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Competitive relaxation processes of oxygen deficient centers in silica

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We report an experimental study on the temperature dependence, from 6 K up to 300 K, of the 4.4 eV emission excited at 7.6 eV via the conversion between two different types of oxygen deficient centers in silica. The photoluminescence undergoes a thermal quenching above 50 K, its amplitude decreasing by a factor of 10, not correlated with changes from 2.1 ns down to 1.4 ns of its lifetime. These experimental features are explained with the occurrence of two nonradiative processes arising from the 7.6 eV excited state: one pumping the 4.4 eV emission and the other accounting for alternative relaxation pathways. The competition between these two rates can be expressed in terms of an Arrhenius law fitting the luminescence quenching with an activation barrier of 29 meV.

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The optical properties of diamagnetic oxygen deficient centers (ODC) in silica are one of the most controversial aspects in the field of defects in this high-gap amorphous insulator.[1,2] Two ODC species have been distinguished by their optical absorption (OA) and photoluminescence (PL) features: ODC(I) associated with an OA at 7.6 eV (E band) and ODC(II) associated with the OA at 5.0 eV ($B_{2\alpha}$ band) and 6.9 eV and a PL at 4.4 eV related to the inverse transition of the $B_{2\alpha}$ band.[1,3–6] It was seen that these two defects stably coexist in as-grown oxygen deficient silica, where the experimentally measured ratio of 7.6 eV absorption/5.0 eV absorption is of the order of 10^3-10^4.[7] A link between these ODC variants was put forward by the observation that under excitation at 7.6 eV of ODC(I) the emission at 4.4 eV [typical of ODC(II)] can be excited, which suggests the effectiveness of conversion processes between these two centers.[8–12] However, time decay measurements at $T=45$ K showed different lifetime values for this emission: 4.2 and 2.1 ns by exciting at 5.0 and 7.6 eV, respectively.[10] In this view, Nishikawa *et al.*[10] proposed a two-configuration model: following the excitation at 7.6 eV, ODC(I) undergoes a conversion towards an unstable ODC(II) from which both the 4.4 eV emission and a back-conversion towards ODC(I) takes place, thus explaining the shorter lifetime. Since then, the ODC(I)-ODC(II) interconversion has met the consent of other researchers on the basis of both optical measurements and *ab initio* simulations.[1,11,13,14]

The reliability of the proposed interconversion processes, even if it rationalizes the link between the 7.6 eV absorption and the 4.4 eV emission, lacks suitable experiments looking for their dynamics. In this work we are concerned with the temperature-dependence examination to find out the relaxation processes occurring from the excited states of ODC(I) up to the emission of the 4.4 eV PL band. We stress that any quantitative analysis of this emission, under vacuum uv excitation, has been until now prevented by distortion due to the strong absorption at 7.6 eV in oxygen-deficient silica.[10–12] To overcome this difficulty, we employ samples with a low content of ODC(I) defects that can be induced in stoichiometric samples after controlled exposure to particles or ionizing radiation.[15,16]

Our measurements were performed on a synthetic wet silica specimen Corning 7940,[17] having sizes of $5\times5\times0.5$ mm^3, irradiated by 2.5 MeV β rays at a dose of 1.2×10^8 Gy by using a Van de Graff electron accelerator. This irradiation produced the growth of the absorption E band, having a peak energy at 7.62 ± 0.03 eV, full width at half maximum (FWHM) of 0.64 ± 0.03 eV and amplitude of 6 ± 1 cm^{-1} at room temperature and a $B_{2\alpha}$ band whose amplitude of $\sim5\times10^{-2}$ cm^{-1} was estimated by the uv excitation spectrum of the 4.4 eV emission. For the sake of comparison we have also investigated the synthetic dry silica oxygen deficient Suprasil 300,[18] $5\times5\times1$ mm^3 sizes, which, as already reported in Ref. 11, has a native OA at 7.54 ± 0.02 eV, FWHM$=0.53\pm0.02$ eV, amplitude of 15.5 ± 0.5 cm^{-1}, while the $B_{2\alpha}$ band, as well measured by the 4.4 eV PL excitation spectrum, is $\sim5\times10^{-3}$ cm^{-1}. It is worth noting that in the β irradiated sample the ratio between the 7.6 eV absorption and the 5.0 eV absorption is about one order of magnitude lower than that in as-grown oxygen deficient silica.

