Photoluminescence spectral dispersion as a probe of structural inhomogeneity in silica

Photoluminescence spectral dispersion as a probe of structural inhomogeneity in silica

Michele D'Amico[1,2]**, Fabrizio Messina**[1]**, Marco Cannas**[1]**,
Maurizio Leone**[1,2] **and Roberto Boscaino**[1]

[1] Dipartimento di Scienze Fisiche ed Astronomiche, Universitá di Palermo, Via Archirafi 36,
I-90123 Palermo, Italy
[2] Istituto di Biofisica, U. O. di Palermo, Consiglio Nazionale delle Ricerche,
Via Ugo La Malfa 153, I-90146 Palermo, Italy

E-mail: damico@fisica.unipa.it

Abstract
We perform time-resolved photoluminescence measurements on point defects in amorphous
silicon dioxide (silica). In particular, we report data on the decay kinetics of the emission
signals of extrinsic oxygen deficient centres of the second type from singlet and directly excited
triplet states, and we use them as a probe of structural inhomogeneity. Luminescence activity in
sapphire (α-Al$_2$O$_3$) is studied as well and used as a model system to compare the optical
properties of defects in silica with those of defects embedded in a crystalline matrix. Only for
defects in silica did we observe a variation of the decay lifetimes with emission energy and a
time dependence of the first moment of the emission bands. These features are analysed within
a theoretical model, previously proposed in D'Amico *et al* (2008 *Phys. Rev.* B **78** 014203), with
an explicit hypothesis about the effect introduced by the disorder of vitreous systems. Separate
estimations of the homogeneous and inhomogeneous contributions to the measured emission
linewidth are obtained. It is found that inhomogeneous effects strongly condition both the
triplet and singlet luminescence activities of oxygen deficient centres in silica, although the
degree of inhomogeneity of the triplet emission turns out to be lower than that of the singlet
emission. Inhomogeneous effects appear to be negligible in sapphire.

1. Introduction

Point defects in amorphous silicon dioxide (SiO$_2$) represent
a fundamental technological issue due to the wide range
of applications of this material in current optical and
electronic technologies. Indeed, the formation of defects,
typically triggered by exposure to ultraviolet (UV) or ionizing
radiation, compromises the performance of SiO$_2$ in optical
components, optical fibres, and metal oxide semiconductor
transistors [1, 2]. On the other side, comparing the properties
of colour centres hosted by an amorphous and a crystal
matrix is an issue of considerable interest for basic solid
state physics, still leaving several unanswered questions
especially concerning the interplay between homogeneous
and inhomogeneous optical broadening [3]. In a crystal,
each member of an ensemble of identical defects experiences
the same local environment and its spectroscopic properties
are properties of the single centre. Hence, the optical
properties of the set of defects, such as the homogeneous

absorption or emission linewidth, determined by the electron–
phonon coupling [1, 2] must be considered as *homogeneous*
properties of the defects. The situation is different in
a glass where, beside the homogeneous features of the
single point defect, different centres are localized in different
environments, possibly featuring a continuous spectrum of
geometric configurations. This statistical distribution of
structural parameters can result in a further broadening of
optical bands (*inhomogeneous effect*). Thus, in an amorphous
solid the observed spectroscopic fingerprint of a set of
nominally identical point defects, i.e. belonging to the same
species, is due to the convolution of both homogeneous and
inhomogeneous effects. No general recipe is available to
discriminate the extent of the former with respect to the latter
and, as a consequence, the prominence of inhomogeneous
or homogeneous effects in determining the optical properties
of defects in glasses has been a debated question for a long
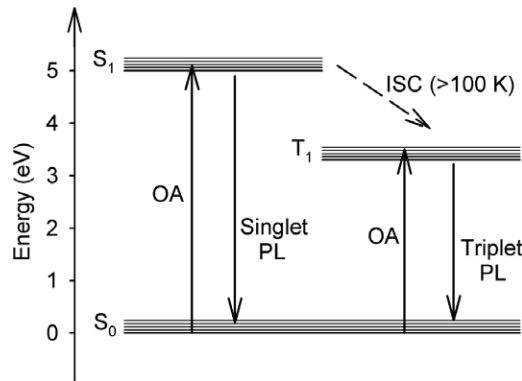time [1, 2, 4].

Figure 1. Schematic representation of electronic levels related to the main optical activities of Ge-ODC(II).

