one of the green excitation spectra; the ridiculously large 1.37eV peak group in the red excitation data in Figure 23; the appearance of other luminescence peaks in the blue and green excitation spectra; and the persistence of the 1.37eV peak in the green excitation data. The prominent dips occur at 520-560nm (~2.3eV) and 680-740nm. Because peaks that should appear in those regions have been muted (or very reduced, in the case of the 450cm\(^{-1}\) Raman peak in the green-excitation data in Figure 23), these dips are inferred to be absorption bands. Reference [31] reports a 2.3eV absorption band that is attributed to Al or Ge impurity centers. Because chemical analyses (see below and Appendix A) show no aluminum content, aluminum cannot be the cause of the observed spectral signature. While germanium was not tested for in the chemical analyses, the high-purity nature of the glass strongly suggests that the observed spectral features are not due to impurities. That these absorption zones are only apparent in special locations on the slides further indicates that the material is spatial highly heterogeneous.

The incredibly large 1.37eV peak set seen in the red-excitation data in Figure 23 is highly unusual and possibly indicates that the spot on the slide used to collect these data is a highly enriched zone of the causing phenomenon or a critical center for that phenomenon. Additionally, it appears that there are multiple peaks around 1.37eV, at least three, that together form a peak complex centered at \(~1.37eV\). Multiple additional unidentified photoluminescence peaks also appear at other photon energies in these special locations in the material; these likely contain important information about the nature of these unique radiation centers. Finally, while other features that appear in the blue and red excitation spectra are significantly different at these special spots, the 1.37eV peak remains relatively unchanged in green excitation spectra.
Figure 22: Set of three spectra taken at the same spot on a Quartz Scientific GE124 slide. Note the unusual spectrum under blue excitation.
Figure 23: Three spectra collected at the same spot on a Quartz Scientific GE124 slide. Note the prominent gaps in the blue- and green-excitation spectra and the ridiculously large 1.37eV peak complex in the red-excitation data.
Chemical Analysis

Complete XRF composition data for a Pyromatics Fused Quartz slide, a Ted Pella GE124 slide, a Quartz Scientific GE124 slide, and a sample of bulk GE124 provided by Pyromatics are presented in the partitioned tables in Appendix A. In comparing these values with the vendor-reported values in Tables 1 and 2, it is apparent that the slides contain significantly higher impurity abundances than is reported by the suppliers. However, no major element impurities (Ca, Na, K, etc.) were detected, and trace element concentrations are all less than 10ppm. With such low concentrations, it is highly unlikely that a trace element is causing the unidentified luminescence in GE124. Furthermore, no significant differences between the trace element composition of Esco S1-UV Fused Silica and that of the GE124 slides can be discerned. Because the Esco material does not show the two unidentified luminescence peaks, the trace elements present in the GE124 slides are almost certainly not the cause of the anomalous luminescence.

Structural Analysis

X-ray diffraction analysis shows no unexpected crystalline structure within GE124. Figure 24 shows the x-ray diffraction pattern for a Quartz Scientific sample. The data only show a broad peak centered at approximately 21°, which is due to amorphous silica [32]. Therefore, no long-range crystalline structure is present within GE124, and the anomalous peaks are therefore not due to any effects from long-range or global structure.
VI. Discussion

Cause of Anomalous GE124 Peak

Based on the chemical composition data, the anomalous photoluminescence observed at and around 1.37eV is almost certainly not due to compositional impurities. For trace elements to play a significant role in the generation of the spectroscopic anomalies, concentrations higher than ~10ppm as well as significant compositional differences from the Esco S1-UV Fused Silica would be expected. Instead, the unidentified GE124 luminescence is likely due to an unidentified or unreported silica network defect (or a combination of defects). Based on the presence of the NBOHC spectral signature, the GE124 must have been deformed or stressed in some way during the fabrication process in order to introduce broken bonds. The individual GE124 slides must be
cut from larger blocks of the glass, so cutting the material could have introduced NBOHC defects along the surface and near the surface of the glass. Based on the presence of the ODC spectral signature, the GE124 melt must also have been deprived of oxygen during the fabrication process. Because the manufacturing process can have such significant effects on the GE124 photoluminescence spectra, another unrealized fabrication-induced defect or phenomenon that also has a unique luminescence effect could certainly be present in the glass.

