



HAL
open science

Temperature dependence of luminescence for different surface flaws in high purity silica glass

Jessica Fournier, Pierre Grua, Jérôme Néauport, Evelyne Fargin, Veronique Jubera, David Talaga, André del Guerzo, Guillaume Raffy, Stéphane Jouannigot

► To cite this version:

Jessica Fournier, Pierre Grua, Jérôme Néauport, Evelyne Fargin, Veronique Jubera, et al.. Temperature dependence of luminescence for different surface flaws in high purity silica glass. *Optical Materials Express*, 2013, 3 (1), pp.1-10. 10.1364/OME.3.000001 . hal-00806313

HAL Id: hal-00806313

<https://hal.science/hal-00806313>

Submitted on 11 Apr 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Temperature dependence of luminescence for different surface flaws in high purity silica glass

J. Fournier,^{1,2,3,*} P. Grua,¹ J. Néauport,¹ E. Fargin,^{2,3} V. Jubera,^{2,3} D. Talaga,^{3,4}
A. Del Guerso,^{3,4} G. Raffy,^{3,4} and S. Jouannigot⁵

¹Commissariat à l'Energie Atomique, Centre d'Études Scientifiques et Techniques d'Aquitaine,
BP2, F-33114, Le Barp, France

²CNRS, Université de Bordeaux, ICMCB, 87 Avenue du Dr. A. Schweitzer, Pessac, F-33608, France

³Univ Bordeaux, ISM, UMR 5255, 351 Cours de la Libération, 33400 Talence, France

⁴CNRS, ISM, UMR 5255, 351 Cours de la Libération, 33400 Talence, France

⁵Laboratoire des Composites Thermo-Structuraux, 3 Avenue de la Boétie, 33600 Pessac, France
*fargin@icmcb-bordeaux.cnrs.fr

Abstract: In situ temperature dependence of the Photoluminescence under 325nm irradiation is used to investigate defect populations existing in different surface flaws in high purity fused silica. Five photoluminescence bands peaking at 1.9, 2.1, 2.3, 2.63 and 3.11 eV have been detected in the spectral area ranging from 1.6 up to 3.6 eV. The Gaussian deconvolution of spectra allows dividing the five luminescence bands in two categories. The former corresponds to bands showing a significant intensity enhancement while temperature decreases; the latter corresponds to bands remaining insensitive to the temperature evolution. Such a behavior brings new information on defects involved in laser damage mechanism at 351 nm in nanosecond regime.

©2012 Optical Society of America

OCIS codes: (140.3330) Laser damage; (180.2520) Fluorescence microscopy.

References and links

1. W. H. Lowdermilk, "Status of the National Ignition Facility project," Proc. SPIE **3047**, 16–37 (1996).
2. M. L. André, "Status of the LMJ project," Proc. SPIE **3047**, 38–42 (1996).
3. N. Bloembergen, "Role of cracks, pores, and absorbing inclusions on laser induced damage threshold at surfaces of transparent dielectrics," Appl. Opt. **12**(4), 661–664 (1973).
4. J. Fournier, J. Néauport, P. Grua, E. Fargin, V. Jubera, D. Talaga, and S. Jouannigot, "Evidence of a green luminescence band related to surface flaws in high purity silica glass," Opt. Express **18**(21), 21557–21566 (2010).
5. L. Skuja, "Optically active oxygen-deficiency-related centers in amorphous silicon dioxide," J. Non-Cryst. Solids **239**(1-3), 16–48 (1998).
6. L. Vaccaro, M. Cannas, and R. Boscaino, "Phonon coupling of non-bridging oxygen hole center with the silica environment: Temperature dependence of the 1.9 eV emission spectra," J. Lumin. **128**(7), 1132–1136 (2008).
7. N. Trukhin and K. M. Golant, "Absorption and luminescence in amorphous silica synthesized by low-pressure plasmachemical technology," J. Non-Cryst. Solids **353**(5-7), 530–536 (2007).
8. Y. Sakurai and K. Nagasawa, "Excitation energy dependence of the photoluminescence bands at 2.7 and 4.3 eV in silica glass at low temperature," J. Non-Cryst. Solids **290**(2-3), 189–193 (2001).
9. J. Néauport, P. Cormont, L. Lamoignon, C. Ambard, F. Pilon, and H. Bercegol, "Concerning the impact of polishing induced contamination of fused silica optics on laser induced damage density at 351 nm," Opt. Commun. **281**(14), 3802–3805 (2008).
10. L. Vaccaro, M. Cannas, and R. Boscaino, "Phonon coupling of non-bridging oxygen hole center with the silica environment: Temperature dependence of the 1.9 eV emission spectra," J. Lumin. **128**(7), 1132–1136 (2008).
11. H. Nishikawa, T. Shiroshima, R. Nakamura, Y. Ohki, K. Nagasawa, and Y. Hama, "Photoluminescence from defect centers in high-purity silica glasses observed under 7.9-eV excitation," Phys. Rev. B Condens. Matter **45**(2), 586–591 (1992).
12. H. Nishikawa, T. Shiroshima, R. Nakamura, Y. Ohki, K. Nagasawa, and Y. Hama, "Photoluminescence from defect centers in high-purity silica glasses observed under 7.9-eV excitation," Phys. Rev. B Condens. Matter **45**(2), 586–591 (1992).
13. M. Kalceff, "Cathodoluminescence microcharacterization of the defect structure of irradiated hydrated and anhydrous fused silicon dioxide," Phys. Rev. B **57**(10), 5674–5683 (1998).