PL activity was investigated with pulsed excitation light ranging from 4.5 to 9.0 eV using the synchrotron radiation (SR) at the SUPERLUMI station on the I beamline of HASYLAB at DESY (Hamburg).[19] The emitted light was analyzed by a 0.5 m monochromator (Czerny-Turner mounting) equipped with a photomultiplier (Hamamatsu R2059 model). PL emission and excitation spectra were measured under multibunch operation and detected within a time window of 21 ns correlated with the arrival of SR pulses. Excitation spectra were corrected for the spectral efficiency of the exciting light. Transient time decay was measured under single-bunch operation, using 1024 channels for scanning the time interval of 192 ns between adjacent pulses, pulse width of 130 ps. The temperature was varied from 6 K up to 295 K by using a sample chamber with a continuous helium-flow cryostat.

Figure 1 shows the temperature dependence of the 4.4 eV PL activity excited in the uv and vacuum-uv range. At low temperature, $T=10$ K, the excitation profile consists of a band at 5.0 eV, associated with the $B_{2\alpha}$ absorption of ODC(II), and a composite structure at higher energy domi-

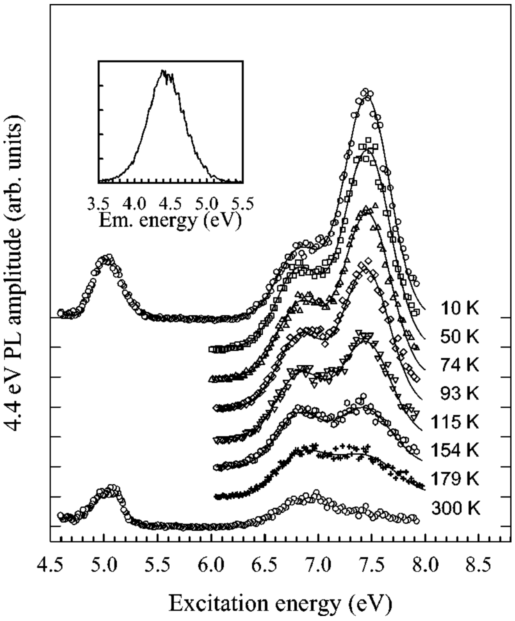

FIG. 1. Photoluminescence activity under uv and vacuum-uv excitation as measured in the β-irradiated Corning 7940 sample. We report the excitation spectra on varying the temperature from 10 K up to 300 K; solid lines represent the two Gaussian best fit for energy above 6.0 eV. In the inset is shown the emission spectrum excited at 7.4 eV and detected at $T=10$ K.

nated by the ODC(I)-related band peaked at 7.45 ± 0.02 eV and FWHM$=0.67\pm0.03$ eV. This is seen by the best fit procedure with two Gaussian components, the second taking into account the 6.9 eV transition from ground up to second excited singlet state in the ODC(II) defect.[6,10–12] We stress that, owing to the low absorption in this spectral region (~0.15 optical density at 7.6 eV) the curve shown in Fig. 1 represents the undistorted vacuum-uv excitation spectrum of the 4.4 eV emission. Hence, through the comparison with the absorption values at 5.0 and 7.6 eV, we argue that, at $T=10$ K, the excitation efficiency from the ODC(II) is higher by a factor ~50 than the ODC(I). On increasing the temperature, we observe the decrease of the 4.4 eV PL amplitude more pronounced on exciting at the higher energy component. At room temperature, the peak at 7.5 eV disappears and only the ODC(II)-related bands at 5.0 and 6.9 eV are observed.

The temperature dependence of the transient behavior of the 4.4 eV emission under pulsed excitation at 7.6 eV is shown in Fig. 2. The curves refer to different temperatures, from 6 up to 182 K, show similar features characterized by comparable decay times of a few nanoseconds. In fact, taking into account the lifetime τ corresponding to the decrease down to $1/e$ of the maximum value, we measure $\tau=2.1\pm0.1$ ns at $T=6$ K down to $\tau=1.9\pm0.1$ ns at $T=182$ K.