In previous papers, we reported optical measurements on a particular kind of point defect in silica, the so-called oxygen deficient centre of the second type or ODC(II), performed at several temperatures both by time-resolved and stationary luminescence techniques. These studies suggested that the spectroscopic properties of ODCs are significantly conditioned by inhomogeneous effects [5–8]. Also, ODC(II)s have been observed only in the amorphous phase of SiO_2, thus being an interesting model system to investigate glassy-specific inhomogeneous effects. The ODC(II) exists as an intrinsic defect or in two extrinsic varieties, and its most commonly accepted structural model consists of a twofold coordinated atom $(=X^{\bullet\bullet})$ [9–11], where X can be either an Si, a Ge or an Sn atom, belonging to the same isoelectronic group. In particular, the Ge-ODC(II) defects are responsible for intense optical activity in the visible–ultraviolet (vis–UV) range which is currently associated with the variation of refraction index in the fibre Bragg gratings after UV writing [2].

In figure 1, the main optical absorption (OA) and photoluminescence (PL) transitions for Ge-ODC(II) are schematically shown. A broad nearly Gaussian OA band centred at ~5.1 eV, assigned to the transition between the ground electronic singlet state (S_0) and the first excited singlet (S_1) state, excites a fast (lifetime in the ns range) PL band centred at ~4.3 eV, due to the inverse $S_1 \rightarrow S_0$ transition [11, 12]. Due to a partial admixture of S_1 and the first excited triplet state (T_1), at $T > 100$ K it is also possible to populate the T_1 state from S_1 by a phonon assisted process called inter-system crossing (ISC). The subsequent radiative decay from T_1 towards S_0 gives rise to an additional PL emission centred at ~3.1 eV. The lifetime of this band is slow (in the range of μs) due to the forbidden spin selection rules for this $T_1 \rightarrow S_0$ transition [12, 13]. It is also possible to populate the T_1 state directly from the ground S_0 state by exciting it with photons of ~3.7 eV energy. This process has a very low absorption cross section and bypasses the ISC channel, giving rise to the same 3.1 eV phosphorescence band independently of the temperature of the system and with the same lifetime as the $S_0 \rightarrow S_1 \rightsquigarrow T_1 \rightarrow S_0$ process [12].

In a recent paper [14] we introduced a new experimental investigation approach, based on time-resolved luminescence measurements, which was able to yield an estimation of

the homogeneous and inhomogeneous linewidth of the fast (ns lifetime) Ge-ODC(II) luminescence band due to decay from the S_1 state. In this paper we generalize our analysis applying it to the same model defect, i.e. the Ge-ODC(II) in silica, measuring also the 'slow' band assigned to the de-excitation from the T_1 state. This phosphorescence band is excited, directly populating the first triplet electronic state to avoid possible inhomogeneous effects arising from the ISC process [6, 15]. Our aim is to find out whether our approach is applicable also to a slow (μs lifetime) triplet emission band and if the extent of inhomogeneous effects affecting triplet and singlet emission processes are comparable or not. Finally, in order to compare the results with those obtained in a system where inhomogeneous effects should be absent, we report the same study performed on the PL of point defects in crystalline sapphire. Although the luminescence activity of defects in irradiated or doped sapphire has been extensively studied in the past, several aspects about the decay kinetics, defect interconversion processes, band attributions and structural models of the emitting defects are not clear yet [16–18].

2. Experimental details

We report measurements performed on Infrasil301 fused silica, hereafter named I301, provided by Heraeus Quartzglas[3]. This material features a 1 ppm concentration of Ge impurities, a consistent portion of which are arranged as Ge-ODC(II) defects in the as-grown material [12, 14, 19]. For comparison with defects in a crystal, we also used an as-grown commercial sapphire sample (α-Al_2O_3) provided by A D Mackay Inc. (Broadway, New York) and rod flame polished[4].

Low temperature (25 K) photoluminescence measurements were done in a standard back-scattering geometry in high vacuum within a helium continuous flow cryostat, under excitation by a pulsed laser and detected by an intensified charge-coupled device detector as described in detail in the experimental section of [14].

