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Thermostimulated luminescence and electron spin resonance in X-ray- and photon-irradiated oxygen-deficient silica

A.N. Trukhin [a,*], J. Troks [a], D.L. Griscom [b]

[a] *Institute of Solid State Physics, University of Latvia, Kengaraga St. 8, LV-1063 Riga, Latvia*
[b] *ImpactGlass Research International, 3938 E. Grant Road #131, Tucson, AZ 85712, USA*

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Abstract

Influences of oxygen-deficiency on radiation properties of high-purity, low-OH fused silica were studied. It is found that thermostimulated luminescence (TSL) peaks are different for photo (7.7 eV) and X-ray excitation at 77 K. X-ray excitation produces TSL peaks at 125 and 170 K corresponding to the anneal temperatures of two types of self-trapped holes centers STH_2 and STH_1, respectively, detected by electron spin resonance (ESR). Oxygen-deficiency apparently increases the number of electron traps, stabilizing a larger number of STHs in the continuous defect-free silica network than is observed in similarly X-irradiated stoichiometric silica glasses. Photoexcitation of oxygen-deficient glass at 7.7 eV produces TSL peaks at 105 and 200 K, presently attributed to STHs at perturbed sites in the immediate vicinity of oxygen-deficiency centers (ODCs). High temperature TSL peaks at 240 and 400 K are produced by both types of irradiations and are followed by ESR detection of E' centers only. All observed TSL and ESR signals were proportional to the level of oxygen-deficiency. The main spectral band in TSL near 2.7 eV is a triplet–singlet transition, ascribable to the twofold-coordinated silicon center (ODC(II)) modified by its nearest structure. It is proposed that this recombination process results when a thermally detrapped STH encounters an electron trapped at the site of ODC(I), and is transmuted into a modified ODC(II):e^-. In principle, any such ODC:e^- defect should be paramagnetic. However, no trapped-electron centers were detected by ESR in the present experiments. Based on the recent work of others, the E'_α centers that were observed are believed to be trapped hole centers. Thus, for reasons unknown, the postulated ODC(II):e^- centers, which may be the primary electron traps in oxygen-deficient silicas, appear to be ESR-silent.

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1. Introduction

Oxygen-deficiency profoundly affects many properties of silica glass. One of them is the optical absorption in the range of transparency, including two well-known bands at 5 and 7.6 eV (for an in-depth review, see [1]). If the 5 eV absorption band in pure and oxygen-deficient silica is well argued to arise from lone twofold-coordinated silicon centers [2–4], opinions on the nature of 7.6 eV band are far more divided [5–11]. There is near universal acceptance that the 7.6 eV band arises from some sort of an 'oxygen-deficiency' in silica (see [1]), and a case has been made that it is Rydberg-like transition from a Si–Si bonding orbital to a Si 4s state [5–7]. Still, it has been cautioned that the complicated set of experimental data does not allow the 7.6 eV band to be ascribed to such a simple point defect [8,10,11] such as neutral oxygen vacancy. Nevertheless, many workers have shown that photon irradiation at 7.6 eV of silica samples displaying a 7.6 eV absorption band leads to creation of E' centers [6,9], as measured by electron spin resonance (ESR), and this result has been

* Corresponding author. Tel.: +371 7 260 686; fax: +371 7 132 7781.
E-mail address: truhins@latnet.lv (A.N. Trukhin).

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used as an argument for the neutral-oxygen-vacancy nature of the 7.6 eV band [6,9]. However, in [8,12] it was shown that the E' center is not the sole product of phototransformation of the precursor defect, and it was therefore argued that the simple relaxed oxygen vacancy is not an adequate model of the defect responsible for the band at 7.6 eV.

Here we report studies of radiation-induced optical properties and ESR spectra of the corresponding electron and hole traps of silica samples prepared with deliberately high levels of oxygen-deficiency and we compare the effects of in-band photoirradiation of such samples with those of non-selective ionizing X-ray irradiations. Specifically, we present the results of electron spin resonance (ESR), thermostimulated luminescence (TSL), and photo and X-ray excited luminescence (PL and XRL, respectively) studies of the trapped charge states in Si-doped silicas irradiated at 80 K. Radiation-induced optical absorption spectra of these samples have been reported elsewhere [8].

