

Clarifying Glass Luminescence at Near-Infrared Excitation

Marisia A. Fikiet¹, David Tuschel², Vladimir V. Ermolenkov¹, and Igor K. Lednev¹ 

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Abstract

Glass is a unique material that is often encountered in chemical and biological studies as a convenient sample holder (vial or microscope slide in particular). If the sample is probed with light in fluorescence and Raman spectroscopic experiments, the contribution from glass is often present and can obscure the spectra from the analyte of interest. It is important to understand the nature of glass photoemission properties to control this potential interference. The Raman spectrum of glass is dominated by peaks around 500 and 1000 cm^{-1} at the excitation with UV and visible light. A strong broad emission band centered at 880 nm appears when glass is irradiated with near-infrared light, a popular 785 nm laser light in particular. We proved experimentally in this study that this broad band is due to glass photoluminescence and not Raman scattering. In addition, three narrow components were found to contribute to this band, which have different excitation profiles indicating that they originate from three different species or the same species experiencing three different types of local environments. It has been hypothesized that these peaks could be due to the presence of rare earth impurities in the glass. Further study is necessary to identify these luminescent centers.

Keywords

Luminescence, Raman spectroscopy, glass, glass properties, near-infrared, NIR

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Introduction

Glass is often used in spectroscopy as a sample holder or substrate. The emission spectra of glass is very well understood when excited with visible light, but as the excitation wavelength lengthens to the infrared range, the spectrum of glass develops a large spectral feature centered at 880 nm. Research into the identity of this spectral feature is lacking, although it has been labeled as fluorescence in several publications.^{1–3} The goal of this paper is to probe this spectral feature and determine whether it is due to Raman scattering or luminescence.

Silicon dioxide glass is an amorphous material with no long-range translational symmetry.⁴ The material that is commonly referred to simply as glass belongs to a class of materials known as silicates.⁵ The structural core of silicates are the interconnected SiO_4 tetrahedra.⁶ The solid state glass structure occurs when the SiO_4 tetrahedra are chemically bound together in the fashion of a polymer without forming the repeating unit cells of a crystal.⁵ Unlike a distinct chemical compound, SiO_2 glass is not a material of unique stoichiometry or solid state structure. Other elements such as B, P, Ti, or Fe can be present as impurities at

stoichiometrically significant amounts and reside in the position normally occupied by Si in the SiO_4 tetrahedra.⁷ Furthermore, there can be other chemical species present such as H_2O , O_2 , OH^- , or N_2 that alter the solid state structure of the glass and thus its physical properties. The presence of elemental or chemical impurities and solid state structural defects such as dangling bonds can affect the degree of polymerization of the SiO_4 tetrahedra and the coordination of O atoms around the central Si or other elemental impurity.⁷ Elemental and chemical impurities along with structural defects affect the solid state structure and the spectroscopic properties of SiO_2 glass.

Silicate glasses have been extensively studied by Raman spectroscopy.⁸ The Raman spectrum of noncrystalline SiO_2 glass consists of broad bands caused by inelastic light scattering from phonons throughout the Brillouin zone.⁹

¹Department of Chemistry, University at Albany, Albany, USA

²Horiba Scientific, Piscataway, USA

Corresponding author:

Igor K. Lednev, University at Albany State University of New York, 1400 Washington Ave., Albany, NY 12222, USA.

Email: ilednev@albany.edu

The selection rules for Raman scattering of crystalline materials dictate that only those phonons at the Brillouin zone center will be Raman active. However, when a material is disordered and there is no long-range translational symmetry, those selection rules are relaxed and phonons throughout the Brillouin zone are Raman active.⁹ The Raman spectrum of an amorphous or disordered material will often look very much like the phonon density of states of the same compound.⁹ Consequently, the Raman spectrum of SiO₂ glass consists of broad bands associated primarily with the stretching and angle bending modes of the structurally varying SiO₄ tetrahedra.⁷ The spatially varying degrees of Si to O coordination determined by the number of bridging oxygens in the polymer network also contribute to the broadness of the Raman bands (Fig. 1).⁹

A Raman spectrum of SiO₂ glass consists primarily of first-order Raman bands in the region from approximately 200 to 1200 cm⁻¹.¹⁰ The vibrational analysis of the glass spectra are of course imprecise, however general but reasonable assignments of bands to vibrational modes can be made.⁸ The cluster of bands below 600 cm⁻¹ has been attributed to the presence of Si–O–Si and oxygen breathing modes.^{8,10} Those bands between approximately 900 and 1200 cm⁻¹ have been assigned to antisymmetric stretching modes of the SiO₄ tetrahedra.¹⁰ Beyond 1200 cm⁻¹, the next occurrence of bands of moderate strength occurs between 2300 and 2900 cm⁻¹. It is expected that the appearance of these bands can be attributed to some degree to overtones of the fundamental band around 1150 cm⁻¹ (second-order Raman scattering).¹⁰ These spectral features are commonly observed when using visible blue, green, or even red excitation. However, a different spectrum emerges when using 785 nm excitation.³