The luminescence from the triplet excited state of Ge-ODC(II) in the I301 sample was collected under laser excitation (energy density per pulse of 1.00 ± 0.02 mJ cm^{-2}) at 330 nm (3.75 eV), corresponding to the $S_0 \rightarrow T_1$ absorption peak, and using a 300 grooves mm^{-1} grating (blaze at 500 nm) with a 4 nm spectral bandwidth. The PL decay was followed by performing different acquisitions with the same integration time $t_W = 15$ μs but at different delays t, going from 0 to 300 μs from the laser pulse.

The luminescence of the sapphire sample was acquired using a 230 nm (5.40 eV) excitation wavelength (energy density per pulse of 1.00 ± 0.02 mJ cm^{-2}), and a 150 grooves mm^{-1} grating (blaze at 300 nm) with a 8 nm spectral bandwidth. The decay was followed varying t from 0 to 400 μs and with $t_W = 4$ μs. All the spectra were corrected for spectrograph dispersion and for instrumental response.
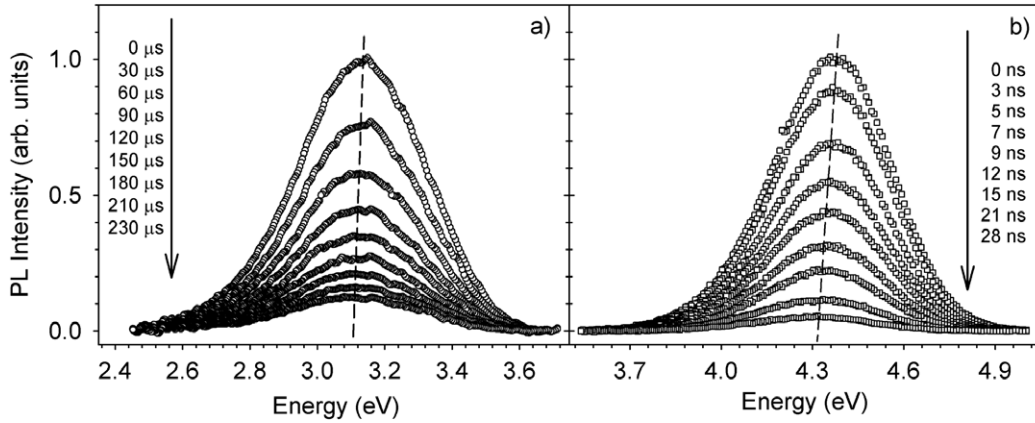
Figure 2. (a) Time evolution of the lineshape of the triplet Ge-ODC(II) luminescence signal ($T_1 \rightarrow S_0$ transition) at 25 K excited at 3.75 eV. (b) Time evolution of the lineshape of the singlet Ge-ODC(II) luminescence signal ($S_1 \rightarrow S_0$ transition) adapted from [14]. Different spectra detected at different time delays from the laser pulse are shown. The dashed line follows the position of PL peaks as a guide to the eye.
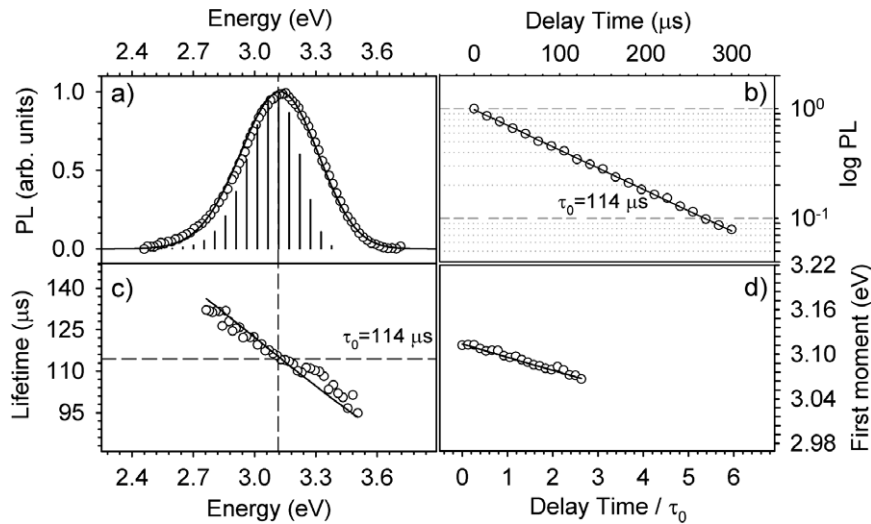

Figure 3. Panel (a): luminescence emission lineshape of triplet Ge-ODC(II) activity ($T_1 \rightarrow S_0$ transition) as measured at $T = 25$ K upon excitation at 3.75 eV, immediately after the end of the laser pulse ($t = 0$). Panel (b): decay kinetics observed at the peak emission energy ($\sim$3.1 eV). Panel (c): decay lifetimes as a function of the emission energy. Panel (d): first moment of the emission band as a function of time delay. The continuous lines represent the results of the fitting procedure by our theoretical model (see section 4).