2. Experimental details

The high purity silica samples for investigation were variations on Russian KS-4V [10]. The method of preparation and purification in all cases was based on recrystallization (cristobalitization) of synthetic silicon dioxide and electrofusion. A high level of oxygen-deficiency in some samples was provided by reaction of the cristobalite with silicon vapor [10]. The oxygen-deficient sample studied here contained about 0.015 wt% Si. For comparison, a sample of KS-4V type melted under normal oxidizing conditions was used. Samples with dimensions $10 \times 10 \times 1$ mm^3 were used for TSL measurements. The measurement temperature could be varied from 60 to 700 K. Photoexcitation was performed in vacuo using light from a deuterium discharge lamp passed through a vacuum monochromator. An X-ray tube with a tungsten anode (15 mA, 40 kV) was used to study the influences of ionizing radiation.

The thermostimulated luminescence was measured by slow heating (0.1 K/s) of the sample after irradiation at 80 K. The luminescence spectra were measured by a MDR-2 monochromator with a 1200-lines/mm grating for the range 2–6 eV. Samples with dimension $2 \times 2 \times 2$ mm^3 were used for ESR measurements. The ESR spectrometer was a PE-1307 operating at 9.4 GHz. The magnetic field modulation frequency was 100 Hz. ESR spectra were recorded at 77 K immediately following 10-min X-ray exposure and also following a subsequent anneal at 200 K.

3. Results

The TSL curves for X-ray (curve 1) and photo excitation (curve 2) for the oxygen-deficient sample are presented in Fig. 1. After X-ray excitation we observe peaks at 125, 170, 240 and 400 K. After photoexcitation at 7.7 eV we observe a weak TSL peak at 105 K, a very broad peak at 200 K, and apparently the same peak as for X-ray excitation at 400 K. The main detected XRL band is situated in the blue at 2.7 eV with a long UV tail to ~4.6 eV (see inset to Fig. 1), which we will argue is a mark of a modified twofold-coordinated silicon. There is good correspondence between band positions and shapes of XRL and TSL, whereas 7.7 eV-excited PL displays a prominent UV emission band at 4.4 eV together with a weaker blue band near 2.7 eV.

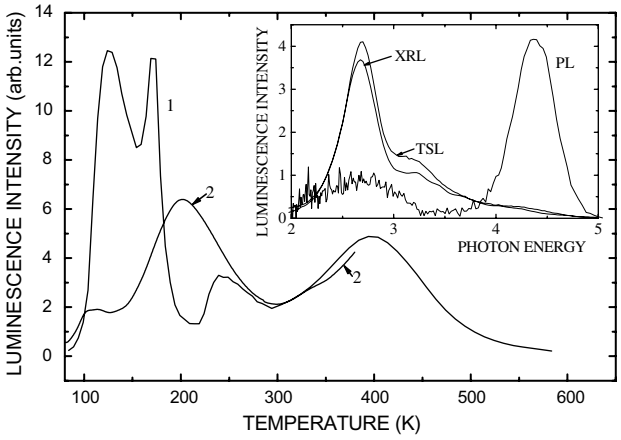

Fig. 1. Thermally stimulated luminescence (TSL) in KS-4 V silica with excess silicon (0.015 wt%) recorded at 2.7 eV after irradiation by X-rays (curve 1) and 7.7 eV photons (curve 2) at 77 K. Insert: luminescence spectra of samples of the same material continuously excited by X-rays (XRL) and by 7.7 eV photons (PL) with comparison to the spectrum of the TSL. The temperature was ~80 K for XRL and PL and ~120 K for TSL.

