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Spectral and kinetic properties of the 4.4-eV photoluminescence band in a-SiO$_2$: Effects of γ irradiation

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Spectral and decay properties of the photoluminescence (PL) emission in the range 3.5–5.0 eV are investigated in various types of silica (a-SiO$_2$), as grown and after γ irradiation. We report experimental results on the ultraviolet (5.0 eV) absorption, on the emission and excitation spectra of the stationary PL, excited by ultraviolet (5.0 eV) and vacuum ultraviolet (6.0–8.5 eV) light, on the decay times of the transient PL emission, at room temperature, and at 10 K. Our results show that γ irradiation causes the appearance of a PL band, centered at 4.37 eV, which can be excited at 5.0 eV and at 6.8 eV. This band, which is induced in all the investigated samples, brings a close similarity to the PL band α_I that is peculiar of unirradiated oxygen-deficient natural silica. However, small but appreciable differences between the two bands can be inferred from our experimental data. The results are consistent with an energy level scheme with two singlet-singlet transitions. We tentatively ascribe the small differences between the two PL bands to different dynamic environments surrounding the intrinsic and the γ-induced centers. [S0163-1829(96)02434-4]

I. INTRODUCTION

Several kinds of intrinsic and extrinsic point defects influence the optical properties of high-purity silica (a-SiO$_2$), manifesting themselves as optical absorption (OA) bands and photoluminescence (PL) emissions.[1] Some defects are formed during fabrication, others are generated in the manufactured material by external agents, e.g., drawing, heat treatments, ionizing radiation.

Point defects in silica have been the subject of intensive studies for more than three decades. Nevertheless, several aspects of their structure and generation mechanisms are far from being thoroughly understood. Actually, the relations between optical bands and specific defects with defined structures are often a matter of controversy. This is true in particular for the OA band B_2 at 5.0 eV and the associated PL activity observed in high-purity silica.

The B_2 band was originally observed by Mitchell and Paige.[2] More recent PL studies[3,4] allowed to distinguish between two OA bands, centered at 5.02 and 5.15 eV and labeled $B_{2\alpha}$ and $B_{2\beta}$, respectively. It is now well established[3,5,6] that the $B_{2\alpha}$ band can excite the PL emission centered at $\approx$4.4 eV (α_I), whereas the $B_{2\beta}$ band excites the PL band at $\approx$4.2 eV (α_E).

It is universally accepted that the defect responsible for the band $B_{2\alpha}$ and for the related α_I PL emission is generated by oxygen deficit,[7–9] but the exact structural model is still an open question. Skuja[10,11] hypothesized a twofold coordinated Si (O-$\ddot{\text{Si}}$-O) with two singlet-to-singlet transitions at 5.0 eV and at 7.0 eV, both effective in pumping the PL emission at 4.4 eV. Other authors[3,7,12] have proposed the oxygen vacancy ($\equiv$Si—Si$\equiv$), with a singlet-triplet transition at 5.0 eV ($B_{2\alpha}$) and a singlet-singlet transition at 7.6 eV (E band). However, the correlation of the E band with the $B_{2\alpha}$ band and the PL emission α_I is controversial.[8,13–17]

The PL activity at 4.4 eV is modified when the material is exposed to neutrons, to uv, to x rays, or to high doses of γ rays.[6,9,18–23] Generally, the intensity of the PL emission increases after irradiation and this has been interpreted as the growth of the α_I band and ascribed to the increased number of oxygen-deficient centers. At a variance to this interpretation, Amossov *et al.*[9] reported that the increase of the PL emission at 4.4 eV is not correlated with the variation of the companion PL band at 2.7 eV and concluded that the defects induced by the radiation are substantially different from those in the as-grown material.