3. Results

We show in figure 2(a) the time-resolved spectra of the triplet ($T_1 \rightarrow S_0$) PL activity of Ge-ODC(II) in the I301 silica sample. For comparison purposes, in figure 2(b) analogous measurements performed on the singlet ($S_1 \rightarrow S_0$) PL emission of the same defects (adapted from [14]) are shown. The dashed lines drawn in figure 2 follow the emission peaks at different time delays t and we observe a non-verticality of their slopes, indicating an experimental detectable red shift of both luminescence bands during the decay.

In figures 3(a) and 4(a) we report the signal acquired at $t = 0$ for the two PL activities of the Ge-ODC(II), corresponding to the most intense spectra in figures 2(a) and 2(b), respectively. The triplet PL band of Ge-ODC(II), as acquired immediately after the end of the laser pulse, is peaked at $\sim$3.1 eV and features a 0.44 eV width (full-width at half

maximum, FWHM), while the singlet band features a $\sim$4.4 eV peak position and a 0.45 eV FWHM.

Analogous time-resolved measurements were carried out on the PL activity in the sapphire sample for purposes of comparison, and we report in figure 5(a) the spectrum acquired for $t = 0$. The PL band observed in sapphire, as acquired immediately after the end of the laser pulse, peaks at $\sim$2.9 eV and features a 0.61 eV FWHM. The spectroscopic parameters of the signal in figure 5(a) are consistent with a luminescence signal previously observed in the literature, and associated either with the so-called P-centre (an anion–cation vacancy pair featuring a charge transfer transition) as proposed by a few works [20, 21] or with an extrinsic defect as proposed in [22]. However, it is worth noting that the detailed structural model of the centre responsible for the observed luminescence is not relevant here. Indeed, for the purposes of the present work we are going to discuss this signal only as a model of a slow
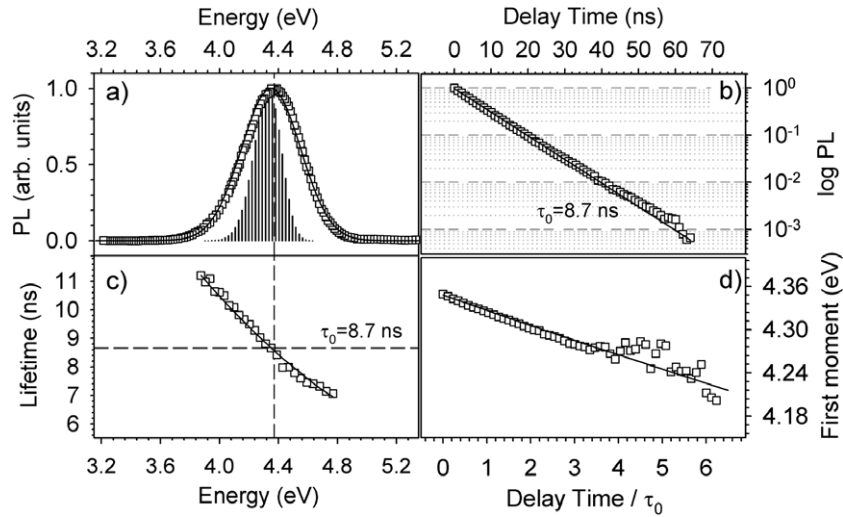
Figure 4. Panel (a) luminescence emission lineshape of singlet Ge-ODC(II) activity ($S_1 \rightarrow S_0$ transition) as measured at $T = 25$ K upon excitation at 5.17 eV, immediately after the end of the laser pulse ($t = 0$). Panel (b) decay kinetics observed at the peak emission energy (~4.4 eV). Panel (c) decay lifetimes as a function of the emission energy. Panel (d) first moment of the emission band as a function of time delay. The continuous lines represent the results of the fitting procedure by our theoretical model (see section 4). All these data are rearranged from [14].
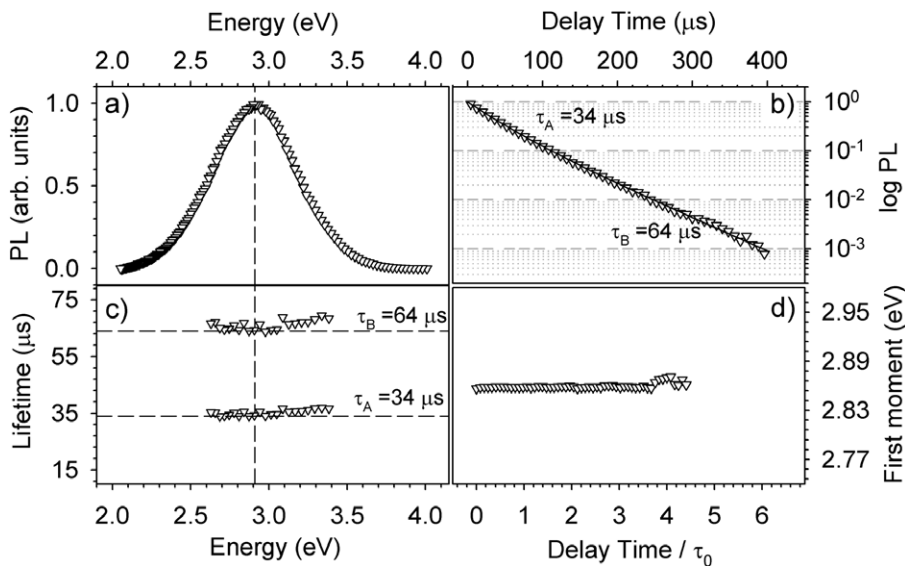