The ESR spectra of silica samples with and without oxygen-deficiency are presented in Fig. 2. It is seen that X irradiation under identical conditions produces a much more intense ESR signal in the sample with the high level of oxygen-deficiency (Fig. 2, diamonds) relative to the stoichiometric sample (Fig. 2, circles and lines). In order to better understand the natures of these ESR signals, we have compared them with a spectrum taken from literature [13]

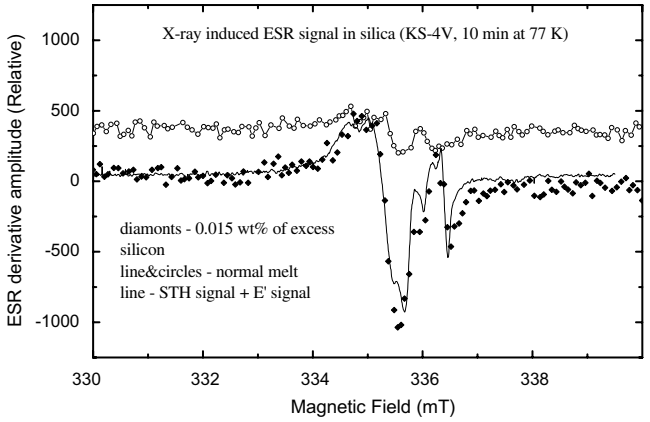

Fig. 2. X-ray-induced ESR signals in KS-4 V silica at 77 K. Diamonds: silica doped with 0.015 wt% of excess silicon. Lines and circles: normal stoichiometric melt. Line without symbols: ESR signal for a Suprasil W1 fused silica sample exposed to X-rays at 77 K and recorded at 110 K (from Ref. [13]).

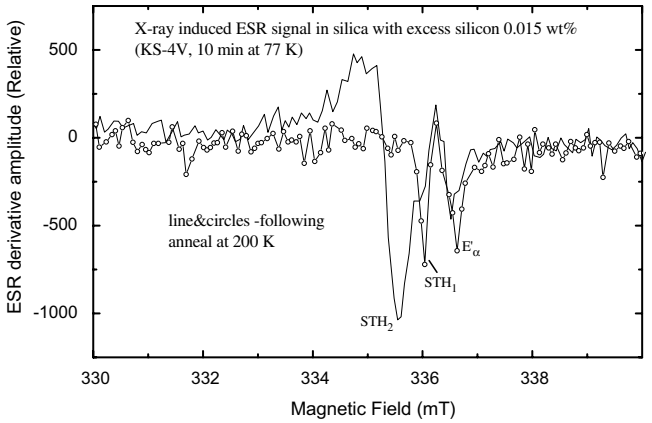

Fig. 3. X-ray-induced ESR signals in KS-4 V silica with excess silicon 0.015 wt% at 77 K. Line without symbols: immediately following irradiation without warming. Lines & circles: following anneal at 200 K.

(Fig. 2, unbroken curve). Excellent agreement can be noted in the case of the sample with 0.015 wt% Si doping.

In Fig. 3 we illustrate some influences of annealing on the ESR signal of the oxygen-deficient sample. The curve without symbols corresponds to the as-irradiated condition at 77 K without anneal; the lines and circles show the result of heating to 200 K. It is seen that this annealing step substantially bleached the main signal, leaving only two sharp lines on the high-field side. Only the highest-field line, attributable to E' centers, was also detected after irradiation at room temperature.

4. Discussion

4.1. Si doping appears to create additional electron traps, which in turn stabilize larger numbers of self-trapped holes

Although the signal-to-noise ratios were not high in any case, the Si-doped sample of the present study clearly exhibited much stronger ESR signals than the undoped sample. The spectrum of Fig. 2 (diamonds) proves to be almost identical, except for noise and some over-modulation, to the self-trapped-hole-plus-E' center spectrum of the paper [13], reproduced as the continuous curve in Fig. 2. Moreover, the parts of the spectrum corresponding to positive g shifts were strongly bleached at 200 K (Fig. 3), as they must be if they are really due to self-trapped holes (STHs) [13]. Since STHs are typical of normal 'defect free' silica glasses [13], the higher strength of the STH spectrum in the oxygen-deficient sample would seem to imply that adding Si to the glass creates additional electron traps which stabilize larger populations of STHs.