In this paper we are concerned with the effect of γ irradiation on the PL band at 4.4 eV. Synthetic high-purity dry silica is a material particularly suitable for this investigation, since it, as-grown, exhibits neither OA bands nor PL emission in the energy range of our interest. We find that exposure to γ rays, even at so low doses as 1 Mrad, induces a PL band centered at $\approx$4.4 eV. We report experimental results on the emission and excitation spectra of this PL band, excited by uv and vacuum uv (vuv) light, and on its transient decay (in the time scale of ns). The effect of lowering the temperature down to 10 K on the lifetime has also been investigated. We carry out a comparison of the γ-induced PL band with the intrinsic α_I PL band, as observed in an oxygen deficient silica type. The similarity between the two bands suggests a structural similarity between the intrinsic and the γ-generated defects. However, the two bands exhibit a few quantitative differences, in particular as for the peak energies, the excitation spectra, and the decay times. The measured differences are small, but larger than the experimental uncertainties. We tentatively relate them to a slight different vibrational environment surrounding the two centers. Finally, to examine the interplay between the γ-generated band with the α_I and α_E bands, we have examined the effect of γ irradiation in the oxygen deficient sample and in a natural dry silica, characterized by the presence of the $B_{2\beta}$ OA band.

The properties of the investigated samples and the experimental techniques are described in Sec. II. The experimental

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results are reported in Sec. III. Finally, in Sec. IV we discuss our results in the frame of the models mentioned above.

II. MATERIALS AND METHODS

We have examined the characteristics of the PL emission in the range 3.5–5.0 eV in several types of silica, including natural and synthetic, wet and dry. Here we report the results obtained in three representative materials, hereafter denoted as S300, I301, and QC. S300 and I301 symbolize Suprasil 300 and Infrasil 301, respectively.[24] The former is a synthetic dry silica (type IV), which, as manufactured, has no OA band nor PL emission in the energy range of our interest. The latter is a natural dry silica (type I); it exhibits the $B_{2\beta}$ OA band[3] centered at 5.15 eV with a full width at half maximum (FWHM) of 0.46 eV, by which one can excite the α_E PL emission peaked at 4.26 eV. Finally, QC denotes an oxygen-deficient natural dry silica (type I), used for the production of spectrophotometric cells,[25] characterized by a predominant $B_{2\alpha}$ OA band,[3] centered at 5.05 eV and with a FWHM of 0.36 eV, which excites the α_I PL emission at 4.42 eV.

The materials were supplied as slabs ($50\times50\times1$ mm^3) with the major surfaces optically polished. Samples of $5\times5\times1$ mm^3, cut from the slabs, were γ irradiated in a ^{60}Co source at room temperature, at the dose rate of 0.75 Mrad(Si)/h. In the following the samples will be referred to as S300/D, QC/D, or I301/D, where D indicates the accumulated dose in Mrad(Si) and $D=0$ represents the unirradiated sample. Samples of the same silica type, exposed to different γ doses, originate from the same slab.

The OA measurements mentioned above were performed using a Cary 2300 spectrophotometer (185–2800 nm). The OH content was verified by measuring the absorption at 2730 nm.

Steady-state PL emission in the range 3.5–5.0 eV, excited by uv light, was measured by a Jasco PF-770 instrument, mounting a Xenon lamp of 150 W, with a bandwidth of 5 nm for excitation and 3 nm for emission. To maximize the emission signal, we adopted the so-called 45°-backscattering-geometry, in which the sample is placed with the major faces at 45° with respect to the exciting beam and the PL light is collected in the direction opposite to the reflected beam. The experimental spectra were fitted to Gaussian curves to determine the peak energy and the full width at half maximum (FWHM); we estimated the accuracy as ±0.01 and ±0.02 eV for the peak energy and for the FWHM, respectively.