Figure 5. Panel (a) emission lineshape of sapphire PL activity as measured at $T = 25$ K upon excitation at 5.40 eV, immediately after the end of the laser pulse ($t = 0$). Panel (b) decay kinetics observed at the peak emission energy (~2.8 eV). Panel (c) decay lifetimes as a function of the emission energy. Panel (d) first moment of the emission band as a function of time delay.

luminescence of a defect in a crystalline oxide and, as we will see, it presents a ~μs lifetime.

From all time-resolved measurements one can extract the lifetime dispersion curves, namely the dependence of the decay lifetime on emission energy. To this end, the lifetimes were obtained by a fitting procedure of PL data at a given emission energy, carried out with a single exponential function for the triplet activity of Ge-ODC(II), and with a double exponential function for sapphire PL activity. The same procedure had already permitted us to study the lifetime dispersion curve of singlet PL activity of Ge-ODC(II) [14]. Representative decays measured at the band peak energies, 3.1 eV, 4.4 eV

and 2.8 eV for triplet Ge-ODC(II), singlet Ge-ODC(II) and sapphire PL signals, are reported with relative fitting curves in figures 3(b), 4(b) and 5(b), respectively. The experimental low temperature (25 K) was chosen to ensure purely radiative decays from the excited electronic state, especially to prevent the activation of the ISC process from the excited singlet ODC(II) state (see figure 1).

The lifetime of the triplet Ge-ODC(II) (figure 3(c)) varies from ~130 to ~100 μs for emission energies increasing from 2.8 to 3.5 eV, while that of the singlet Ge-ODC(II) (figure 4(c)) varies from ~11 to ~7 ns in the 3.8–4.8 eV range [14]. Finally, in the sapphire sample lifetime dispersion is not observed.

Indeed, the two lifetimes characterizing the luminescence decay are independent of the emission energy: they remain fixed to $\tau_A = 34\ \mu$s and $\tau_B = 64\ \mu$s all over the range of the PL band[5].

The observed energy dependence of the luminescence lifetime is expected to cause a progressive red shift of the first moment of the band, due to different temporal evolutions of different parts of the PL band. From measured spectra we have thus calculated the time dependence of the first moment of the luminescence bands; the results are reported in figures 3(d), 4(d) and 5(d) for triplet Ge-ODC(II), singlet Ge-ODC(II) and sapphire activities, respectively. The horizontal axes represent the time delay from the laser pulse in units of the lifetime τ_0: for both Ge-ODC(II) activities τ_0 is defined as the lifetime of the PL signal at the central emission energies, 114 μs and 8.7 ns for triplet and singlet decay respectively. For sapphire activity τ_0 is chosen to be the mean value of the two experimental lifetimes τ_A and τ_B. We observe that the slow PL activity in silica features an approximately linear red shift of the band as a function of time. Hence, the result originally observed for the singlet PL activity [14] is now generalized to the triplet luminescence as well, whereas the first moment of the PL activity in sapphire has a constant value consistent with the results found for the lifetimes.