Based on observations discussed in the Results section, the spatial distribution of the photoluminescence-inducing phenomenon (or phenomena) is highly heterogeneous. The unique spots on the sample slides where the 1.37eV peak is more intense than the GE124 Raman signature and where the absorption bands become apparent very likely hold important information about the specific nature of the cause of the anomalous luminescence. Two important observations are that the 532 nm excitation wavelength falls within one of the absorption bands and that the 1.37eV peak set is most consistent in the green. This correlation could suggest a link between the 520nm-560nm absorption band and the sharper 1.37eV peak; however, correlation does not imply causation. The fact that the 488 nm excitation wavelength does not excite the sharper 1.37eV peak corroborates this inference, but the fact that the 780 nm excitation wavelength does not fall within an absorption band but still excites the sharp 1.37eV peak complicates this idea. Specifically, the lack of correlation between the observed presence of the absorption bands and the enlarged 1.37eV peak group in the red excitation spectra (Figures 22 and 23) adds significantly difficulty to assigning an association between the two phenomena. Additionally, the absorption bands are only observed at specific spots on the samples, while the 1.37eV peak group is always observed in some form. If they were clearly related, one would expect the absorption bands to be more obvious in all of the collected spectra. Finally, the high variability in the 1.37eV peak complex shape in the red excitation data in comparison to invariability of the 1.37eV peak complex shape in the green excitation data cannot be simply explained in terms of the absorption bands. This observation in particular implies further complications in the luminescence-generating process.

The presence of additional unidentified luminescence peaks in the spectra from the special sample spots (Figures 22 and 23) likely holds important information for deciphering the cause and nature of the anomalous luminescence center. Further study will be necessary to decrypt that information.
The anomalously small FWHMs of the identified peaks in the high purity silica luminescence spectra could indicate that the presented peak identification is incorrect, that GE124 displays a higher structural order than other high purity silica glasses, or that the processes causing the observed spectral lines involve are purely electronic transitions instead of vibronic (involving loss of energy to phonons) [33]. Because the silica network is disorganized, a wide range of energies can be lost to phonons in the luminescence process, and therefore the resulting luminescence line width will be very large. However, purely electronic transitions avoid this broadening. Such transitions create zero-phonon lines, which usually are only excited at relatively low temperatures using special techniques such as spectral hole-burning or fluorescence line narrowing [33]. Somehow, in the experiments in this study, the observed luminescence could be due to purely electronic transitions, although this seems highly improbable given that these experiments were conducted under room-temperature conditions with the involvement of no special techniques. Alternatively, GE124 could have a higher order than usual glass. In amorphous materials, inhomogeneous broadening causes asymmetric spreading of spectroscopic peaks; the broadening in this case is caused by statistical irregularities in the glass network at radiation centers due the amorphous nature of the material [34]. With a higher order material, the effect of statistical network irregularities would be diminished and the FWHMs of the peaks would be decreased, although perhaps not all together that substantially since homogeneous broadening still plays an important and dominant role in determining peak FWHM [34]. It is, however, difficult to find a reason that GE124 would have a higher structural order than other glass materials. Furthermore, the XRD scan for this material does not show any features that could indicate long-range order, and the presence of an ODC peak is characteristic of amorphous silica [34]. For the peaks to have such small FWHMs, GE124 would need to have a fundamentally amorphous structure but also have a more developed intermediate order than most other high purity silica glasses. As Figure 25 shows, the FWHMs of Quartz Scientific GE124 and Esco S1-UV Fused Silica are almost identical. Either similar phenomena exist in both materials, or there is an aspect of the experimental setup that has effects that have not yet been fully understood.
Figure 25: Comparison of the QSI GE124 NBOHC peak FWHM and the Esco S1-UV Fused Silica NBOHC peak FWHM. Note that the FWHMs are almost identical and are both an order of magnitude less than the FWHM values reported in the literature. It is important to note that Esco S1-UV Fused Silica does not always show the NBOHC peak.

Recommendation for Alternative Experimental Materials

Based on the Raman signatures for the considered window materials (Figures 9 – 16), Esco Optics S1-UV Fused Silica is the best material to use in the biophysics experiments. With a low intensity, flat Raman spectrum between 1200cm$^{-1}$ and 2000cm$^{-1}$ when illuminated with 780nm laser light (Figure 12), this material is an ideal glass for these experiments. The Corning 7980 supplied by Quartz Scientific (Figure 16) would also be a useful glass for the biophysics experiments; however, the company custom manufactured this product for another client, and the sample used in this study was surplus from that order. Since Quartz Scientific does not usually supply 7980 slides, using the Esco Optics S1-UV Fused Silica as a window material is more effective and dependable.

Due to their irregular and intense spectra, all other samples are not suitable for use. As was first discovered by the Kwok Lab in trying to use the material for the biophysics experiments, GE124 (Figures 9 – 11) displays anomalous fluorescence that would mask the Raman signature from the lipid bilayers. The spectra observed from Esco Pyrex (Figure 13), Corning 7980 (Figure 14), and Corning 7979 (Figure 14) are all far too irregular and display too great a signal intensity in the region of interest to be used as window materials. Esco S1-UV Fused Silica (Figure 12), however, meets the requirements of an ideal experimental material, at least when excited with the laser that would be used in the biophysics experiments (the Ti:Sapphire laser tuned to 780 ± 10nm). With 532nm and 780nm excitation wavelengths, the sample only significantly shows a well behaved silica Raman spectrum (other small features are
negligible and may not be reproducible). When illuminated with 488nm light from the argon ion laser, Esco Fused Silica does display a large, anomalous fluorescence band. However, because the biophysics experiments will be conducted with red / near-infrared light, the anomalous peak that only shows up with blue light will not be a problem.