In fact, there is considerable evidence in the literature that introduction of special electron traps into otherwise pure silica glass greatly enhances STH yields upon irradiation at cryogenic temperatures. First, the reference spectrum of Fig. 2 (unbroken curve taken from [13]) corresponds to a material (Suprasil W1) rich in interstitial oxygen molecules. Based on data for STHs induced in Suprasil W1 by 6.4 eV photons, it was proposed in [14] that such a sub-band-gap irradiation can only have produced large concentrations of STHs by electron transfer from network oxygens to interstitial oxygen molecules, producing interstitial O_2^- molecular ions (which are not detectable by ESR due to their weak and poorly defined crystal-field interactions with the glass network [15]). Second, the high strength of an oxygen-hole-center signal (retrospectively recognized as due to STHs) in a sol–gel silica glass X-irradiated at 77 K was attributed in [16] to efficacious electron trapping on Ge impurities; (indeed, strong ESR spectra of Ge(1,2) trapped-electron centers were also recorded in this experiment [16]).

4.2. What are the electron traps in oxygen-deficient silicas?

The nature(s) of the additional electron traps resulting from Si doping are not immediately apparent from our data since, aside from STHs and E' centers, no other paramagnetic species are detected – and most E' centers have been generally thought of as trapped-hole centers [17–20].

The $E'_{\alpha 1}$ center [17], which is a strong component of the present E' center spectra, was recently proposed to be the result of electron trapping on a two-coordinated silicon [19]. However, an even more recent paper has reported a reliable determination of the ^{29}Si hyperfine structure (hfs) of a stable E'_{α} center variant that clearly identifies it as due to an unpaired electron in a dangling sp^3 orbital of a three-coordinated silicon ($O_3 \equiv Si\bullet$, where '$\equiv$' denotes three bonds to three network oxygens and '$\bullet$' represents the unpaired spin); and it was demonstrated to result from *positive* charge trapping [20]. Furthermore, Buscarino [20,21] showed from studies of the 5 eV-excited 4.4 eV photoluminescence band that in at least four different low-OH silica samples the concentration of two-coordinated silicons was about one order of magnitude lower than the combined concentrations of E'_{γ} plus E'_{α} centers generated by γ irradiation and subsequent isothermal annealing at 630 K. Thus, (1) the E'_{α} center variant that is stable to 630 K (we shall call the $E'_{\alpha HT}$ center; 'HT' for high temperature) cannot arise from an electron trapped on a two-coordinated silicon as proposed in [19] and (2) there are insufficient two-coordinated silicons – ODCs(II) – to account for the majority of the trapped electrons. Regardless of trapping sites, Buscarino's studies of γ-irradiated dry silicas annealed to ~630 K demonstrate that in dry, oxygen-deficient silica samples trapped-electron centers have no ESR signature, in either the standard first-harmonic or high-power second-harmonic modes of detection [20,21].

In contrast to Buscarino's room-temperature irradiations and high-temperature anneals, our present ESR experiments were performed at 77 and 200 K after irradiation at 77 K, so the $E'_{\alpha 1}$ centers [17] that we observe could conceivably be different in nature than $E'_{\alpha HT}$. (Because the notation of [17] has become obsolete, we propose to rename the $E'_{\alpha 1}$ defect as $E'_{\alpha LT}$.) There are two notable

experimental differences between $E'_{\alpha LT}$ and $E'_{\alpha HT}$: (1) the measured mean values of g_2 are different $\{g_2(E'_{\alpha LT}) = 2.0013$ [17–19] and $E'_{\alpha HT} = 2.0009$ [20, 21]$\}$ well outside of experimental error and (2) $E'_{\alpha LT}$ is white-light bleachable [17] whereas $E'_{\alpha HT}$ is not [20,21].