4. Discussion

The comparison between results on the oxygen deficient centres in SiO$_2$ and the defects in sapphire suggests that the distribution of lifetimes measured for different emission energies and the corresponding red shift of the first moment of the band as a function of delay time are peculiar features of defects embedded in amorphous solids as opposed to defects in crystals, where such effects are not observed. This characteristic behaviour of 'amorphous defects' can be conveniently referred to as *luminescence dispersion*. A similar result had been pointed out in a previous work [14] by comparing the PL properties of the $S_1 \rightarrow S_0$ transition of Ge-ODC(II) with those of F-type centres in lithium fluoride. While featuring comparably fast (ns) lifetimes, the decay properties of these two systems turned out to be very different: a strong luminescence dispersion was found for Ge-ODC(II) [14], while the decay lifetime of F-centres in LiF was found to be independent of emission energy and the luminescence peak independent of time [14].

The present results yield a strong generalization of previous findings. Indeed, data reported in section 2 demonstrate that the PL dispersion effect occurs both for the fast (ns) singlet and for the slow (μs) triplet luminescence of the Ge-ODC(II), thus being independent of the temporal range of the decay kinetics as well as of the nature of the transition. Also, dispersion effects are absent in sapphire defects, similarly to what was previously observed in LiF [14],

and notwithstanding the double exponential decay kinetics, which may suggest the coexistence of two slightly different varieties of the optically active centre.

On the whole, our results suggest luminescence dispersion to be a general optical property which allows us to clearly discriminate the behaviour of defects embedded in amorphous solids from those in crystalline ones. At least, this appears to be true for oxides. Also, it is worth stressing that the lifetime of a PL band of defects in a solid is widely regarded as a strong fingerprint of the defect, which can be used to unambiguously recognize it by time-resolved PL measurements. It is worth noting that, without taking account of the lifetime dispersion effects evidenced here, lifetime differences as large as $\sim$30% in amorphous systems can wrongly be regarded as signatures of different defects.

More detailed information can be obtained from these experimental results when analysed in the framework of the theoretical model proposed in [14] based on the standard background for the description of point defects' optical activities in a solid matrix [1, 3] and where the presence of different environments, which can accommodate different members of an ensemble of point defects in an amorphous matrix, can be mapped into a Gaussian distribution (centre $\widehat{E_0}$ and half-width σ_{in}) of the zero phonon energy E_0 [14]. E_0 represents the energy difference between the ground and first excited electronic state both in the ground vibrational sub-level. The peak PL emission energy E_e can be equivalently used as a statistically distributed parameter instead of the zero phonon energy. Indeed, these two spectroscopic features are linked by the relation $E_e = E_0 - S$ where S is the half Stokes' shift, that is the half-difference between the peak of absorption and luminescence bands and which is assumed to be undistributed like the other homogeneous parameters (the homogeneous half-width σ_{ho} and the oscillator strength f). Hence, the Gaussian distribution of E_0 implies a Gaussian distribution of E_e with the same half-width σ_{in} and centred at $\widehat{E_e} = \widehat{E_0} - S$.

On this basis, it is possible to write a quantitative expression of the PL emitted by the ensemble of colour centres in an amorphous solid [14] and one can numerically integrate it in order to simulate the time-resolved PL spectra, $L_s(E, t)$, as a function of the four parameters $\widehat{E_e}$, σ_{in}, σ_{ho}, f. From $L_s(E, t)$, the simulated decay lifetime $\tau_s(E)$ and the kinetics $M_{1s}(t)$ of the first moment can be easily calculated by using the same procedure applied to the experimental data $L(E, t)$. For further details we refer to the original paper [14].