14. Y. Sakurai and K. Nagasawa, "Green photoluminescence in γ -irradiated oxygen-surplus silica glass," *J. Appl. Phys.* **86**(3), 1377–1381 (1999).
15. M. R. Kozlowski, C. L. Battersby, and S. G. Demos, "Luminescence investigation of SiO₂ surfaces damaged by 0.35 μ m laser illumination," *Proc. SPIE* **3902**, 138–144 (2000).
16. S. G. Demos, M. Staggs, K. Minoshima, and J. Fujimoto, "Characterization of laser induced damage sites in optical components," *Opt. Express* **10**(25), 1444–1450 (2002).
17. H. Nishikawa, E. Watanabe, D. Ito, Y. Sakurai, K. Nagasawa, and Y. Ohki, "Visible photoluminescence from Si clusters in γ -irradiated amorphous SiO₂," *J. Appl. Phys.* **80**(6), 3513–3517 (1996).
18. Y. Sakurai, "Photoluminescence band near 2.2 eV in γ -irradiated oxygen-deficient silica glass," *J. Non-Cryst. Solids* **342**(1-3), 54–58 (2004).
19. Y. Sakurai, "Effect of thermal heat treatment on oxygen-deficiency-associated defect centers: relation to 1.8 eV photoluminescence bands in silica glass," *J. Appl. Phys.* **95**(2), 543–545 (2004).
20. H. Nishikawa, R. Tohmon, Y. Ohki, K. Nagasawa, and Y. Hama, "Defects and optical absorption bands induced by surplus oxygen in high purity synthetic silica," *J. Appl. Phys.* **65**(12), 4672–4678 (1989).
21. M. Guzzi, M. Martini, M. Mattaini, F. Pio, and G. Spinolo, "Luminescence of fused silica: observation of the O₂⁻ emission band," *Phys. Rev. B Condens. Matter* **35**(17), 9407–9409 (1987).
22. L. Skuja, "Direct singlet-to-triplet optical absorption and luminescence excitation band of the twofold-coordinated silicon center in oxygen-deficient glassy SiO₂," *J. Non-Cryst. Solids* **167**(3), 229–238 (1994).
23. C. Giansante, G. Raffy, C. Schäfer, H. Rahma, M.-T. Kao, A. G. L. Olive, and A. Del Guerso, "White-light-emitting self-assembled nanofibers and their evidence by microspectroscopy of individual objects," *J. Am. Chem. Soc.* **133**(2), 316–325 (2011).
24. J. Fournier, PhD thesis (University of Bordeaux, 2011).
25. T. A. Laurence, J. D. Bude, N. Shen, T. Feldman, P. E. Miller, W. A. Steele, and T. Suratwala, "Metallic-like photoluminescence and absorption in fused silica surface flaws," *Appl. Phys. Lett.* **94**(15), 151114 (2009).
26. L. N. Skuja and A. N. Trukhin, "Comment on 'Luminescence of fused silica: observation of the O₂⁻ emission band'," *Phys. Rev. B Condens. Matter* **39**(6), 3909–3911 (1989).
27. K. Ramseyer and J. Mullis, "Factors influencing short-lived blue cathodoluminescence of α -quartz," *Am. Min.* **75**, 791–800 (1990).
28. M. Leone, R. Boscaino, M. Cannas, and F. M. Gelardi, "Low temperature photoluminescence spectroscopy relationship between 3.1 and 4.2 eV bands in vitreous silica," *J. Non-Cryst. Solids* **216**, 105–110 (1997).
29. Y. Sakurai, "The 3.1 eV photoluminescence band in oxygen-deficient silica glass," *J. Non-Cryst. Solids* **271**(3), 218–223 (2000).
30. M. Kohketsu, K. Awazu, H. Kawazoe, and M. Yamane, "Photoluminescence centers in VAD SiO₂ glasses sintered under reducing or oxidizing atmospheres," *Jpn. J. Appl. Phys.* **28**(Part 1, No. 4), 615–621 (1989).