The use of 785 nm excitation yields a spectrum consisting of the aforementioned Raman bands; however, a very

intense broad band consisting of at least four spectral components extending from approximately 1000 to 2300 cm⁻¹ now appears. This broad band is absent in spectra acquired with 532 and 633 nm excitation from the same glass sample.³ In fact, this dominant spectral feature apparently only appears in the Raman spectrum when excited with long wavelength radiation in the 780 nm wavelength region. Plotting the 785 nm excited Raman spectrum on an absolute wavelength scale reveals that the aforementioned 1000 to 2300 cm⁻¹ band of the Raman shift scale appears at absolute wavelengths between approximately 850 and 950 nm.

The overwhelming strength of this band and its appearance only when excited with light from a particular region of the near-infrared (NIR) suggest that it may well arise from photoluminescence and not Raman scattering, although a resonance enhancement of Raman scattering might potentially explain the appearance of this band at NIR excitation only. A simple and straightforward experiment involving a tunable excitation would be sufficient to clarify this dilemma, but an instrument with this capability is not easily available. We used a special experimental configuration involving a handheld Raman instrument and an external tunable laser source for this experiment.

Materials and Methods

Samples

The two samples used were a .5-in. piece of Teflon and a block of five glass slides (Fisher Scientific) taped together in order to give thickness. Both samples were cleaned with ethanol to remove any residues before spectral measurements. Aluminum tape masks were put on both samples. The aluminum foil mask had a pin hole in it to help position

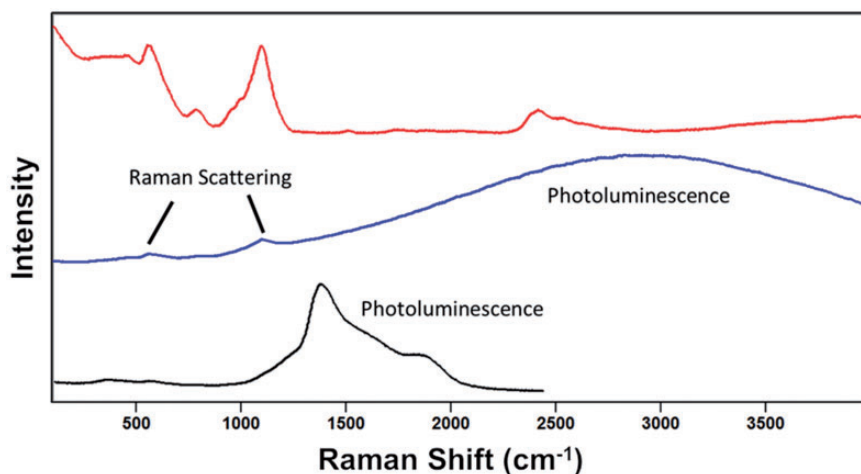


Figure 1. Raman spectra of glass microscope slide obtained using excitation wavelengths of 532 nm (red spectrum), 638 nm (blue spectrum), and 785 nm (black spectrum). Copyright 2016 with permission from Wrights Media.³

the focused laser beam on the sample and make sure the spectrometer is collecting emitted (photoluminescence and/or Raman scattering) light from the correct spot on the sample.

Instrumentation and Experimental Setup

An Indigo S tunable Ti sapphire laser (Positive Light) was used as the external laser in a range from 758 to 785 nm. A Cbex Handheld Raman instrument (Snowy Range) was used as the detector. The laser power of the Cbex laser was set to zero so its laser did not interfere. The lasers and detector were set up as shown in Fig. 2.

One second accumulations were taken of the Teflon at the excitation with the tunable laser at 785 nm and 775 nm. One second accumulations were taken of the glass at the excitation with the tunable laser at 785, 775, 764.9, and 758 nm. The instrument response was assumed to not change significantly over the small region measured.