The PL activity and its transient decay, with pulsed excitation light ranging from 4.5 to 9.0 eV, was investigated using the synchrotron radiation (SR) at the SUPERLUMI station on the I-beamline of HASYLAB at DESY (Hamburg, Germany).[26] The integrated PL emission and excitation spectra were measured under multibunch operation, with a 0.25 and 5.0 nm excitation and emission bandwidth, respectively. The PL light was dispersed by a 0.5 m Czerny-Turner monochromator over a 256-channel diode array, with a channel width of 0.45 nm. Experimental data were normalized to the source intensity and corrected for the system response. The experimental spectra were analyzed by the same procedure as described above; however, in this case, owing to the lower signal-to-noise ratio, the peak energy and the FWHM were determined with larger uncertainties, ±0.02 and ±0.04 eV, respectively. The time decay of transient PL was measured under single-bunch operation, using 512 channels for scanning the time interval (≈192 ns) between adjacent SR pulses. The SR pulse width was ≈0.5 ns. The measurements were carried out both at 300 and 10 K, by using a sample chamber with a helium-flow cryostat.

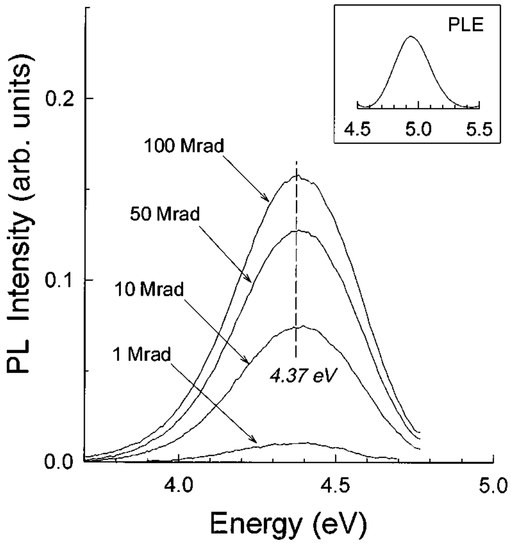

FIG. 1. PL emission spectrum excited at 5.0 eV in the samples S300/D, with D ranging from 1 to 100 Mrad(Si). The inset shows the PLE spectrum as detected in the most irradiated sample S300/100 for the emission energy of 4.4 eV.

III. EXPERIMENTAL RESULTS

A. Stationary PL excited at 5.0 eV

First, we consider the effect of γ irradiation in synthetic silica S300. As noted above, neither OA bands nor PL emission were detected in the as-manufactured sample (S300/0). A PL band, excited at 5.0 eV, could be observed in the irradiated samples S300/D, as shown in Fig. 1 for D ranging from 1 to 100 Mrad/(Si). The growth kinetics is apparently nonlinear.[23] In all the irradiated samples, this band is centered at 4.37 eV and has a FWHM of 0.45 eV. In the inset of Fig. 1 we report the PL excitation (PLE) profile, as measured in the sample S300/100 for the emission energy 4.4 eV. The PLE spectrum is peaked at $E_{\mathrm{exc}}=4.95$ eV and has a FWHM of 0.34 eV. Unfortunately, a reliable measurement of the corresponding OA band (at ~5.0 eV) was prevented by the overwhelming tails of the much more intense OA band (5.8 eV) of the E' centers.[21,23,27]

The PL band centered at 4.37 eV, induced by γ irradiation and hereafter referred to as α_R band, closely resembles the intrinsic PL band α_I, usually observed in unirradiated oxygen-deficient-type silica.[3,5,9,15,21] This is evident if the PL and PLE spectra in Fig. 1 are compared to the corresponding ones measured in our unirradiated sample QC/0 (Fig. 2, dashed curves). However, in spite of the similarity, a significant difference is that the band α_I, as detected in the sample QC/0, even if has the same FWHM of 0.45 eV, is peaked at a slightly higher energy (4.42 eV). Analogously, the PLE profile detected in the sample QC/0 (inset of Fig. 2) has the