1. Introduction

High purity silica glasses are widely used in various high-tech applications, especially in the manufacturing of UV optics used in high power laser facilities, such as NIF [1] or LMJ [2]. Fused silica exhibits large transparency from IR to UV as well as a high bulk damage threshold at 351 nm. Despite these qualities, laser damage can appear at fluences of a few J/cm² at 351 nm in nanosecond regime thus limiting lifetime of these laser optical components. Therefore, lots of efforts are made in order to understand damage mechanisms. Subsurface fractures induced by the polishing process are commonly admitted to be laser damage precursors [3], nevertheless the origin of absorption triggering damage on such defects remains to be established.

In this paper, we investigate the evolution of photoluminescence with temperature on various surface flaws using confocal microscopy. We have chosen excitation energy of 3.8 eV, close to the photon energy of 3.5 eV which is associated with the wavelength of 351 nm. Such an excitation wavelength is retained because the laser induced damage mechanisms we want to study occur at 351 nm. Two types of surface flaws on polished fused silica samples are considered: indentation and laser damage sites. Our aim is to obtain temperature dependent spectra in order to improve the description of fused silica defects and their links with luminescence bands. It must be noted that more bands could be involved in the deconvolution of spectra, but our choice is closely related with the dispersion of experimental results; in fact we have retained only bands having a systematic occurrence. For indentations as well as laser damage sites, we have previously reported that photoluminescence experiments using single excitation energy of 3.8 eV give rise to 5 bands, centered at 1.9, 2.1, 2.3, 2.7 and 3.1 eV in the 1.6-3.6 eV spectral range [4]. For both types of flaws, we herein

report experimental results on the thermal behavior of luminescence spectra, in the 90 K-300 K temperature range.

A brief outline of the actual knowledge upon thermal behavior of these luminescence spectra can be drawn through a comparison between several experimental results found in literature.

The evolution of the 1.9 eV band, attributed to the NBOHC (Non Bridging Oxygen Hole Center [5]), has been studied by Vaccaro *et al.* in photoluminescence experiments [6]. For the two excitation energies, being of 2.17 eV and 4.77 eV, they have shown an increase of this band intensity by a factor superior to 4 as temperature decreases from 300 K to 4 K. In a previous paper [4], we have reported the existence of a green luminescence band at 2.3 eV, which was observed in different surface flaws. According to the literature, the 2.3 eV band could be due to the STE (Self Trapped Exciton) relaxation, this defect having an emission band between 2.2 and 2.6 eV, since it shows a very weak intensity level at room temperature, but much stronger below 150 K [7]. The temperature dependent experiments that we have driven are appropriate in order to validate or invalidate of this hypothesis.

The 2.7 eV band has been described to show different thermal behavior for different excitation wavelength [8]. For 355 nm excitation (3.49 eV), the intensity of this band increases as temperature is shown to decrease, while it increases with temperature for 241-266 nm excitation wavelengths (4.66-5.15 eV). These facts are consistent with the assumed attribution of this band to the ODC(II) defect (Oxygen Deficient Center [5]).

The paper is organized as follows. In Section 2, we describe the sample preparation methods, and the equipment used for confocal luminescence involving the temperature change. Section 3 is devoted to the luminescence spectra and deconvolutions. Results are discussed in Section 4 and conclusions are drawn in Section 5.

2. Experimental arrangement

2.1 Sample preparation methods

Experiments were conducted on 10 mm diameter-4 mm thick high purity super polished fused silica samples. Samples were polished with a process ensuring low cerium content in the silica surface [9]. Indentations and laser damage surface flaws were generated on different samples for further photoluminescence analysis [4]. Before measurements, all the samples were thoroughly cleaned in order to prevent external pollution on studied surfaces and surface flaws, which could interact with the excitation radiation. The methods used to clean samples, make indentations and laser damage are detailed elsewhere [4].

2.2 Photoluminescence confocal microscopy

Photoluminescence spectra were carried out on a LABRAM HR-800 spectrometer, a high resolution Raman spectrometer with luminescence confocal microscopy capabilities [4]. Luminescence is excited by a continuous laser at 325 nm (3.82 eV) from 93 K to 293 K. To make these measurements, we have used a nitrogen cooled watertight plate (LINKAM). Before decreasing temperature, the system is purged in order to avoid water condensation during 10 min at 313 K under nitrogen flux. Moreover, it is necessary to wait 10 minutes in order to stabilize the temperature prior to measurement. Spectra are recorded each 20 K step and a ramp of 1 K/min is used to increase temperature. A laser of 1 mW power is used and the pinhole is opened at 300 μm because of the weakness of the luminescence emitted by the samples. For all measurements, the obtained spectra were corrected from the spectral response of the spectrometer and the detector sensibility.

3. Results

3.1 Indentations

The acquisition of luminescence spectra were made on a site located in the central region of an indentation. The 93, 193 and 293 K spectra are presented in Fig. 1(a).