Results and Discussion

Raman spectroscopy is based on the inelastic light scattering, and Raman shift is for the most part independent on the wavelength of the incident light used. Elastic light scattering is also known as the Rayleigh scattering and occurs at the wavelength of the incident light. So if the incident wavelength is changed, the wavelengths of the Rayleigh, Stokes, and anti-Stokes Raman scattering also change. Normally, Raman shift is plotted instead of absolute wavelength to make Raman spectra taken with different incident wavelengths comparable. However, if two Raman spectra of the same compound were taken at two different excitation wavelengths and the scattered light intensity is plotted against an x-axis of absolute wavelength, the Raman peaks would have appeared to shift from one spectrum to the other.

Photoluminescence is often seen in Raman spectra as an annoying byproduct, as it is not the result of scattered photons. The wavelength of a photon that is the result of photoluminescence is independent of the wavelength of the

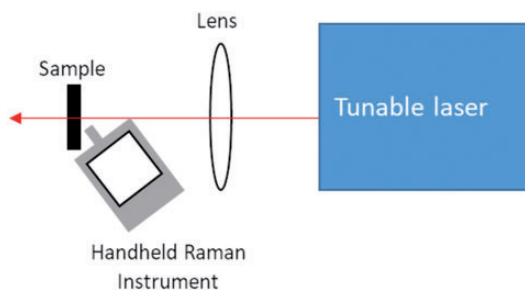


Figure 2. Experimental setup of a tunable laser, handheld Raman instrument, and the sample.

incident photon in most cases. Therefore, if two different incident wavelengths are used to create photoluminescence, there will be no peak shift in the resulting spectra. The purpose of this experiment was to show that the emission peak between 850 and 950 nm that appears when glass is irradiated with a laser light of 785 nm is due to photoluminescence and not due to Raman scattering. This was done by taking spectra of glass and Teflon at various excitation wavelengths. Teflon was used as a control. First, spectra at two different excitation wavelengths were taken of Teflon. The Raman spectrum of Teflon is well documented with peaks at around 731, 1216, 1300, and 1380 cm^{-1} .¹¹ In absolute wavelength values, these peaks are calculated to appear at 832, 867, 874, and 880 nm for 785 nm excitation and 822, 856, 862, and 868 for an excitation at 775 nm excitation. As can be seen in Fig. 3, the spectrum of Teflon at 785 nm excitation shows all four expected peaks in the range of 820 to 950 nm including those around 832.9 nm and a triplet at 866.6, 874.6, and 880.1 nm. When the incident light wavelength is changed to 775 nm, the peaks shift to lower wavelengths as expected with the main peak at 824.3 nm and the triplet at 857.8, 864.4, and 868.9 nm. The spectra of Teflon are quite noisy due to the non-traditional instrument configuration. However, the peak shift due to the change in incident wavelength is easily seen and demonstrates the point well.

Spectra of glass were taken in a similar way to the Teflon spectra. Additionally, glass spectra were taken at 764.9 nm and 758 nm excitation wavelengths. The emission spectra of glass can be seen in Fig. 4.

Glass shows a relatively narrow emission band centered around 880 nm. By looking at the spectra taken at different excitation wavelengths, it can be seen that there is no

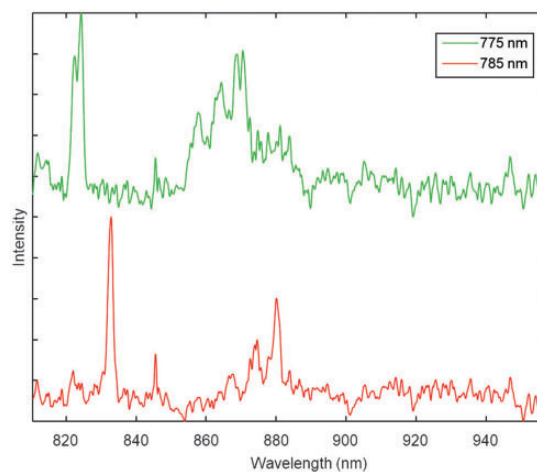


Figure 3. Raman spectra of Teflon at two different excitation wavelengths. Spectra were baseline corrected with an automated weighted least squares algorithm with an order of 3, normalized by total area, and smoothed with a Savitzky–Golay algorithm with a filter width of 15 and a polynomial order of 3.