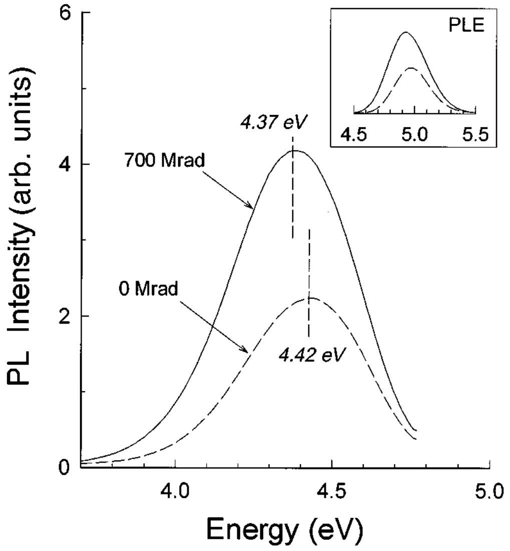

FIG. 2. PL emission spectrum excited at 5.0 eV in the as-grown sample QC/0 (dashed curve) and in the irradiated sample QC/700 (full curves). The emission maximum at 4.42 eV in the as-grown sample is shifted to 4.37 eV after γ irradiation. The inset shows the corresponding PLE spectra as detected at the emission energy of 4.4 eV. The PLE spectra peak at 4.98 eV and at 4.94 eV, respectively.

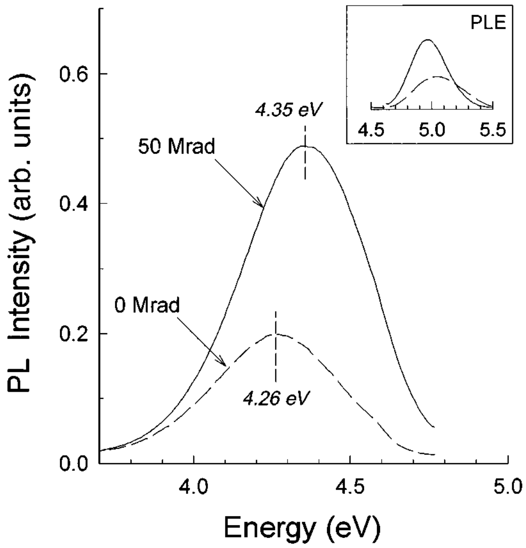

FIG. 3. Effect of γ irradiation on the PL and PLE (inset) spectra in the sample I301. The as-grown sample (I301/0, dashed spectra) exhibits the α_E band (4.26 eV) with a PLE spectrum peaked at 5.06 eV. In the irradiated sample (I301/50, full curves) the band α_R dominates with an emission maximum at 4.37 eV and an excitation maximum at 4.98 eV.

same width of 0.34 eV as in the sample S300/1000 (inset of Fig. 1), but is centered at $E_{\mathrm{exc}}=4.98$ eV.

To evidence the reliability of this difference, we report in the same Fig. 2 the PL and the PLE spectra as detected in the irradiated sample QC/700. As shown, after heavy γ exposure, the PL band recovers the same properties as the α_R band observed in the irradiated synthetic samples S300/D: its center is now at 4.37 eV and its PLE has shifted its maximum to 4.94 eV.

To complete this subsection, we report that the growth of the α_R PL band under γ exposure is unaffected by the presence of centers $B_{2\beta}$, responsible for the spectrally neighboring α_E band. This is shown in Fig. 3, where we report the PL and PLE spectra, as detected in our unirradiated sample I301/0 and in the irradiated one I301/50. As expected,[3,5,6,28] the band α_E observed in the as-grown material is well distinguishable from both the bands α_1 and α_R: it is centered at 4.26 eV and has a FWHM of 0.47 eV; its PLE spectrum is peaked at 5.05 eV and has a FWHM of 0.45 eV. In the irradiated sample, the γ-generated α_R band overcomes the original α_E band and has essentially the same properties as in the other two samples (Figs. 1 and 2). In fact, in Fig. 3 the emission spectrum is peaked at 4.35 eV with a FWHM of 0.44 eV; the PLE spectrum is peaked at 4.98 eV with a FWHM of 0.36 eV.