The ideal behavior from Esco Fused Silica is reproducible between different slides. Figure 26 shows two Raman spectra for two different Esco Fused Silica samples with red illumination. As is apparent in this figure, the low, flat signal is the region of interest is constant across different pieces of glass. Therefore, Esco Fused Silica is the material that should be implemented in these biophysics experiments.

Figure 26: Raman spectra from two different samples of Esco S1-UV Fused Silica. Both display a well behaved Raman signature and low intensity in the region of biophysical interest. These two characteristics, along with the reproducibility of the spectral signature, make Esco Fused Silica the ideal window material for the biophysics experiments.

VII. Conclusion

Anomalous luminescence peaks at 1.7eV and 1.37eV that have not been previously reported in the literature have here been recognized within GE124 fused quartz glass. The 1.37eV luminescence is comprised of at least three sub-peaks: a low, broad peak that is excited by 780nm, 532nm, and minimally 488nm laser light; a sharp peak at 1.37eV that sits on top of the broad base and that is excited by 532nm and occasionally 780nm laser light; and rarely a third peak that is only occasionally visible under 780nm excitation. The lack or presence of certain observed features in the GE124 luminescence spectra indicates that the slide material is highly spatially heterogeneous. Absorption bands observed at specific points on sample slides and associated extra luminescence peaks may hold important information about determining the
exact cause of the 1.37eV photoluminescence, although it is unclear if any correlation between the appearance of the absorption bands and the 1.37eV peak group’s structure exists. At present the exact cause of these luminescence effects cannot be determined; however, they are clearly not due to impurities and are most likely due to silica glass network defects.

In searching for a suitable window material for use in the Kwok Lab biophysics experiments, this study finds that Esco S1-UV Fused Silica is the best material. Under 780nm excitation, this glass has a low, flat signal in the spectroscopic region in which the lipid bilayer signals are expected to be observed.

Further research will be necessary to determine the cause of the anomalous 1.37eV luminescence. Since the photoluminescence is most likely a silica glass network defect or combination of defects, electron paramagnetic resonance (EPR, a technique analogous to NMR) may be a useful tool in determining the characteristics and possibly the identity of the defect or defects. However, this technique also only works with defect centers that are paramagnetic, more fundamentally ones that involve an unpaired electron. If the defect centers are not paramagnetic, then EPR will not be helpful in assessing the cause of the 1.37eV peak set. At a more basic level, annealing the GE124 would ideally heal any defects, so the disappearance of the 1.37eV signal from annealed samples would be a clear indication that the anomalous luminescence is caused by network defects. The annealing point for GE124 is reported as 1140°C [5] or 1215°C [7], so a controlled, clean oven that can reach these temperatures will be required. Additionally, x-ray irradiation may also be a useful test to determine if the 1.37eV peak complex is defect-related; if x-ray irradiation makes the 1.37eV peak group more prominent, then the peak set is clearly caused by defects. A first-order test with a piece of GE124 shows that, when irradiated for more than 40 minutes with x-rays, the glass takes on a notable gray hue. Using x-ray-producing equipment at the College, irradiation tests with controlled dosages could be easily performed in order to test the spectroscopic effects of such a process. In both the annealing experiment and the x-ray irradiation experiment, a lack of change in the 1.37eV peak group does not necessarily provide any useful information. Regardless of the outcome of these experiments, a determination of the specific cause of the 1.37eV peaks, either a specific defect or otherwise, will be difficult and will require much further experimentation.
VIII. Acknowledgements

We wish to express our sincere gratitude towards Esco Optics (http://www.escoproducts.com/). They were very helpful in our search for usable materials, and they provided us with free samples of Corning 7980 and 7979. Because of the quality of their products, the Kwok Lab will be showing its thanks in a more substantial way in the future.

IX. References

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    Chichester, 2005).
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X. Appendix A

The following table presents the XRF data collected for a Pyromatics Fused Quartz slide, a Ted Pella GE124 slide, a Quartz Scientific GE124 slide, and a piece of bulk GE124 provided by Pyromatics. Negative values indicate that the measurement is invalid because the concentrations in the material are below the detection limits. The upper two blocks contain data from a standard analysis, which provides major element oxide data in weight percent and trace element concentration in parts-per-million by weight. The lower three blocks contain data from a ProTrace analysis, which provides trace element data in parts-per-million by weight. The extremely high silica content and minimal impurity content of these samples, combined with the pure, undiluted form of the material (usually Geology samples are mixed with flux to promote melting for analysis), makes it very hard to perform a careful analysis. For this reason, the concentration data are not necessarily accurate, as should be visible in the >100% silica values reported in some cases. However, the fact that the XRF did have difficulty analyzing these samples, and the data showing consistently high silica with almost no other elements, strongly suggest that no significant impurities are present in GE124.

### Standard Analysis

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