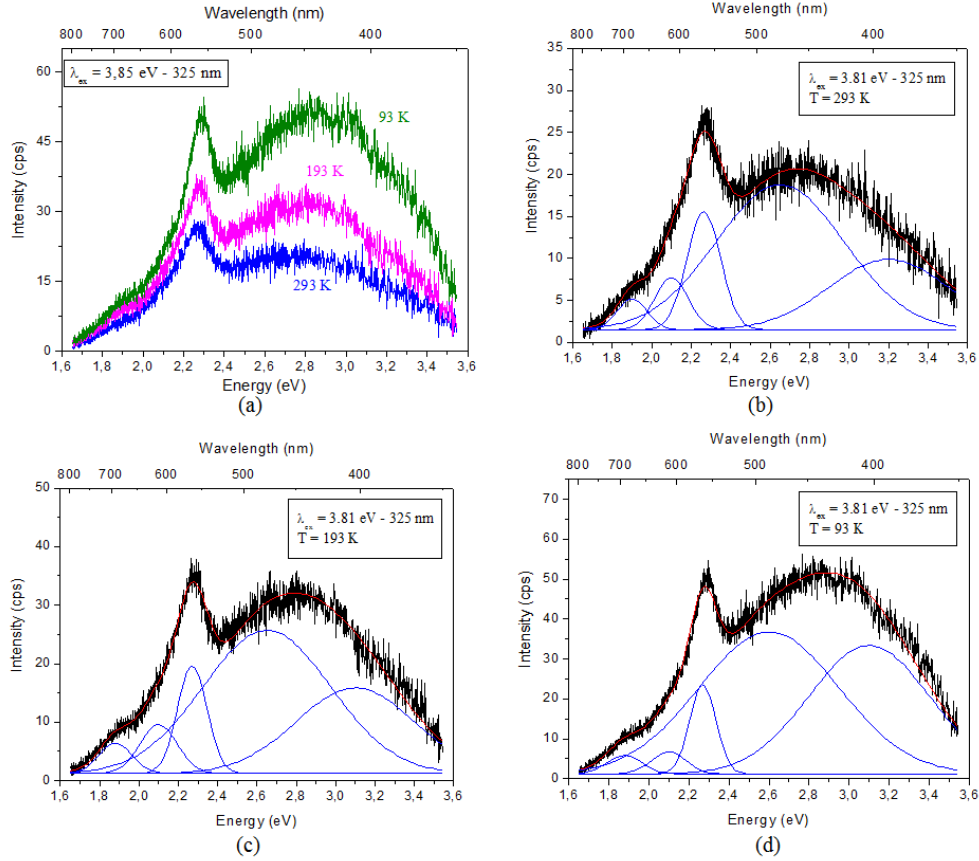


Fig. 1. Photoluminescence spectra for an indentation excited with 3.81 eV photons. (a) comparison of the three spectra, (b) 293 K, (c) 193 K, (d) 93 K. (Experimental signal (black), fitted signal (red) Gaussian components of the fitted signal (blue)).

The spectra present two main contributions: a narrow band peaking at 2.3 eV and a wider one centered on 2.8 eV. This figure reveals also a global increase of luminescence as the temperature decreases. We can observe a change in the intensity ratio between these two main contributions. In order to identify what the predominant effect is, experimental signals were analyzed with a multi-parameter Gaussian function and results of deconvolution are shown in Figs. 1(b), 1(c) and 1(d). The number of components introduced in the fitting model is consistent with the experimental signal reported previously in such silica materials [4]. For the three temperatures, spectra are composed of five bands centered at 1.89 eV (656 nm), 2.10 eV (590 nm), 2.28 eV (551 nm), 2.65 eV (451 nm) and 3.10 eV (400 nm). The corresponding fitting parameters are summarized in Table 1. As no significant displacement or shape of the emission bands can be noticed in this range of temperature as evidenced by Fig. 1(a), we have also considered that the positions and the widths of the bands are constant for each temperature. This method makes possible comparisons between results obtained for indentations and laser damage.

Table 1. Parameters Used for Spectral Deconvolutions of Thermal Dependent Luminescence Reported on Indentations

Position (eV)	FWHM (eV)	Temperature	Surface (a.u.)
1.89	0.19	293 K	0.92
		193 K	1.15
		93 K	1.58
2.10	0.18	293 K	2.10
		193 K	2.26
		93 K	2.43
2.28	0.15	293 K	3.05
		193 K	3.71
		93 K	5.19
2.63	0.55	293 K	11.37
		193 K	16.72
		93 K	25.24
3.11	0.55	293 K	7.87
		193 K	12.07
		93 K	24.40

The spectra presented in Fig. 1 and deconvolution parameters gathered in Table 1 show a strong increase of the highest energy bands (3.1 eV and 2.63 eV) as the temperature decreases. Concerning the three other bands, there is few or no evolution with temperature, especially for the 2.10 eV band. In order to throw into relief these behaviors, we have reported in Fig. 2 the normalized surfaces of each band as functions of temperature, the weight of a band being well characterized by its surface. Because of its stability with respect to temperature, the 2.10 eV band has been chosen as a constant, thus we have normalized the surface of each band by the 2.10 eV band surface. As mentioned before, we can see that there is no significant evolution of the 1.90 and 2.25 eV normalized band intensities with the decrease of temperature. For the 2.63 and 3.11 eV bands, we can observe an increase by a factor 2 of the band surfaces as temperature decreases.