Nevertheless, despite these differences, there is adequate evidence that neither $E'_{\alpha LT}$ nor the E'_{γ} variant into which it is converted by white-light bleaching [17] is a trapped electron center. This evidence comes from comparison of the isochronal anneal curves of X-ray- and 6.4 eV-photon-induced paramagnetic defect centers in another low-OH silica (Suprasil W1) [14]. In the case of the X-irradiated sample of [14], the total oxygen-associated trapped hole centers ($STH_1 + STH_2 +$ peroxy radicals) was an order of magnitude greater than the total E' centers, yet both totals shared the same exponential – $\propto \exp(-T/130\ K)$ – isochrona decay behavior from 110 to ~260 K. In [14], this 'universal' decay law (also seen in a high-OH silica) was tentatively ascribed to 'detrapping of electrons from a range of shallow traps not detectable by ESR.' Strongly supporting this notion was the fact that Suprasil W1 samples subjected to 6.4 eV-photon irradiation to a comparable dose of deposited energy yielded comparable STH_1, STH_2, and peroxy radical concentrations (but no E' centers), the total of which suffered no decay at all upon an equivalent sequence of isochronal anneals all the way to 290 K [14]. As explained in Section 4.1, the (much more stable) ESR-silent electron traps in *that* case were inferred to be interstitial oxygen molecules, which are peculiar only to oxygen-rich synthetic silicas such as Suprasil W1.

Buscarino's silica samples, like our present one, were *oxygen-deficient* and possessed OH contents <5 ppm [21] (in our case <200 ppb); they differed, however, in having aluminum impurities ~10–100 ppm (in our case <100 ppb). However, Al impurities serve as *hole* traps, so the electron traps are likely to have been the same in their case as in ours; and no ESR-active trapped electron centers were observed in either case. As noted in Section 4.1, increasing levels of oxygen-deficiency are inferred to result in increasing numbers of electron traps. Buscarino has shown [20,21] that there were too few two-coordinated silicons in his samples to serve as such traps; however, he did find that the number of oxygen vacancies (identified and quantified by means of the 7.6 eV absorption band) outnumbered the radiation-induced E' centers in his samples typically by a factor of ~10 to 20 [21].

Thus, ODCs(I) – oxygen vacancies after [6,7] – are the prime suspects for the trapping sites of the ESR-silent trapped electron centers of Buscarino's studies [20,21] and also in the case our present study.

4.3. Thermal bleaching of ESR spectra is consistent with model interpretations

After heating to 200 K, the remaining ESR signals in the present Si-doped sample (Fig. 3, circles) consist of two sharp features, the high-field member of which, though overmodulated, appears to be due almost entirely to $E'_{\alpha LT}$ centers. The sharp feature at slightly lower field corresponds within measurement error to the position of the g_1 peak of the STH variant STH_1 (2.0027 [13]) and is tentatively identified as arising from this source, even though unlike the STH_1 and STH_{mixed} spectra of [13,14] the g_2 peak is unresolved and the spectrum is stable above 200 K. But in support of this notion, room-temperature-stable STHs have been identified in pressure-densified silica [19]. And, a metastable STH_1-like spectrum (also with an unresolved g_2 peak) recorded at room temperature for an as-sputtered high-purity SiO_2 thin film has recently been argued to arise from STHs in highly distorted environments [22].

Otherwise, the principal part of the ESR spectrum induced at 77 K in the Si-doped sample of Fig. 1 (diamonds) was totally removed by the 200 K anneal (see Fig. 2). This principal part is identical within experimental accuracy to the STH variant termed STH_2 in [13], which has been found to decay by a factor of ~50 upon annealing for 5 min at 190 K in undensified bulk silica glasses [14].