The behaviour shown in figure 3 for silica PL activity can be examined in the frame of the above theoretical model (as already done in [14] for data of figure 4). To this end, we have performed numerical integration, varying the above-mentioned parameters, to obtain a set of three theoretical curves which simultaneously fit the shape of the PL band, the dependence of the decay lifetime as a function of the emission energy and the kinetics of the first moment. The continuous lines in figure 3 represent the results of our fitting procedure, while the histogram shows the discrete Poissonian homogeneous lineshape of half-width σ_{ho} as obtained by our fitting procedure. Since the PL dispersion effect found here

---

[5] It is worth noting that the double exponential behaviour of P-centre luminescence in sapphire is unknown to the best of our knowledge. In [20] the authors found a lifetime of $\sim$50 μs which is consistent with the mean of the two lifetimes found here. It is beyond the aim of this paper to investigate the reason behind these decay features.

Table 1. Upper section: best fitting parameters obtained by our theoretical model for the investigated triplet PL activity of Ge-ODC(II). Lower section: values of λ, σ_{tot}, $\hbar\omega_p$ and H, as calculated from best fitting parameters.

$\widehat{E}_e$ (eV)	σ_{in} (meV)	σ_{ho} (meV)	f
3.08 ± 0.05	140 ± 8	125 ± 16	$(3.3 \pm 0.5)10^{-5}$
$\lambda(\%)$	σ_{tot} (meV)	$\hbar\omega_p$ (meV)	H
56 ± 4	188 ± 9	52 ± 14	6 ± 2

for Ge-ODC(II) is not evidenced in sapphire luminescence, we argue that in a crystal, besides a few imperfections due to dislocations or strain, the inhomogeneous effects (and thus the related width) are virtually absent. As a consequence, the red shift of the first moment of the PL band and the dispersion of lifetimes are not possible, consistent with experimental results (see figure 5).

The upper part of table 1 lists the best parameters obtained by our fitting procedure for the triplet luminescence of Ge-ODC(II). In the lower part of table 1 we also report the parameter $\lambda = \sigma_{\text{in}}^2/\sigma_{\text{tot}}^2$ which estimates the degree of inhomogeneity. We remark here that this parameter gives $\lambda = 78\%$ for the singlet transition of Ge-ODC(II) [14]. On the one hand, these results for the parameter λ evidence that inhomogeneous effects strongly affect both the electronic transitions of the ODC(II) defects in silica. On the other hand, the value of λ for triplet emission of Ge-ODC(II) (56%) is smaller than that found for singlet emission (78%). Hence, the width of the inhomogeneous distribution turns out to be greater for the $S_1 \rightarrow S_0$ transition than for the $T_1 \rightarrow S_0$ one. This finding can be qualitatively visualized by comparing figure 3(c) with figure 4(c). In fact, the relative lifetime increase observed by moving leftwards by a FWHM on the horizontal axis is lower ($\sim$20%) for the triplet PL than ($\sim$33%) for the singlet PL band.

This result leads to an important consideration about the meaning of inhomogeneity: the inhomogeneous width has to be considered as a property of a specific electronic transition occurring at the defect site, rather than a property of the defect. As a matter of fact, the physical property of the defect which lies at the root of inhomogeneity effects is the site-to-site distribution of the structural parameters, such as bond angles and lengths. In this sense, the statistical distribution of E_e should be regarded as a convenient, and synthetic, representation of inhomogeneity effects; the form and width of such a distribution are determined in principle by the detailed dependence of the emission peak E_e on the microscopical structural parameters. Only quantum mechanical calculations can investigate the form of this mapping function, and may allow us to understand why it ultimately results in a larger degree of inhomogeneity affecting the $S_1 \rightarrow S_0$ transition as compared to the $T_1 \rightarrow S_0$ transition of Ge-ODC(II). Also, more experimental investigations are needed to find out whether this difference between triplet and singlet emissions is a general property of defects in amorphous systems or a peculiar feature of oxygen deficient centres in silica.

Finally, the value of the oscillator strength found here for the triplet band of Ge-ODC(II) is in excellent agreement with

the value 1.2×10^{-5} which was reported in a review paper about oxygen deficient centres in silica [12]. From data in the upper part of table 1 we can also calculate the Huang–Rhys factor $H = S^2/\sigma_{\text{ho}}^2$, the vibrational frequency $\hbar\omega_p = \sigma_{\text{ho}}^2/S$ and the total width (from $\sigma_{\text{tot}}^2 = \sigma_{\text{in}}^2 + \sigma_{\text{ho}}^2$) [14]. All these quantities are summarized in the lower part of table 1 and are obtained by using $S = 0.30$ eV for the half Stokes' shift of the triplet PL band. The values of S were estimated experimentally by measuring the half-difference between the spectral positions of the excitation energies and emission peaks. The result for the vibrational frequencies shows that the Ge-ODC(II) couple with very low frequency modes, in accordance with previous experimental and computational results [8, 14, 23, 24].