B. PL excited in the vuv

To further investigate the properties of the intrinsic α_I band and of the γ-generated one, α_R, we performed PL measurements under vuv excitation, using a SR facility. The possibility of exciting the 4.4 eV PL by high-energy light (5.5–8.0 eV) has been reported previously by other authors.[15,18,29,30]

The results obtained in our samples S300/100, QC/0, and QC/700 are shown in Fig. 4. The PL spectra were measured for $E_{\mathrm{exc}}=6.8$ eV and confirm the differences between the two bands α_I and α_R: the former [dashed spectrum in Fig. 4(a)] is peaked at 4.42 eV, the latter at 4.37 eV in both the irradiated samples, QC/700 [full curve in Fig. 4(a)] and

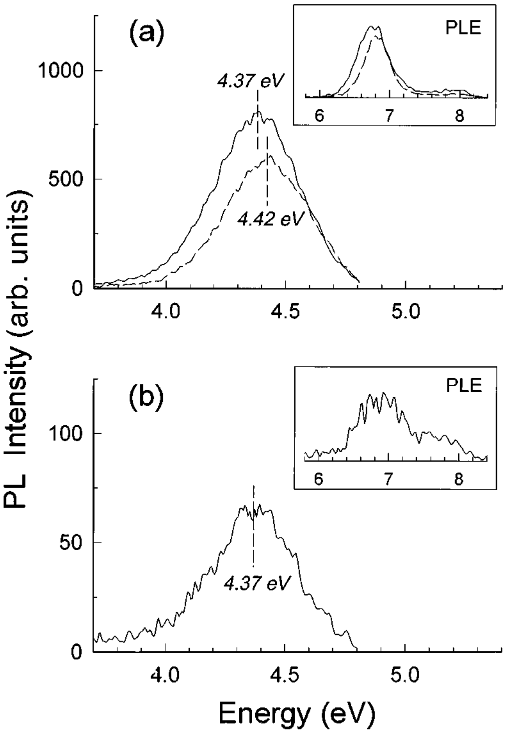

FIG. 4. High energy (6.0–8.0 eV) excitation of the PL emission at 4.4 eV at $T=300$ K: (a) as-grown sample QC/0 (dashed spectrum) and irradiated sample QC/700 (full spectrum); (b) sample S300/100. The insets report the corresponding PLE spectra, measured by detecting the emission at 4.4 eV.

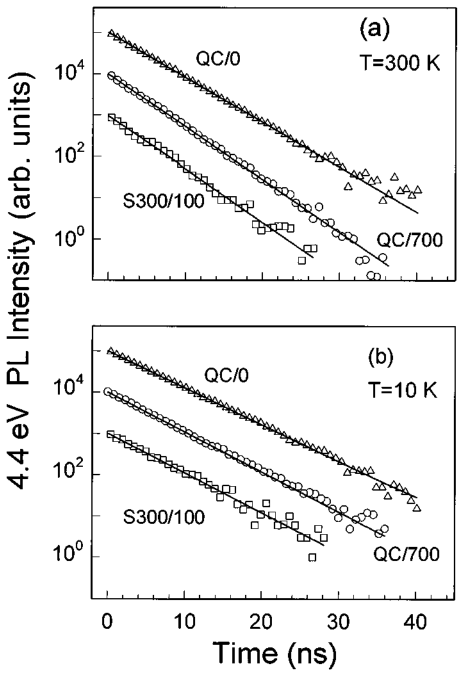

FIG. 5. Kinetics of the PL emission at 4.4 eV excited at $E_{\mathrm{exc}}=5.0$ eV: (a) $T=300$ K; (b) $T=10$ K. Data were taken in the samples: QC/0 (△), QC/700 (○), and I301 (□). For viewing purposes, the initial values of the decay curves are scaled by decades. Full lines plot the exponential functions with the decay time τ determined by best fitting.