4.4. Low-temperature thermoluminescence peaks correspond to STH detrapping

The X-ray-induced thermoluminescence curves of the Si-doped silica sample (Fig. 1, curve 1) exhibit peaks at about 125 and 170 K (as well as at 240 and 400 K). The positions of these first two peaks correspond with the temperatures at which STH_2 and STH_1 respectively anneal by ~20% after 5 min at the respective temperature [14]. The 125-K TSL peak is asymmetrical, with a high-temperature tail extending to ~200 K for a scanning time from 100 to 200 K of ~17 min. By comparison, the result of 5-min isochronal anneals at 20 K intervals up to 200 K is extrapolated from the data of [14] (where the last data point was at 190 K) to STH_1 and STH_2 concentrations reduced by one and two orders of magnitude, respectively. Since the STHs are (with one possible exception[1]) the only defects in silica, intrinsic or extrinsic, known to decay in the range 125–170 K (see relevant references collected in [23]), the X-ray-induced TSL peaks in this range are almost certainly determined by thermal detrapping of STHs. It has been shown

[1] Fig. 1 of Ref. [17] portrays isochronal anneal data for X-ray-induced 'E'_{α} centers' in Suprasil W1, which are seen there to decay with increasing temperatures above 100 K according to a concave-downward curve on a semi-log plot, reaching ~45% of the initial intensity after an anneal at 160 K. It is to be noted that this behavior essentially mimics the decay of STH_2 in the same material [14], so in this case the decay of $E'_{\alpha LT}$ could have resulted if $E'_{\alpha LT}$ were a trapped electron center co-induced with an equal number of STHs. However, the original spectra and measurement conditions pertinent to $E'_{\alpha LT}$ in Fig. 1 of [17] have been lost, so the method by which the $E'_{\alpha LT}$ component was separated from the omnipresent E'_{γ} component no longer known. In any event, the 'E' center' spin-concentration data of [14] for X-irradiated Suprasil W1 – which represent an average of *all* E' centers, not just $E'_{\alpha LT}$ – show an *exponential* decay with increasing isochronal temperature below 200 K (see Section 4.2).

elsewhere [8] that these distinctive TSL peaks monotonically increase in intensity with increasing levels of Si doping up to at least 0.015 wt% – consistent with our conclusion from the present ESR data that increased silicon excess (oxygen-deficiency) results in higher numbers of electron traps, which in turn support higher numbers of STHs.

4.5. Oxygen-deficiency may enhance the number of STH_2 trapping sites in the vicinity of ODCs(I)

Normally, Si-doping-enhanced STH yields would be expected to occur mostly in 'normal' parts of the glass network distant from the oxygen-deficiency-related electron traps, at least when all defects are induced by X-rays, thereby assuring that most electrons (holes) are created above (below) their respective mobility edges. However, this notion seems to be belied by the fact that the 'STH_2' TSL band at 125 K, as well as the TSL band at 400 K, grows much faster with progressively larger Si-doping levels (when comparing the areas under the curves) than the 'STH_1' band at 170 K, which dominates in the stoichiometric glass (Fig. 8 of Ref. [8]). That is, the 125 and 400 K bands might be associated with distortions in the glass network introduced at the same time as the excess silicon. If so, it seems likely that these distortions would occur near the sites of the introduced ODCs. In fact, it has been argued [24] that the accepted model for STH_2 (i.e., the model that is implied by its g matrix [13,22]) requires the presence of some SiO_4 tetrahedra with Si–O–Si dihedral (torsion) angles typical of those in α quartz and therefore atypical of dihedral angles in normal silica glasses. Since ODCs(I) typically outnumber ODCs(II) in dry oxygen-deficient silicas by two to three orders of magnitude [20,21], irradiation of these glasses may result in abundant ODC(I) + electron – STH_2 close pairs.

