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# Time resolved photoluminescence associated with non-bridging oxygen hole centers in irradiated silica

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**Abstract**

We report time resolved photoluminescence spectra of irradiated silica under excitation with a laser tunable in the visible and UV range. The investigated samples exhibit the emission band at 1.9 eV associated with non-bridging oxygen hole centers, whose spectral and kinetics properties do not depend on the kind of irradiation (γ, β and neutrons). The 1.9 eV luminescence decay follows a multi-exponential curve with a characteristic lifetime that increases from 8.9 μs to 10.4 μs on increasing the emission energy. This dependence accounts for the blue-shift of the emission band during its decay and is interpreted as due to the inhomogeneous properties of silica leading to a distribution of kinetics features of this defect.


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## 1. Introduction

Radiation induced generation of oxygen dangling bonds in silica is one of the main causes of their transparency loss in visible and UV range [1]; hence, it is particularly relevant in several device applications requiring stable optical transparency such as radioactive environments [2,3]. This defect is usually named non-bridging oxygen hole center (NBOHC) and its structure is denoted by ≡Si–O·, where (≡) stands for bonds with three oxygen atoms and (·) indicates an unpaired electron [4,5]. Optical studies of NBOHC take advantage of its peculiar photoluminescence (PL) at 1.9 eV, associated with several absorption bands centered around 2.0 eV, 4.8 eV and 6.5 eV, whose time decay occurs in ~10 μs [5–7]. In turn, spectral and kinetics features related to this emission are widely investigated to derive spectroscopic parameters (width, stokes shift, quantum yield, lifetime) useful to better clarify the optical properties associated with this defect, both homogeneous arising from the electronic structure and inhomogeneous due to the interaction with the amorphous silica network [8–12].

Acquisition of time resolved PL spectra has been proven to be a unique method to study these properties in conjunction [13–16]. However, most works on this issue are limited to experiments with pulsed lasers working at a specific wavelength, not suitable for a fine-tuning with the excitation spectrum. The purpose of the present paper is to find out the PL of NBOHC using a laser tunable in the visible and UV range and to single out the inhomogeneity effects on the decay kinetics.

## 2. Experimental

We investigated three samples of synthetic wet silica Suprasil 1 (S1), OH content $\sim 5 \times 10^{19}$ cm$^{-3}$, supplied by Heraeus [17], shaped with square surface $5 \times 5$ mm$^2$ optically polished, where NBOHC are induced after exposure to different kinds of radiation:

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- S1/γ (thickness 0.5 mm) irradiated with a γ dose of $2 \times 10^6$ Gy by a $^{60}$Co source (energy $E_\gamma = 1.17$ MeV, $E_\gamma = 1.33$ MeV) at the Dipartimento di Ingegneria Nucleare, Palermo University.
- S1/β (thickness 1 mm) irradiated with a β dose of $5 \times 10^9$ Gy by a Van de Graff electron accelerator ($E_\beta = 2.5$ MeV) at the Laboratoire de Solides Irradiés, Palaiseau, France
- S1/n (thickness 1 mm) exposed to a neutron fluence of $1.6 \times 10^{17}$ n/cm$^2$ at TRIGA MARK II reactor ($E_n > 3.5$ MeV), at LENA laboratory, Pavia University.

For all these irradiations the penetration depth in silica is much larger than the samples thickness [3]. Hence, NBOHC are expected to be uniformly distributed in our samples and their concentration, measured on the basis of the absorption coefficient at 2.0 eV [11], is $(2.4 \pm 0.6) \times 10^{17}$ cm$^{-3}$ in S1/γ, $(4.1 \pm 0.5) \times 10^{18}$ cm$^{-3}$ in S1/β and $(2.7 \pm 0.5) \times 10^{18}$ cm$^{-3}$ in S1/n.