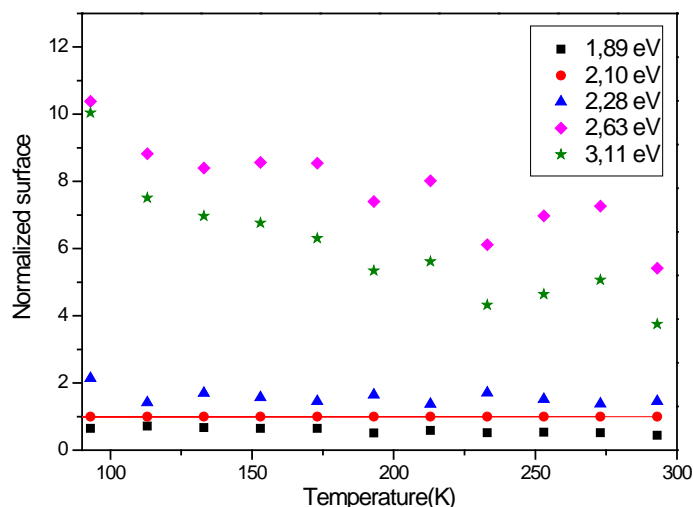


Fig. 2. Normalized surface of each luminescence band as a function of temperature for an indentation.

3.2 Laser damage

The same methodology was used for laser damage sites on similar silica samples. Figure 3(a) shows the luminescence spectra obtained on laser damages for the three temperature values of

293, 193 and 93 K. All spectra are recorded inside the laser damage. Spectra show large variations with temperature. The presence of three main contributions around 1.9, 2.3 and 3.1 eV is observed. We can notice an increase of intensities in 1.9 and 3.1 eV contributions as temperature decreases. On the contrary, the 2.3 eV level does not seem to be influenced by temperature variations. This evolution is similar to the one observed for indentations.

The Gaussian deconvolutions of these spectra are presented in Figs. 3(b), and 3(c) and 3(d) and fitting parameters are summarized in Table 2. The spectra are composed of the 5 bands centered at 1.90 eV (652 nm), 2.10 eV (590 nm), 2.31 eV (537 nm), 2.63 eV (471 nm) and 3.15 eV (393 nm) respectively.

The 2.10 eV band, as for indentations, does not significantly evolve with temperature and will therefore be chosen again as the reference for normalization. The evolutions of normalized surfaces with respect to temperature are reported in Figs. 4(a) and 4(b), pointing out the characteristic behaviors of the 3.15 and 2.63 eV bands. It can be seen that the surface of the 3.15 eV band, the most strongly modified one, is multiplied by a factor 15 as temperature decreases from 293 K to 93 K, while the intensity of the 2.63 eV band is multiplied by 4 for the same temperature change. The 1.90 eV intensity increases slightly in comparison with the two previous bands.