4.6. The situation changes when activation of the Si-doped glass is taken with 7.7 eV photons

The low-temperature TSL peaks induced by 7.7 eV photons (Fig. 1, curve 2) are located at slightly different positions (at 105 K and at 200 K) vis-a-vis the STH-associated peaks at 125 and 170 K induced by X-rays (curve 1). These 'new' peaks are likely related in some way to the defect giving rise the 7.6 eV band (universally recognized as arising from ODCs(I) [1–4]), which is selectively excited in this experiment. However, it remains possible that the peaks at 105 and 200 K are due respectively to the same two defects (STH_2 and STH_1) that we argue must be respectively responsible for X-ray-induced TSL peaks at 125 and 170 K. Given the inference of Section 4.5 that the enhanced 125 K peak may result from structural distortions favoring STH_2 trapping near ODCs(I) introduced by Si doping, it is proposed that the peaks at 105 and 200 K could be STH-type centers located in more acutely distorted regions of the glass network very near to ODCs(I). Indeed, since the 7.7 eV excitation responsible for the 105 and 200 K TSL peaks is in-band with the absorption of the ODC(I) defect, the STHs associated with this selective excitation are more likely to be localized near ODC(I)s than would be the case in the X-ray-excited samples. By inspection of the relative intensities in Fig. 1, these photoexcited STHs would comprise a small number STH_2s of less-than-normal stability (105 eV peak) and a large number of STH_1s of greater-than-normal stability (200 eV peak).

In any event, the 7.7 eV excitation used here is a lower energy than the photoconductivity band gap of silica at ~9.0 eV [25,26]. Thus, there remains the question of where the ground and excited states of ODC(I) lie with respect to the mobility edges [22,27,28]. In our model, the ground state of ODC(I) must lie somewhat above the mobility edge for hole transport, so that upon in-band photon excitation, the hole may tunnel onto a near-neighbor bridging oxygen where it would be immobilized, in most cases as a strain-stabilized STH_1. In this view, most of these holes would be thermally released to move back to ODC(I):e^- only on heating to 200 K (peak in curve 2 of Fig. 1). In the meantime, the recombination of electron with hole comes through lowest excited state of ODC(I) (S_1^I) would remain 'bottlenecked' (trapped in an excited state) due to the escape of the hole originally created in ODC(I) (S_0^I).

4.7. Luminescence spectra

The 7.7 eV-excited photoluminescence emission spectrum of Fig. 1 (inset) seems to suggests that, at the time the radiative transition takes the form of an excited two-fold-coordinated silicon, which de-excites principally via the $S_1^{II} \rightarrow S_0^{II}$ (4.4 eV) channel and weakly via the $T_1^{II} \rightarrow S_0^{II}$ (2.7 eV) channel [1,8,29,30]). In any event, these radiative transitions are understood to belong to ODC(II) and not ODC(I), even though it was the absorption band of the latter that was excited [1,29,30].

By contrast, under X-ray excitation, we observe mainly the ODC(II) triplet–singlet luminescence at 2.7 eV [1,2,8,11]. The singlet–singlet emission band of the two-coordinated silicon, clearly observed at 4.4 eV in the PL process, is nearly absent in both XRL and X-ray-excited TSL, i.e., it is very broad and spectrally spread in the recombination processes apparent in XRL and TSL [8,11]. This difference between mostly-blue bands observed in XRL and TSL on one hand and the mostly-UV emission of the PL on the other is tentatively explained as being due to different structure of the emitting centers. We suggest that in the case of the PL a lone twofold-coordinated-silicon-center is manifested, whereas in XRL and TSL a 'modified' twofold-coordinated silicon participates.

4.8. Nature of the modified twofold-coordinated-silicon center

Nishikawa et al. [29] proposed a 'two-configuration ODC' scheme whereby an ODC(I) excited to the S_1^I state

may lower its energy by converting to an ODC(II) in its S_1^{II} state (see review of evidence and arguments in [1]). This scheme was explicitly put forward to explain the reason why the 4.4 eV PL can be excited in the 7.6 eV band with time constant (~2 ns) shorter than that excited at 5 eV (4.5 ns) and is correlated in different samples with the magnitude of this absorption band [11]. Our arguments made above regarding the TSL and XRL lead us to either Nishikawa's model [29] or an earlier model [11] wherein ODC(II)-like defects are created at ODC(I) sites in oxygen-deficient silicas by both X-rays and 7.7 eV photons.