PL time resolved experiments were performed using the following set up. The excitation light is provided by a pulsed laser VIBRANT OPOTEK (pulse width ~5 ns, repetition rate 10 Hz) tunable in the range 210–2400 nm. In the present work the laser wavelength was varied from 510 nm to 690 nm and from 210 nm to 350 nm, the pulse energy being maintained to be 0.5 mJ and 0.2 mJ in the two ranges, respectively. Samples were mounted in the holder in the so-called 45° back-scattering geometry and were excited uniformly along their thickness by the laser beam (spot size ~1 mm$^2$). The emitted light was spectrally resolved by a monochromator equipped with a grating with 300 grooves mm$^{-1}$ and 500 nm blaze, and then acquired by an intensified charge coupled device camera driven by a delay generator setting the acquisition time window $W_T$ and the delay $T_D$ with respect to the arrival of laser pulse. All spectra were detected with a 10 nm bandwidth and corrected for the monochromator dispersion.

## 3. Results

Fig. 1 shows time resolved spectra of the PL at 1.9 eV acquired in the S1/n sample under pulsed excitation at $E_{exc} = 4.77$ eV and $E_{exc} = 2.07$ eV, with $W_T = 1$ μs and $T_D$ ranging up to 80 μs. Regardless $E_{exc}$, we observe that the PL decay is almost completed over 80 μs, and the emission peak shifts towards higher energies on increasing $T_D$.

To better evidence the PL lineshape evolution, decay kinetics monitored at different emission energies are reported in Fig. 2(a) and (b) for the two excitation energies. All curves are described by a not-single exponential function, and their decay gets slower on increasing $E_{em}$, regardless the excitation. The lifetime τ, measured as the time necessary to reduce the PL intensity to $1/e$, increases from $\tau = 9.0 \pm 0.3$ μs ($E_{em} = 1.77$ eV) to $\tau = 10.4 \pm 0.3$ μs ($E_{em} = 1.94$ eV) under $E_{exc} = 4.77$ eV and from $\tau = 8.6 \pm 0.3$ μs ($E_{em} = 1.77$ eV) to $\tau = 9.9 \pm 0.3$ μs ($E_{em} = 1.94$ eV) under $E_{exc} = 2.07$ eV. In the inset are plotted the PL lineshapes recorded at different $T_D$ from 1 μs to 75 μs, that indicate a monotonous blue-shift during the decay: from $1.90 \pm 0.01$ eV to $1.93 \pm 0.01$ eV under $E_{exc} = 4.77$ eV and from $1.91 \pm 0.01$ eV to $1.94 \pm 0.01$ eV under $E_{exc} = 2.07$ eV.

Time resolved spectra detected in the S1/γ and S1/β samples show analogous features. In fact, for each $E_{em}$, we measure similar lifetimes, regardless the sample and the excitation energy. The emission dependence of lifetime is reported in Fig. 3, where the bar length accounts for the dispersion of measured values and is comparable with our experimental uncertainty.

Finally, we address to the excitation dependence of time resolved spectra. In Fig. 4 we report the integrated intensity of PL band detected as a function of excitation energy for three different $T_D$; the curves are normalized to their maximum amplitude both in the visible and UV range. The excitation PL profile results to be independent on $T_D$ over the two investigated ranges. The visible excitation shows a

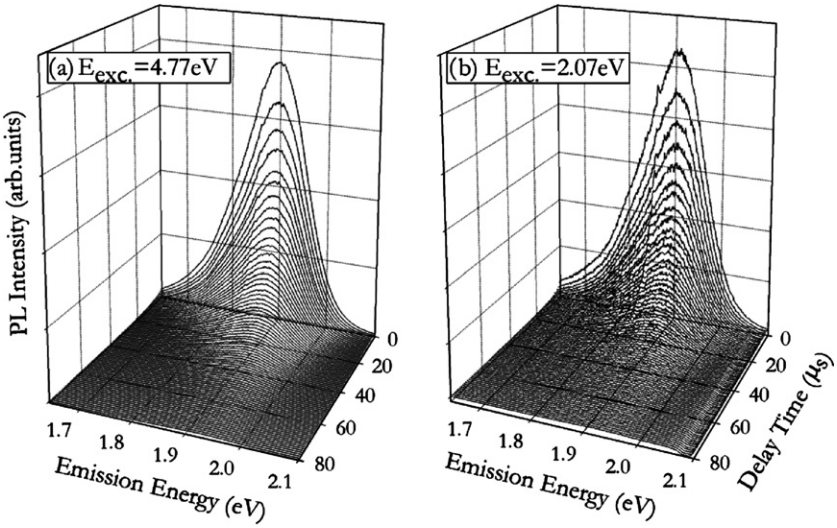


Fig. 1. Time resolved PL spectra acquired at different delays in S1/n sample under excitation at 4.77 eV (a) and 2.07 eV (b).