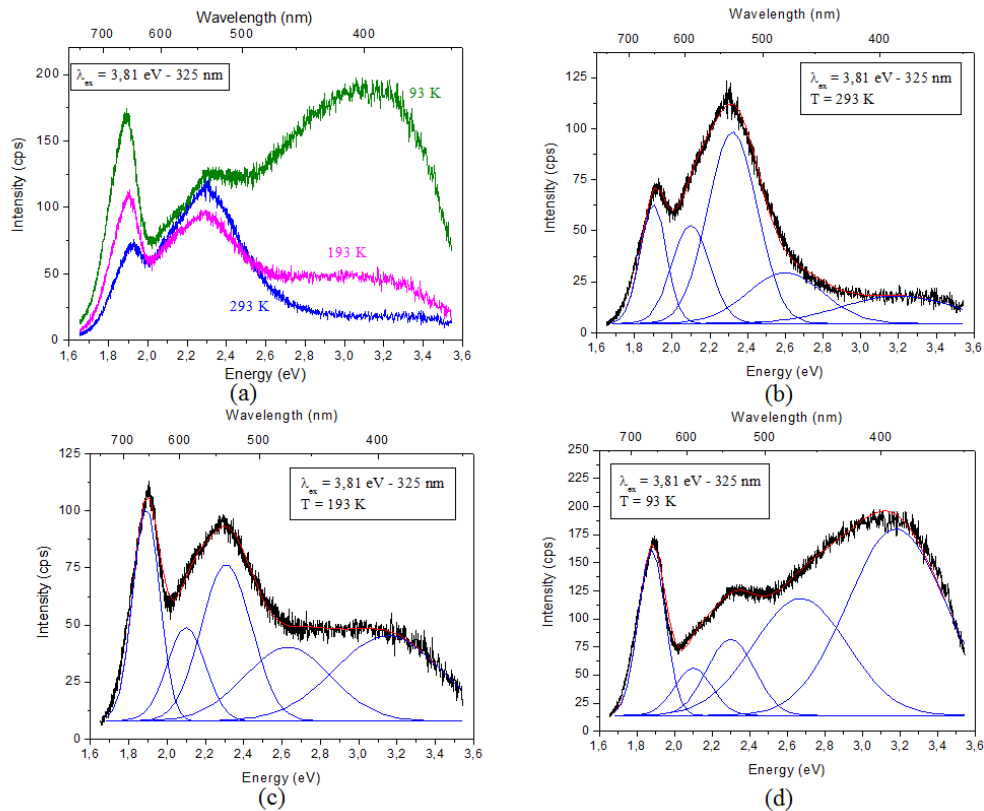


Fig. 3. Photoluminescence spectra for an indentation excited with 3.81 eV photons. (a) comparison of the three spectra. (b) 293 K. (c) 193 K. (d) 93 K. Experimental signal (black), fitted signal (red) Gaussian components of the fitted signal (blue).

Table 2. Parameters Used for Spectral Deconvolutions for the Three Temperatures

Position (eV)	FWHM (eV)	Temperature	Surface
1.90	0.14	293 K	10.43
		193 K	16.55
		93 K	25.99
2.10	0.20	293 K	8.22
		193 K	7.54
		93 K	7.53
2.31	0.30	293 K	35.71
		193 K	25.29
		93 K	23.12
2.63	0.55	293 K	12.00
		193 K	19.54
		93 K	58.63
3.15	0.55	293 K	8.46
		193 K	25.16
		93 K	116.82

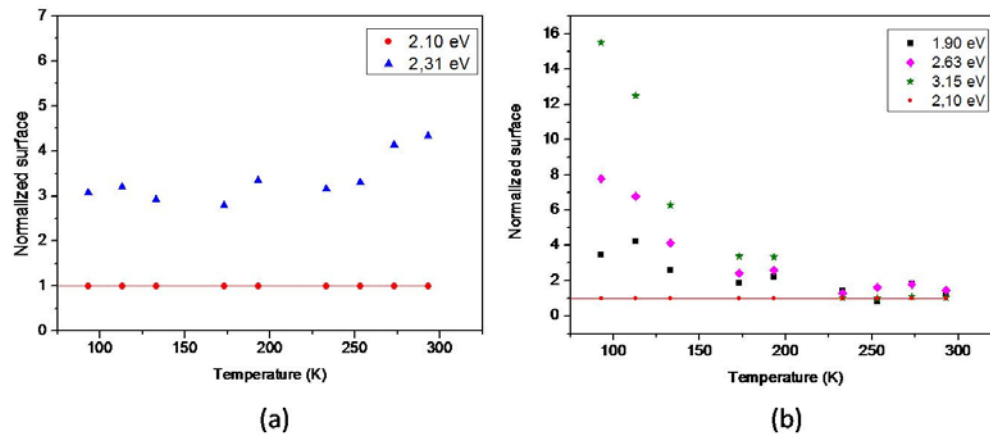


Fig. 4. Normalized surface of each luminescence band as a function of temperature for laser damage on silica materials. (a) 2.10 eV and 2.31 eV band. (b) 1.90, 2.63 and 3.15 eV band.

4. Discussion

Deconvolutions of luminescence spectra for both laser damage and indentations show the presence of five common luminescence bands. The temperature decrease leads to a global increase of luminescence intensity. A detailed analysis shows that some bands are more sensitive than others to temperature variations. In the indentation, the intensities of the 2.6 and 3.1 eV bands increase, in a more pronounced way for the second one. In laser damage, the intensities of three bands peaking at 1.9, 2.63 and 3.15 eV show an intensity enhancement, particularly the 2.63 and the 3.15 eV bands. For the two kinds of flaws, the 2.1 band shows a very strong stability and the 2.3 eV band remains almost unchanged.

4.1 The 1.9 eV band

Concerning indentations the 1.90 eV band does not show a significant evolution as temperature decreases down to 93 K; in laser damage, the surface of this band tends to increase as the temperature decreases, but very weakly. The Vaccaro *et al.* results showing strong changes of the 1.9 eV band intensity with temperature [10], differ substantially from ours. As well as the use of pristine fused silica samples, this is likely due to the selected excitation energies (2.17 and 4.77 eV in their experiments). In fact, the 2.17 and 4.77 eV energies match the well known absorption bands of the NBOHC, whereas the 3.81 eV excitation energy we used is located in the tail of the absorption band of this defect [5], and

the temperature domain they explored was larger (from 4 K to 300 K). Thus, the differences relative to the thermal behavior that we have observed are not in complete contradiction with Vaccaro *et al.* results showing only a weak increase of this band for a 4.77 eV excitation from 300 K down to 100 K. However we cannot totally exclude the involvement of another kind of defect yielding a 1.9 eV luminescence band.