S300/100 [Fig. 4(b)]. The PL emission in sample S300/100 is certainly caused by γ irradiation, since it was not observed in the as-grown material (sample S300/0). The PLE spectra (insets of Fig. 4) refer to the PL light emitted at 4.4 eV and consist of a maximum at $E_{\mathrm{exc}}=6.8$ eV and a shoulder structure extending up to ≈ 8.0 eV. In the next section we will comment on the peculiar shape of these PLE profiles.

C. Transient PL

A further difference between the bands α_I and α_R was noticed when considering the decay of the PL signal in transient measurements. The decay of the PL at 4.4 eV is known to occur in a time scale of the order of ns.[6,15,20,29] Accurate measurements have been reported only recently[15] and limited to the α_I band in oxygen-deficient silica.

Typical decay curves of the PL signal, as detected in our three samples under excitation at 5.0 eV and at $T=300$ K are reported in Fig. 5(a). The decay is exponential in all samples, over a dynamic range of at least three decade of intensity. By a standard fitting procedure, we measured the lifetime $\tau=3.5$ ns for the α_R signal in both the irradiated samples (QC/700 and S300/100), to be compared to the longer value $\tau=4.1$ ns measured in the unirradiated sample QC/0. The same values of τ, within the experimental uncertainty of ± 0.1 ns, were measured for other two values of the excitation energy, $E_{\mathrm{exc}}=6.8$ eV and $E_{\mathrm{exc}}=7.6$ eV (curves not shown).

Finally, we performed transient PL measurements at $T=10$ K. The decay curves of the PL emission, excited at 5.0 eV, are reported in Fig. 5(b). At low temperature, a substantial lengthening of the lifetime occurs; in particular, we determined $\tau=4.6$ ns for the α_R signal in the samples QC/700 and S300/100, and $\tau=4.8$ ns for the α_I signal in QC/0. At variance to the behavior observed at $T=300$ K, at $T=10$ K the lifetime was found to depend on the excitation energy. In particular, for $E_{\mathrm{exc}}=6.8$ eV, we measured essentially the same value of τ (within the experimental uncertainties) for both bands and in all three samples, whereas for $E_{\mathrm{exc}}=7.6$ eV, we revealed a shortening of the lifetime: $\tau=2.4$ ns, $\tau=3.1$ ns, and $\tau=3.4$ ns, in samples S300/100, QC/0, and QC/700, respectively.

In Table I we summarize the experimental values of the relevant quantities, as derived from the measurements reported above.

IV. DISCUSSION AND CONCLUSIONS

According to our experimental results, γ irradiation of silica glasses produces, among others, an optical active defect characterized by the PL band α_R at 4.37 eV, having a PLE spectrum with two maxima at $E_{\mathrm{exc}}=5.0$ eV and $E_{\mathrm{exc}}=6.8$ eV. This PL emission has a short decay time, as measured here.

The effect is quite general and independent on the silica type. The three materials considered above are representative of a large variety of commercial silica, at least as regards the properties of the PL activity at 4.4 eV. In particular, we found that the behavior of Suprasil 1 and Suprasil 311 (type III) (Ref. 24) is the same as S300, that of Puropsil[31] 453 as QC, and that of Homosil, Herasil,[24] Pursil A (Ref. 31) as I301.

The γ-generated α_R band is well distinguishable from the α_E PL band, excited within the $B_{2\beta}$ OA band, observed in many natural silica types, and its growth is independent of the existence of this band in the as-grown material.

The band α_R brings close similarities to the band α_I,

TABLE I. Experimental values of the relevant quantities of the PL emission at 4.4 eV in our three samples, at three different excitation energies.