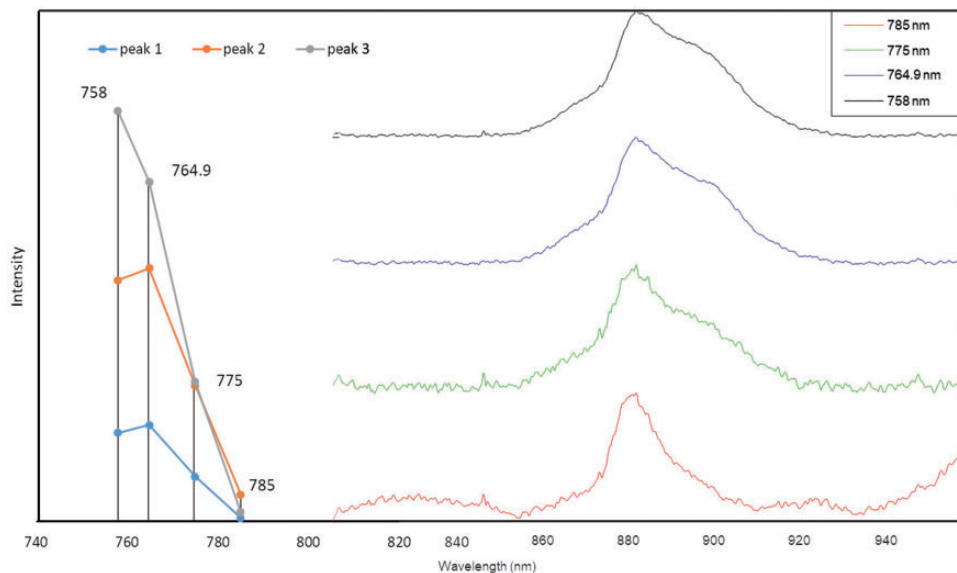


Figure 4. Left are graphed peak height intensities (adjusted for power and accumulation time) of the three fitted peaks (excitation spectra) for various excitation wavelengths. The spectra on the right are of glass obtained at four different excitation wavelengths. Spectra were baseline corrected with an automated weighted least squares algorithm with an order of 3, normalized to total area, and smoothed with a Savitzky–Golay algorithm with a filter width of 15 and a polynomial order of 3.

Table I. Position, width, and height for the three fitted peaks in Fig. 5.

Wavelength	Peak 1			Peak 2			Peak 3		
	Position (nm)	Width (nm)	Height	Position (nm)	Width (nm)	Height	Position (nm)	Width (nm)	Height
758 (196 mW)	867	15	0.010	881	9.32	0.0028	891	28	0.0048
764.9 (222 mW)	868	15	0.0011	881	10.17	0.0030	892	27	0.0040
775 (232 mW)	866	15	0.0053	880	10.49	0.0016	892	28	0.0016
785 (240 mW)	867	7	0.000045	880	10.18	0.00032	890	14	0.00011

shifting of the main peak at about 880 nm as is seen in Teflon. The main peak was the most evident at an incident light wavelength of 785 nm, but when the other excitation wavelength is used, several smaller peaks start to appear. As the incident wavelength shifts to smaller wavelengths, another emission band centered around 890 nm is evident. Gaussian peak fitting was used to visualize this and another smaller peak around 865 nm. Peak fitting was done using GRAMS/AI software with a three-peak constraint. The fitting also shows that the peak around 890 nm cm^{-1} does not shift (and is therefore due to photoluminescence) and increases in intensity as the incident wavelength decreases. Fitting with three peaks was sufficient to approximate well the shapes of spectra obtained at various excitation wavelengths as shown in Fig. 4. Table I summarizes the obtained fitting parameters. There are three peaks present, the first around 867 nm, the next around 880 nm, and the last around 890 nm. The peak positions and widths do not change much with excitation wavelength and shows that we are fitting the

photoluminescent curve with the same peaks for each excitation. The width does change noticeably at 785 nm excitation, but this is also accompanied by a decrease in peak height by an order of magnitude. This width decrease could be because these peaks are relatively small at the 785 nm excitation and their fitting is not as accurate.

We plotted the peak height as a function of the excitation wavelength in the left part of Fig. 4 to characterize the excitation profile for each peak. These profiles have different shapes that should indicate a different nature of the photoluminescent centers responsible for each of the three peaks. Alternatively, these could be the same centers experiencing three different types of local environments or the conformation of the matrix around them.

Again, the fitting results show that three narrow bands with different excitation profiles contribute to the glass luminescence spectrum at NIR excitation. While no one has shown that the spectral feature we present is in fact three overlapping luminescent bands, it has been hypothesized by