4.2 The 2.1-2.3 eV bands

One hypothesis proposed to interpret the 2.3 eV luminescence band is its attribution to the STE defect. This defect was effectively expected by Nishikawa *et al.* [11], for which the 2.3 eV luminescence was observed under 7.9 eV excitation through two photon absorption mechanism, and Kalceff *et al.* [12] in cathodoluminescence experiments. In the last case, an emission was still observed for defects created under electron beam at 298 K, and seemed to be more intense at 5 K. Contrarily to the well known behavior of STE's, which shows a change of several orders of magnitude for luminescence intensity as temperature varies in the 150-250 K range [13], the present study shows that the 2.3 eV band is very weakly influenced by temperature decrease, from the ambient down to 90 K, for both indentation and laser damage. Hence, such results make the STE hypothesis unconvincing and must be ruled out. This conclusion is in agreement with Kalceff *et al.* [12] who proposed the existence of another defect which could be thermally stabilized at 5 K but would develop to others defects at larger temperature. This hypothesis could explain why in our case, further luminescence characterizations performed two months after the creation of indentation, evidenced a large decrease of this emission, the glass being conditioned at 298K during this time. Moreover on our fresh indentation and laser damage, no evolution of the luminescence is observed for each temperature and during the whole series of characterization.

Other hypotheses are proposed, such as the peroxy radical $\equiv\text{Si-O-O}\uparrow$ defect (the arrow represents an unpaired electron) [14], or the peroxy bond $\equiv\text{Si-O-O-Si}\equiv$ defect which could present an absorption band around 3.8 eV [5]. Those hypotheses cannot be turned down, though no direct link has been proved between the presence of such defects and photoluminescence around 2.3 eV.

Kozlowsky and Demos [15,16] have proposed different hypotheses to explain the presence of a band at ~ 2.25 eV, such as Si clusters or E_{δ}' centers [5]. A particular form of Si cluster, that is the E_{δ}' center, has also been detected by electron spin resonance (ESR) [17]. This defect is expected to be at the origin of the green luminescence band observed by Sakurai on the surface of γ -irradiated oxygen-deficient silica glass [18], or Nishikawa *et al.* [17] in γ -irradiated amorphous silica. It would have a width of about 0.4 eV and a lifetime ~ 20 ns.

Sakurai and Nagasawa [14] have also observed a green luminescence band at 2.25 eV on the surface of γ -irradiated oxygen-surplus silica glass. In this case, the bandwidth and lifetime are respectively given ~ 0.2 eV and ~ 200 ns. A correlative photoluminescence band is observed at 2.10 eV band has been observed, and the authors show that at room temperature this band is not visible but appears as temperature decreases to 20 K. Moreover, this photoluminescence band is also shown to appear after heat treatment at 1323 K of oxygen-deficient silica glass [19]. In this last work, the authors proposed that the luminescence could be due to silicon crystalline nanoparticles.

The oxygen excess samples show an absorption band at 3.8 eV [20], this may be ascribed to the presence of O_2^- ions. For silica, most luminescent defects encountered in the literature are considered to be electrically neutral, but some authors have evocated the possible role of O_2^- interstitial ions [20,21]. Itoh *et al.* [13] proposed the creation of $E'-\text{O}_i^-$ pairs where E' is the well-known paramagnetic defect [5] and O_i^- an mobile oxygen interstitial to explain green luminescence observed in silica glass after an electron pulse irradiation. The study of the influence of other factor like irradiation or acid etching of the surface is in progress to improve our understanding of defects at the origin of this green luminescence and why we observe some evolutions of these defects after a long time (a few months) ageing.

4.3 The 2.63 eV and 3.1eV bands

The 2.63eV band, which is usually attributed to the ODC(II) defect (Oxygen Deficient Center [5]), has shown different thermal behaviors for different excitation wavelengths. Sakurai [8] showed this 2.63 eV band intensity decreases as the temperature decreases for UV excitation energies (4.66 eV, 4.84 eV and 5.15 eV), whereas the opposite behavior is obtained for 3.49 eV excitation. Skuja [22] also showed that the intensity at 2.63 eV decreases with increasing temperature under 375 nm (3.31eV) excitation wavelength, but yields the opposite behavior under 248 nm (5 eV) excitation. These observations are consistent with the assumed attribution of this band to the ODC(II) defect: a non radiative relaxation way takes place after 4.66-5.15 eV excitation to produce a low emission at 2.7 eV. The direct emission in the 3.5-4.7 eV range includes precisely the well known 4.3 eV band, and becomes less efficient as temperature increases, to the profit of the low emission at 2.7eV [5]. According with available data for ODC(II) defect excitation spectrum [5], the nearest transition leading to direct emission centred at 2.7eV is a forbidden excitation centred at 3.15 eV between the singlet ground state and the first triplet state, which could explain the inverse temperature behaviour of the emission around 2.63eV band observed under 375nm (3.31eV) excitation. This interpretation would be in accordance with the temperature evolution we observe for this band from laser damage and indentation under 3.82eV (325nm) excitation, though this energy is already far from the required 3.15 eV excitation energy.