Samples	$E_{\mathrm{exc}}=5.0$ eV				$E_{\mathrm{exc}}=6.8$ eV				$E_{\mathrm{exc}}=7.6$ eV	
	E_0 (eV) (± 0.01)	FWHM (eV) (± 0.02)	Lifetimes (ns) (± 0.1)		E_0 (eV) (± 0.02)	FWHM (eV) (± 0.04)	Lifetime (ns) (± 0.1)		Lifetime (ns) (± 0.2)	
			$T=300$ K	$T=10$ K			$T=300$ K	$T=10$ K	$T=300$ K	$T=10$ K
QC/0	4.42	0.45	4.1	4.8	4.42	0.42	4.1	4.6	4.0	3.1
QC/700	4.37	0.46	3.5	4.6	4.38	0.42	3.5	4.6	3.5	3.4
S300/100	4.37	0.45	3.5	4.6	4.37	0.40	3.6	4.5	3.7	2.4

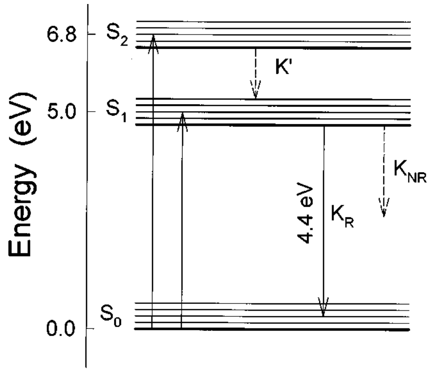

FIG. 6. Energy level scheme used for discussing the results obtained for the PL bands α_I and α_R. Triplet states, responsible for other PL bands, are not considered.

originating from oxygen-deficient centers (ODC's), as regards the peak energy, the PLE spectrum and the decay time. Our experimental results cannot prove a specific structural model, however, they suggest that the γ-induced defect has a structure similar to the ODC. Moreover, the fact that the band α_R is generated also in synthetic silica (as, e.g., S300), clear of optical active defects before irradiation, indicates that the defect is generated by γ rays acting on normal bonds Si-O. It is not surprising that exposure to γ rays can play the same role as the growth in an oxygen-deficient ambience; in fact one of the basic effects of the radiation is the cleavage of the Si-O bonds and the displacement of the oxygen out of its normal position. Our results indicate that doses as low as 1 Mrad can induce detectable PL activity even in the absence of precursors. This is in disagreement with the previously reported statement[9] that this mechanism of defect generation requires γ doses as high as 1000 Mrad.

The observed properties of both bands, α_R and α_I, are consistent with the simple energy level scheme outlined in Fig. 6, consisting in a ground state S_0 and two singlet states S_1 and S_2. Both transitions, at 5.0 and 6.8 eV, are able to excite the PL emission at $\approx$4.4 eV, associated with the decay from S_1 to S_0. A similar energy level scheme was put forward by Skuja[5,14] for an ODC center consisting of a twofold coordinated Si. As displayed in Fig. 6, the decay rate of the excited state S_1 has both radiative (K_R) and nonradiative (K_{NR}) contributions. In this scheme, K_{NR} includes the relaxation rate from S_1 to S_0 through the triplet state (not shown). As an experimental fact, the lifetime of S_1 is independent of the pump energy (5.0 or 6.8 eV), so we can assume $K' \gg K_R$, K_{NR} and $\tau=(K_R+K_{\mathrm{NR}})^{-1}$ for both excitation bands.

The centers responsible for the two bands are expected to have essentially the same electronics properties. However, according to the results in Table I, the two bands exhibit small differences as regards the peak energies, the PLE spectra, and the decay times at $T=300$ K. The differences are above the experimental uncertainties and have been verified in a variety of samples.