In Fig. 3, we summarize the thermal behavior of the 4.4 eV PL under 7.4 eV excitation in the β-irradiated Corning 7940 silica specimen. In the investigated temperature range, the PL amplitude obtained by the above-described best fitting procedure of Fig. 1 decreases by ~1 order of magnitude whereas the lifetime reduction is less than 10%. In the inset, we show the temperature dependence of the PL at 4.4 eV as measured in the Suprasil 300 sample over a range extending up to 240 K. The obtained results are almost consistent with those for the irradiated Corning 7940 sample even if now we find that the lifetime decreases down to 1.4 ns at $T=240$ K. We observe that the temperature dependence of the 4.4 eV emission lifetime, evidenced in the Suprasil 300 sample, agrees with previous experiments.[12]

The energy level scheme sketched in Fig. 4 helps us to interpret the observed features. It includes a ground state S_0

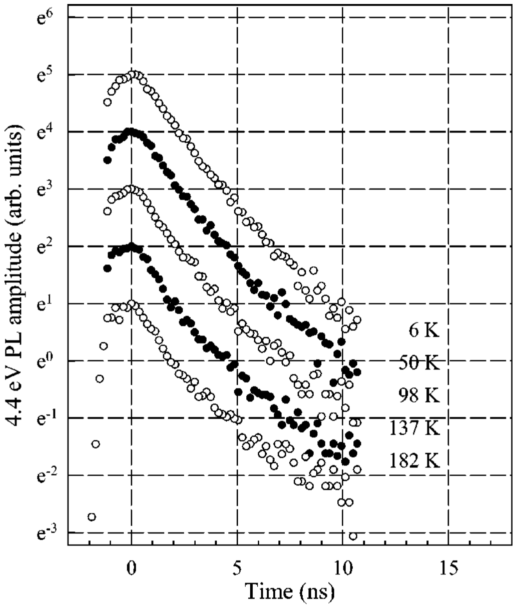

FIG. 2. Time decay of the emission at 4.4 eV excited at 7.4 eV observed for the β-irradiated Corning 7940 sample at various temperatures from 6 up to 182 K. For sake of clarity, the curves are arbitrarily scaled.

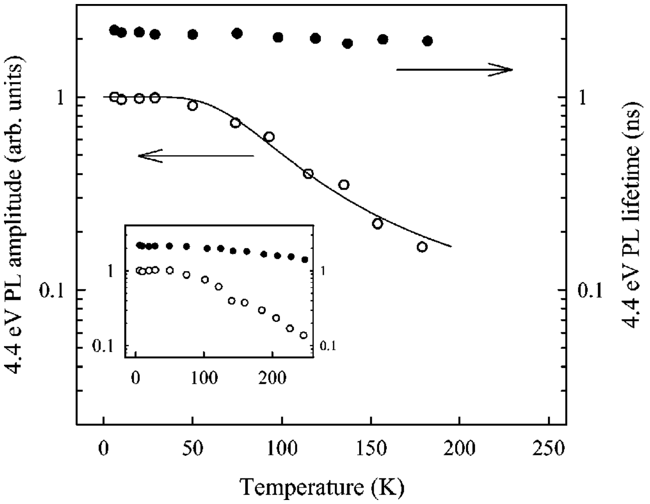

FIG. 3. Amplitude (open symbol) and lifetime (full symbol) temperature dependence of the 4.4 eV emission excited at 7.4 eV for the β-irradiated Corning 7940 sample. Solid line represents the best fit curve of Eq. (3). In the inset we show the thermal behavior of amplitude and lifetime as measured in the unirradiated Suprasil 300 sample.

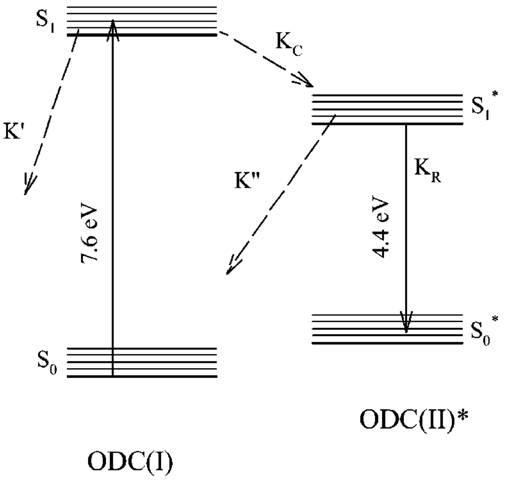

FIG. 4. Schematic diagram of the energy levels and transitions accounting for the luminescence at 4.4 eV excited at 7.6 eV.