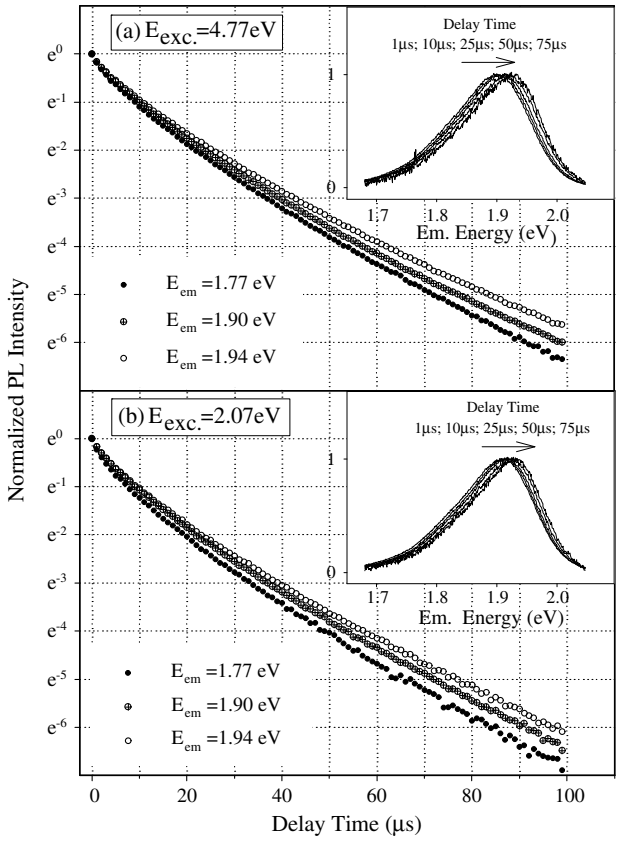


Fig. 2. Semilog plot of the PL decay in S1/n sample excited at 4.77 eV (a) and 2.07 eV (b) and measured at three different emission energies. The insets show the PL spectral shapes detected at different time delays (from 1 μs to 75 μs).

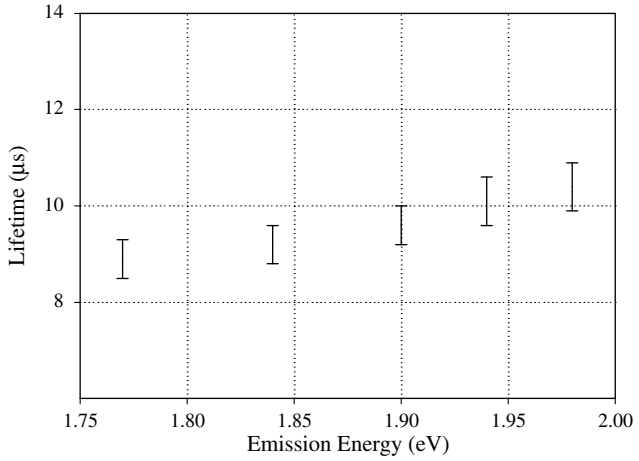


Fig. 3. Lifetime as a function of emission energy under excitation at 4.77 eV and 2.07 eV. For each emission energy the bar length accounts for the dispersion of the experimental values in the investigated S1 samples.

well isolated asymmetric band centered at $1.95 \pm 0.02$ eV with full width at half maximum (FWHM) of $0.18 \pm 0.02$ eV. It is worth noting that these spectral features are not well known so far [16]; in fact, because of the overlap with the emission, the acquisition of excitation spectra around 2 eV requires the use of time resolved