We suggest that these differences are related to little different environments surrounding two essentially similar centers. A possibility is that the two centers differ from each other for their vibrational coupling, which may affect not only the peak energy of the PL emission but also its lifetime. In fact, the difference between the measured values of τ at $T=300$ K ($\tau=3.5$ and 4.1 ns, for the α_I and the α_R band) may be ascribed to the different value of K_{NR}, which represents nonradiative channels for energy relaxation (phonons) and is expected to be rather sensitive to the local environment. This hypothesis may explain also the low-temperature behavior of τ. In fact, on lowering T, due to the narrowing of the phonon spectrum and its shift toward lower frequencies, nonradiative relaxation is expected to lose effectiveness and the lifetime to tend to the value $\tau=(K_R)^{-1}$, peculiar of the defect structure and independent of the vibrational properties of the surrounding. This is in agreement with our experimental observational that both the α_I and the α_R bands have the same lifetime $\tau=(4.6\pm0.2)$ ns at $T=10$ K [Fig. 5(b)]. In this scheme, from our low-temperature measurements, we can derive $K_R \approx 2.2\times10^8$ s^{-1}, in agreement with previously reported values,[15] whereas, from the measurements at $T=300$ K, we get $K_{\mathrm{NR}} \approx 2.7\times10^7$ s^{-1} for the α_I band and $K_{\mathrm{NR}} \approx 6.9\times10^7$ s^{-1} for the α_R band.

Our results on the high-energy PLE profiles (Fig. 4) agree with those reported for the α_I band by Nishikawa *et al.*,[15] with a pronounced maximum at nearly 6.8 eV and a broad shoulder extending up to 8.0 eV. Those authors interpreted this spectrum as the superposition of two bands, at $E_{\mathrm{exc}}=6.9$ eV and at $E_{\mathrm{exc}}=7.6$ eV. They supported this hypothesis also by their observation that the decay of the PL emission excited at 7.6 eV was faster than exciting at 5.0 eV or at 6.8 eV, by nearly a factor 2. For interpreting their results, they suggested an ODC model with two structural configurations, the former with the same energy level scheme as in our Fig. 6, the latter with only one singlet-to-singlet transition at 7.6 eV. In their interpretation, the PL emission at 4.4 eV upon excitation at 7.6 eV results from the conversion from one configuration to the other and is characterized by a shorter decay time because of back-conversion processes. Actually, our low-temperature measurements in all our samples confirm the shortening of the lifetime on increasing the excitation energy to 7.6 eV (Table I). However, we found that the shortening is peculiar of the low-temperature case; in fact at $T=300$ K the lifetime recovers a value independent of the excitation energy ($\tau=4.1$ ns for the α_I band and $\tau=3.6$ ns for the α_R band). This result does not seem to support the two-configuration ODC model. In fact, in the framework of that model, on increasing the temperature the back-conversion rate should fasten and hence the shortening of the lifetime upon excitation at 7.6 eV should be more evident. We have not an alternative explanation for the peculiar shape of high energy PLE spectra. Here we only report that the relative intensity of the shoulder at 7.6 eV with respect to the maximum at 6.8 eV was found to depend on the material type.

A final remark concerns the spectra in Fig. 2 and in Fig. 4(a), where one can notice that in the irradiated sample QC/700 the PL spectra have completely assumed the properties of the α_R band, even if the intensity of the band is higher than in the unirradiated sample only by a factor less than 2. This fact suggests that the concentration of the centers responsible for the α_1 band decreases under γ irradiation. We recall that it has been reported that the OA band $B_{2\alpha}$ and the associated PL emission α_I can be bleached (even if partially) by exposure to uv light.[9,13] A similar effect may be hypothesized for γ photons. Further experimental work is required to make clear this aspect.

In conclusion we have reported experimental results on the PL band α_R induced by γ irradiation in a variety of silica types. We have characterized this band by measurements of stationary PL and transient decay, in the uv and vuv region. We suggest that the center generated by γ rays is very similar to the ODC observed in oxygen-deficient silica, the only difference between the two centers being the vibrational environment. Measurements at low temperature seem to confirm this tentative interpretation. We have also reported experimental results on the properties of the α_I PL band, which are in agreement with those previously reported by other authors,[15] but for our observation that the decay rate of the transient PL is essentially independent of the excitation energy at room temperature; this aspect is relevant for its connection with the interpretation of the high-energy PLE spectrum of this band.

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