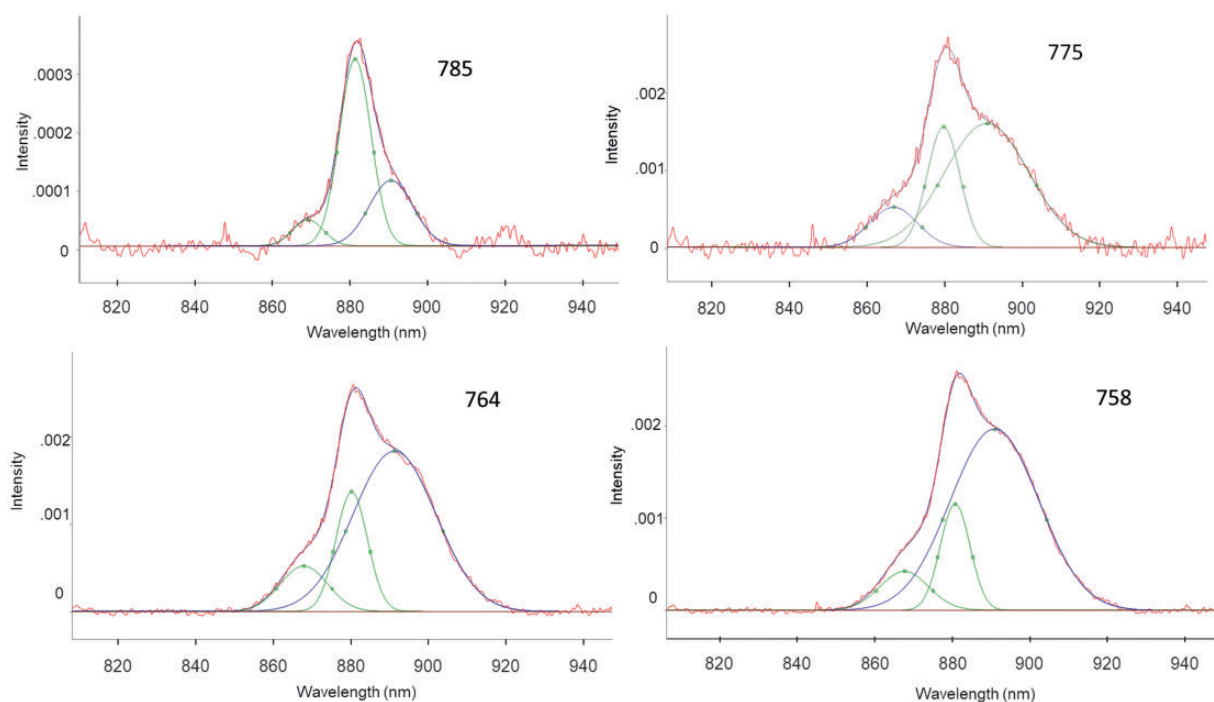


Figure 5. Fitting of the glass spectra with three peaks after preprocessing and the position, width, and height of all the peaks. Height has been adjusted for power and accumulation time.

Kamemoto et al. that this feature is the result of trace amounts of rare earth ions in the glass.¹² Rare earth impurities in glass are known to fluoresce, with the peak positions dependent on the identity of the rare earth ion as well as the ion's local environment (i.e., amount of cross-linking, presence of other ions) and excitation wavelength. The peaks seen in Fig. 5 could be caused by different ions or ions in different environments.^{1,4,13} However, rare earth elements have been shown to have very narrow absorbance bands in other matrixes (NIST SRMS 1920a, 2035, 2036, and 2065). One can speculate that the inhomogeneous broadening, due to coupling of the d orbitals of the rare earth to oxygen atoms in the matrix, can play a role here, but obviously more work must be done to conclude that rare earth impurities are the source of the observed wide luminescence bands. It would be interesting to investigate further the nature of the fluorescent centers responsible for these bands and the identity of the ions potentially causing this photoluminescence, but these questions are beyond the scope of this paper. Additionally, since only one type of glass slide from a single manufacturer was used in our paper, more and varied glass sources should be tested. This should include different types of glasses (i.e., borosilicate, phosphate) and other clear substrates (i.e., quartz).

Conclusion

We proved experimentally here that the wide band centered around 880 nm that appears when glass is irradiated

with 785 nm incident light is due to photoluminescence and not due to Raman scattering. To do this, glass and a Teflon standard were irradiated with different incident wavelengths. The resulting spectra plotted in absolute wavelength showed that the Teflon Raman bands shifted when the incident wavelength was shifted, while the glass band did not shift. This shows that this band from glass is the result of photoluminescence, which has only been speculated on before. Upon further investigation, three components were found to contribute to the band centered at 880 nm. These three overlapping peaks have different excitation profiles indicating that they originate from different species or the same species experiencing three different types of local environments. It has been hypothesized¹² that these peaks could be due to the presence of rare earth impurities in the glass. Further study is necessary to identify these photoluminescent centers.

Conflict of Interest

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ORCID iD

Igor K. Lednev  <https://orcid.org/0000-0002-6504-531X>

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