Moreover, the oscillator strength of this transition is small (about 10^{-7}) and is expected to give rise to a very weak luminescence signal. For comparison 3.82 eV is also situated in the tail of excitation band of NBOHC defect centred at 4.8eV with oscillator strength larger than 10^{-2} . Furthermore, a life time of 10.2 ms is currently admitted for the 2.6 eV emission resulting from ODC (II) defect excitation [5]. However, we performed recent Time-resolved confocal fluorescence microscopy on indentations and laser damage on a set-up previously described [23]. Under pulsed laser excitation at 3.22 eV (385nm) and detecting all the photoluminescence above 405 nm, short-lived emissions with lifetime distributions in the 1-10 ns range [24] were highlighted. These distributions tended to be maximal around 2 ns and 4ns for indentations and laser damage respectively [24]. Laurence *et al.* reported unexpected ultra fast photoluminescence (0.04-5ns) observed under 3.1eV pulsed laser excitation from surface flaws on fused silica [25]. This ultra-fast component could likely be attributed to the 2.63 eV emission band invalidating the ODC(II) defect origin of this luminescence. This would suppose excitation followed by direct emission preserving spin multiplicity without intersystem crossing. For such photoluminescence scheme the emitted intensity usually increases when the temperature decreases.

The correlative 3.1 eV band has first been proposed to be an ODC(II)-type defect built upon a Ge rather than a Si atom, yielding 3.1 eV instead of 2.6 eV luminescence [26]. However, the possibility of Ge implication can be dismissed because of the high purity of our silica samples. Other hypotheses have been formulated elsewhere in order to interpret this band, such as the presence of Al₂O₃ near the surface due to the polishing process [27]. However, we believe that the involvement of Al₂O₃ polishing residues must be ruled out, mainly because of the very strong difference in luminescence intensity between flaws and pristine areas. Finally Skuja [5] suggested this luminescence could be due to ODC(II)-type defect localized on the surface and then in contact with air. Moreover, concerning the evolution of this band, Leone *et al.* [28] have shown that under 248 nm excitation wavelength, the band intensity decreases with temperature decrease, contrarily to our results. Similar observations have been made by Sakurai [29] and Kohketsu [30]. Nevertheless, in these works excitations were made at 4.7 eV, 5 eV, 5.17 eV or 7.7 eV, allowing also a luminescence band at 4.4 eV. Those authors [28,29] have concluded that the 4.4 eV and 3.1 eV bands pertain to the same object, for which the two kinds of electron transitions specified above occur, that is a fast one and a slow one. Hence the change of intensities with temperature was relative to a

balance between the 4.4 eV and 3.1 eV bands; because of the difference in photo excitation energies, these results are not contradictory with ours. In the present results obtained on indentation and laser damage, the thermal behavior of this band and the 2.63 eV band appear correlated, suggesting surface ODC(II)-type defect are at the origin of this photoluminescence, as proposed by Skuja [5].

Very likely, the 2.6 and 3.1 eV emission bands having identical temperature behaviour would derive from the same type of defect electronic transitions which could also invalidate the ODC(II)-type defect origin of this luminescence.

5. Conclusion

Five photoluminescence bands (under 325 nm laser excitation) peaking at 1.9, 2.1, 2.3, 2.63 and 3.11 eV have been detected in the spectral area ranging from 1.6 up to 3.6 eV. Though very low emission was expected for such excitation, we surprisingly obtain the same emission bands already described for VUV excitation [5] or after damage produced by cathodoluminescence [12] or γ irradiation [18,29]. When the temperature increases in the 93 K - 293 K range, both intensities of the 2.63 eV and 3.11 eV emission bands decrease together. The others bands are very little affected by the temperature. If the evolution observed for the 2.63 eV, 3.11 eV and 1.9 eV bands are in agreement with the literature, the attribution to the STE defect of the 2.3 eV band can be firmly invalidated due to the non-evolution of this band with temperature.

Despite the numerous studies concerning the photo luminescence of fused silica in the visible-UV spectral range, a consensus about the \sim 2.2 eV, and 3.1 eV bands is not actually established. Our experiments may bring new insights in order to achieve a better understanding of laser-silica interactions. They also throw into relief the importance of the excitation wavelength on luminescence thermal behavior, and thus emphasize that excitation and absorption spectra are absolutely required in order to elucidate the true defect nature; this is a considerable task and this work is currently in progress. Finally, it seems that one must be very careful for the interpretation of the 2.63 eV band, the width of which in the present work is quite larger than the currently accepted value, and which could be associated to a very fast component of the photoluminescence spectrum.

Acknowledgments

We would like to thank T. Cardinal and A. Garcia for fruitful discussions concerning luminescence spectroscopy, and T. Donval for assistance with laser damage accomplishment.