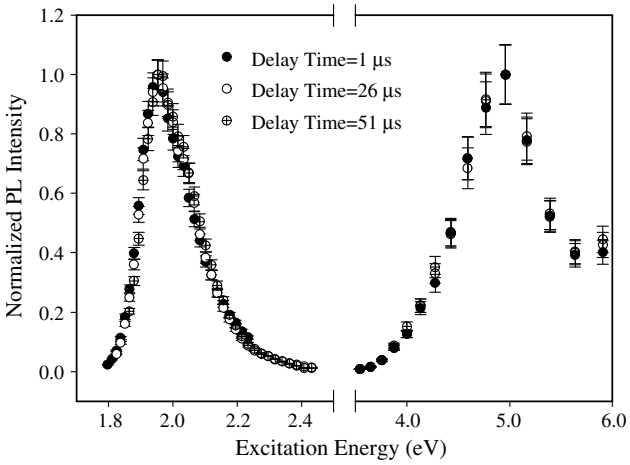


Fig. 4. Integrated PL intensity as a function of the excitation energy measured in the S1/β sample at three different delay times from the excitation pulse. The curves are plotted normalized to their maximum amplitude.

technique. The UV excitation PL profile is characterized by a band peaked around 4.9 eV with FWHM of ~1 eV, superimposed to a component at higher energies, in agreement with the data obtained using standard steady state spectrofluorometer [5,11].

## 4. Discussion

The above reported results show that the decay features of the PL at 1.9 eV, induced in silica samples by several kinds of ionizing radiation, depend on emission energy whereas are poorly influenced by excitation energy. No remarkable difference appears in the comparison among synthetic wet silica samples after different irradiation histories and containing a different concentration of NBOHC, mainly induced by the cleavage of OH bonds [18]. Then, we infer that the observed decay properties are peculiar to a single type of defect (NBOHC) and reflect both homogeneous and inhomogeneous properties. In fact, the measured lifetime (~10 μs) is consistent with an electronic transition between weakly overlapping states [5,9,10]. Moreover, due to the local interaction defect/environment, not equivalent site-to-site, the decay rates are inhomogeneously distributed.

Figs. 2 and 3 indicate that the lifetime increases with the emission energy thus involving the slower depletion of the higher energies PL components that manifests in a blue-shift of the band during its decay. This result proves the existence of a mapping between the spectral components inhomogeneously distributed within the PL band [8], and their lifetime: each subset of NBOHC emitting at $E_{em}$ has a specific $\tau(E_{em})$. We also observe that the overlap of components decaying with different $\tau$ is qualitatively consistent with the not-pure exponential curve decay, as observed both in the present paper and in previous works [5,6,8].

The decay features maintain regardless the excitation channel: (i) visible, in which the 1.9 eV PL is the inverse

transition of the excitation around 2.0 eV; (ii) UV, in which the 1.9 eV PL and the excitation around 4.8 eV do not involve the same levels and a part of absorbed energy is released through a non-radiative decay [5,11]. This finding proves that the lifetime only depends on radiative decay from the excited level and any non-radiative process is not competitive with the emission. Finally, as evident from Fig. 4, the visible and UV excitation profiles do not change their shape during the PL decay. This means that the selective excitation of centers inhomogeneously distributed does not influence their decay. The results suggest that NBOHC, before emitting the PL at 1.9 eV, loses memory of excitation process.

## 5. Conclusion

Time resolved luminescence spectra reported in the present work show that synthetic wet silica samples, exposed to different kinds of radiation ($\gamma$, $\beta$ and neutrons), exhibit the same emission properties at 1.9 eV associated with the generation of NBOHC. The use of a tunable laser in our experimental setup allows to describe in detail the excitation profile in the visible and UV range where are located the bands at 2.0 eV and 4.8 eV. Moreover, the analysis of the time decay evidences inhomogeneous properties of this defect: the decay curves deviate from a single exponential law and the lifetime increases with the emission energy.

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