Our model for the 7.7 eV-excited TSL envisions that the hole initially created in the ground state of the ODC complex has a high probability of tunnelling onto a nearby bridging oxygen where it becomes trapped due to this oxygen state lying above the valence-band mobility edge for hole transport. (The distortion caused by the very close-by oxygen vacancy could well be responsible for raising the energy of this particular hole state.) This momentary hole removal – metastable at cryogenic temperatures – would bottleneck the recombination process for a long enough period of time to permit non-radiative relaxation of the ODC(I):e^- species to a modified ODC(II):e^-, where the energy level lies above the T_1^{II} state of a modified ODC(II). In this case, upon warming the intimately associated STH would detrap and return under coulombic attraction, resulting in the 2.7 eV $T_1^{II} \rightarrow S_0^{II}$ emission of ODC(II), as experimentally observed.

The XRL spectrum would be explained in the same way, except that X-rays surely create *mobile* electrons and holes; and the holes, at least, can self-trap anywhere in the network [13,14,22]. Thus, e–h recombination should then be governed by thermal detrapping of STHs from (mostly undistorted) bridging-oxygen sites. These detrapped holes would then thermally diffuse to the sites of the trapped electrons. We propose that in sufficiently oxygen-deficient silicas the unpaired electrons are trapped at ODC(I) sites that consequently relax into modified ODC(II):e^- species in the exact same manner as proposed in the preceding paragraph for in-band UV excitation of ODC(I) sites. Thus, our model accounts for the identical 2.7 eV $T_1^{II} \rightarrow S_0^{II}$ emission of modified ODC(II)s being observed in both XRL as TSL.

5. Conclusions

By performing ESR studies on the same low-temperature-irradiated silica samples it was found that the quantity of self-trapped holes is higher in an oxygen-deficient sample. This is explained in terms of the creation of traps for electrons by oxygen-deficient centers. Through parallel PL, XRL, and TSL studies, we have gained new insights into the likely mechanism of the TSL and, by extension, the spectrally identical XRL. Specifically, we are now able to propose that free electrons are readily trapped by twofold-coordinated silicons associated with grossly oxygen-deficient sites in the glass network that we term 'modified' ODC(II). Lone twofold coordinated silicons does not participate in the charge trapping and recombination processes. Consistent with nomenclature already in use, these trapped-electron centers may be denoted modified ODCs(II):e^-. The surroundings of modified ODC(II) plays significant role in trapping of electron. The final recombination of trapped electrons with liberated hole that comes from the well known $T_1^{II} \rightarrow S_0^{II}$ transition would then take place with the emission of 2.7 eV light, as observed in our TSL and XRL spectra. The $S_1^{II} \rightarrow S_0^{II}$ transitions also are seen in recombinations, however the S_1^{II} state of modified ODC(II) is greatly affected by the surroundings and does not provide the band shape usually observed in photoluminescence. Our evidence strongly supports the interpretation of TSL peaks at 125 and 170 K as corresponding to the reaction of ODC(II):e^- states with detrapped STH_2s and STH_1s, respectively, created at 'normal' sites throughout the glass network by X irradiation. We tentatively propose that the 7.7 eV-photon-stimulated TSL peaks at 105 and 200 K are due to detrapping of STH_2s and STH_1s, respectively, from distorted sites in the glass network very near to 7.7 eV-excited ODC(I):e^- states that transmute into modified ODC(II):e^- states after the ground-state hole has tunneled onto a nearby bridging oxygen in one of two possible distorted bonding conformations. This is a significant variation on the OCD(I)* → ODC(II)* transmutation as previously inferred [1,8,11,29,30] from other studies; (here, '*' denotes an excited state of an electrostatically neutral center). By analogy, we tentatively attribute the TSL peak at 400 K to detrapping of STH *pairs* (i.e., bipolarons; see, e.g., [28]) which recombine with the remaining ODC(II):e^- trapped-electron centers at elevated temperatures.

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