and an excited state, S_1, connected by the 7.6 eV absorption transition and associated with the ODC(I) defect, and the two states $S_0^\star$ and $S_1^\star$ associated with the unstable ODC(II)* configuration and originating the emission at 4.4 eV. The depopulation of S_1 is governed by the competition between the nonradiative rate K' down to S_0 and the conversion rate K_C towards $S_1^\star$; in turn $S_1^\star$ can relax both radiatively emitting the 4.4 eV fluorescence at the rate K_R and non radiatively at the rate K'' including the back conversion process towards ODC(I).[10] During the SR excitation around 7.6 eV, the 4.4 eV PL quantum efficiency is governed by (i) the pumping term from S_1 proportional to the ratio $K_C/(K_C+K')$; (ii) the relaxation from $S_1^\star$ proportional to $K_R/(K_R+K'')$. After the SR pulse, only the relaxation takes place and the PL kinetics is given by

$$I_{PL}(t)\propto \frac{K_C}{K_C+K'}\,\frac{K_R}{K_R+K''}\,e^{-(K_R+K'')t}. \qquad (1)$$

Integration of Eq. (1) over a time much longer than $(K_R+K'')^{-1}$ gives rise to the integrated PL intensity:

$$I_{\mathrm{PL}}^{\mathrm{Integ}}\propto \frac{K_C K_R}{(K_C+K')(K_R+K'')^2}. \qquad (2)$$

Comparison of Eqs. (1) and (2) with the thermal behavior of the 4.4 eV PL activity, shown in Fig. 3, points out two main aspects:

(i) The lifetime only reduces from 2.1 down to 1.9 ns below 180 K, thus indicating that any variation of the nonradiative rate K'' in this temperature range is negligible in comparison with the sum K_R+K''.

(ii) The integrated amplitude drops down above 50 K. Therefore, this negative change can be mainly related to the competition between nonradiative relaxation rates K_C and K' arising from S_1.

On the basis of the points (i) and (ii), one can hypothesize that the quenching of the 4.4 eV emission is governed by an Arrhenius behavior so that Eq. (2) can be readjusted according to the expression:[20]

$$I_{\mathrm{PL}}^{\mathrm{integ}}(T)\propto[1+A\exp(-\Delta E/k_B T)], \qquad (3)$$

where k_B is the Boltzmann constant while the activation energy ΔE and the preexponential factor A take into account the ratio K'/K_C. The best fit curve of our data in term of Eq. (3) is reported in Fig. 3 (solid line) with $A=27\pm 3$ and $\Delta E=29\pm 3$ meV. It is worth noting that the positive value of ΔE, as obtained by our analysis, means that the crossing $S_1\rightarrow S_1^\star$ is anyway favored (lower activation energy) in comparison with the K' channel.

In the framework of the most commonly accepted model assuming the ODC(I) to be a relaxed oxygen vacancy,[4,5,13,14,21–23] our results are consistent with the hypothesis that, following the 7.6 eV absorption transition, the Si nuclei move away from their ground state distance ~2.3–2.5 Å, thus producing more structural rearrangements through competitive nonradiative processes. In particular, we acknowledge that *ab initio* molecular dynamics computations reported in Ref. 14 have shown the occurrence of two nonradiative relaxation channels from the excited oxygen vacancy towards (i) a twofold coordinated silicon, ODC(II), emitting at 4.4 eV and (ii) a couple of E' centers.

In conclusion, we examined the relaxation processes originating from the two diamagnetic ODC variants in silica upon vacuum-uv excitation. Following the absorption at 7.6 eV, the excited ODC(I), besides pumping the 4.4 eV emission via its conversion into the unstable ODC(II)*, relaxes by an alternative nonradiative channel. The balance between these two deexcitation rates can be accounted for a net phonon-assisted relaxation with an activation barrier of 29 meV, which is the main cause of the observed thermal quenching of the photoluminescence at 4.4 eV.

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