5. Conclusions

We have studied by time-resolved luminescence the extrinsic (Ge-related) oxygen deficient centres in amorphous silicon dioxide. Both the triplet and the singlet PL of the defect feature a dispersion of decay lifetimes within the emission band and a temporal red shift of their first moments. Comparison with a defect in crystalline sapphire demonstrates that these effects are peculiar to a centre embedded in a disordered solid. Experimental findings are analysed within a theoretical frame which models the effects induced by glassy disorder on the optical properties of defects in silica to numerically estimate the homogeneous and inhomogeneous half-width. We find that the degree of inhomogeneity experienced by the triplet luminescence band is appreciably less than by the singlet one.

Acknowledgments

References

[1] Pacchioni G, Skuja L and Griscom D L (ed) 2000 *Defects in SiO$_2$ and Related Dielectrics: Science and Technology* (Norwell: Kluwer–Academic)

[2] Nalwa H S (ed) 2001 *Silicon-Based Materials and Devices* (San Diego, CA: Academic)

[3] Stoneham A M 1975 *Theory of Defects in Solids* vol 1 (Oxford: Clarendon)

[4] Moerner W E (ed) 1988 *Persistent Spectral Hole-Burning: Science and Applications* (*Springer Topics in Current Physics* vol 44) (Berlin: Springer)

[5] Leone M, Agnello S, Boscaino R, Cannas M and Gelardi F M 1999 *Phys. Rev.* B **60** 11475

[6] Cannizzo A, Agnello S, Boscaino R, Cannas M, Gelardi F M, Grandi S and Leone M 2003 *J. Phys. Chem. Solids* **64** 2437

[7] Cannizzo A and Leone M 2004 *Phil. Mag.* **84** 1651

[8] Cannizzo A, Leone M, Boscaino R, Paleari A, Chiodini N, Grandi S and Mustarelli P 2006 *J. Non-Cryst. Solids* **352** 2082

[9] Skuja L N, Streletsky A N and Pakovich A B 1984 *Solid State Commun.* **50** 1069

[10] Nishikawa H, Shiroyama T, Nakamura R, Ohki Y, Nagasawa K and Hama Y 1992 *Phys. Rev.* B **45** 586
[11] Skuja L 1994 *J. Non-Cryst. Solids* **179** 51
[12] Skuja L 1998 *J. Non-Cryst. Solids* **239** 16
[13] Agnello S, Boscaino R, Cannas M, Gelardi F M and Leone M 2000 *Phys. Rev.* B **61** 1946
[14] D'Amico M, Messina F, Cannas M, Leone M and Boscaino R 2008 *Phys. Rev.* B **78** 014203
[15] Agnello S, Boscaino R, Cannas M, Gelardi F M, Leone M and Boizot B 2003 *Phys. Rev.* B **67** 033202
[16] Chen W, Tang H, Shi C, Deng J, Shi J, Zhou Y, Xia S, Wang Y and Yin S 1995 *Appl. Phys. Lett.* **67** 317
[17] Caulfield K J, Cooper R and Boas J F 1997 *J. Phys.: Condens. Matter* **9** 6457

[18] Surdo A I, Kortov V S, Pustarov V A and Yakovlev V Y 2005 *Phys. Status Solidi* c **2** 527
[19] Grandi S, Mustarelli P, Agnello S, Cannas M and Cannizzo A 2003 *J. Sol–Gel Sci. Technol.* **26** 915
[20] Pujats A V, Springis M J and Valbis J A 1980 *Phys. Status Solidi* a **62** K85
[21] Springis M, Kulis P, Veispals A and Tale I 1995 *Radiat. Meas.* **24** 453
[22] Evans B D 1991 *J. Appl. Phys.* **70** 3995
[23] Galeener F L, Leadbetter A J and Stringfellow M W 1983 *Phys. Rev.* B **27** 1052
[24] Umari P, Gonze X and Pasquarello A 2003 *Phys. Rev. Lett.* **90** 027401