

## Experimental evidence of different contributions to the photoluminescence at 4.4 eV in synthetic silica

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1999 J. Phys.: Condens. Matter 11 721

(<http://iopscience.iop.org/0953-8984/11/3/011>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.210

The article was downloaded on 14/05/2010 at 18:37

Please note that [terms and conditions apply](#).

## Experimental evidence of different contributions to the photoluminescence at 4.4 eV in synthetic silica

R Boscaino, M Cannas, F M Gelardi and M Leone

INFN, Unità di Palermo and Dipartimento di Scienze Fisiche e Astronomiche dell'Università,  
Via Archirafi 36, I-90123 Palermo, Italy

Received 18 May 1998, in final form 21 October 1998

**Abstract.** Photoluminescence activity in high-purity synthetic silica samples, both as grown and  $\gamma$ -irradiated, was investigated by exciting in the vacuum-ultraviolet region. An emission band centred at 4.4 eV, excited within the absorption band at 7.6 eV and exhibiting a strong temperature dependence, was unequivocally evident. All of these features, together with its very fast decay time (2.3 ns at  $T = 10$  K) make this emission distinguishable from the well known isoenergetic bands detected in oxygen-deficient or in  $\gamma$ -irradiated silica. Our results are discussed in the light of structural models reported in the literature and seem to be consistent with the occurrence of a change in the structure of a point defect, from the single oxygen vacancy, responsible for the absorption at 7.6 eV, to the twofold-coordinated silicon, giving rise to the photoluminescence at 4.4 eV.

### 1. Introduction

Silica ( $\alpha$ -SiO<sub>2</sub>) is a prototype glass of substantial interest as regards the physics of amorphous materials. In this realm, much attention is currently paid to its point defects, both intrinsic and impurity related. For most of them, the structure, the generation mechanism and the stability within the glass network are still matters of controversy. The interest in point defects is also sustained by the widespread use of silica in the technology of optical and electronic devices. In fact, a concentration of defects as low as a few ppm may compromise the exceptional electric and optical performances of the pure material.

Point defects are responsible for the optical activity of silica in the visible (vis), ultraviolet (uv) and vacuum-uv (vuv) ranges. So, from an experimental point of view, optical absorption (OA) and photoluminescence (PL) spectroscopies are the techniques most commonly used to characterize them. For instance, several optical bands, namely the OA band at 5.06 eV ( $B_{2\alpha}$ ), the PL band at 4.4 eV and the PL band at 2.7 eV, are generally ascribed to an oxygen-deficient centre (ODC) [1, 2]. The exact structure of this centre and its arrangement in the silica network have not been clearly established, but recent '*ab initio*' calculations [3] strongly support the hypothesis, already proposed in the literature [4], of a twofold-coordinated silicon defect (O–Si–O).

As regards the PL emission centred at 4.4 eV, it is now recognized that it results from at least two distinguishable contributions. Non-stoichiometric oxygen-deficient as-grown silica [2, 4–11] exhibits the so-called  $\alpha_1$ -band (where the label stands for intrinsic). Due to its very short lifetime ( $\tau \approx 4.1$  ns at room temperature), the  $\alpha_1$ -emission has to be related to a singlet–singlet transition and, on the basis of its excitation spectrum, is usually associated with the inverse transition of the one giving rise to the OA band  $B_{2\alpha}$  [5, 9].

Recently, we reported experimental evidence [9, 11, 12] that  $\gamma$ -exposure induces in every type of silica a PL band at  $\sim 4.4$  eV, the so-called  $\alpha_R$ -band (where the subscript R stands for radiation induced), having spectral and time features very similar to those of  $\alpha_I$ ; therefore, we argued that the band  $\alpha_R$  originated from essentially the same ODC as is responsible for  $\alpha_I$ , but for a slightly different structural environment which seems to be peculiar to defects generated by  $\gamma$ -radiation [9, 12].

Both PL bands,  $\alpha_I$  and  $\alpha_R$ , can also be excited in the vuv region [4, 5, 9–15]. Their excitation spectrum is rather broad, extending from 6.0 eV to 8.4 eV, with a pronounced maximum at  $\sim 6.9$  eV. Several authors [2, 5, 13–15] have also hypothesized a correlation between the 4.4 eV PL activity and the OA band centred at 7.6 eV (the E band). However, the structural origin of the E band and its eventual correlation with the OA band  $B_{2\alpha}$  and with the PL bands  $\alpha_I$  and  $\alpha_R$  are far from being unambiguously confirmed.

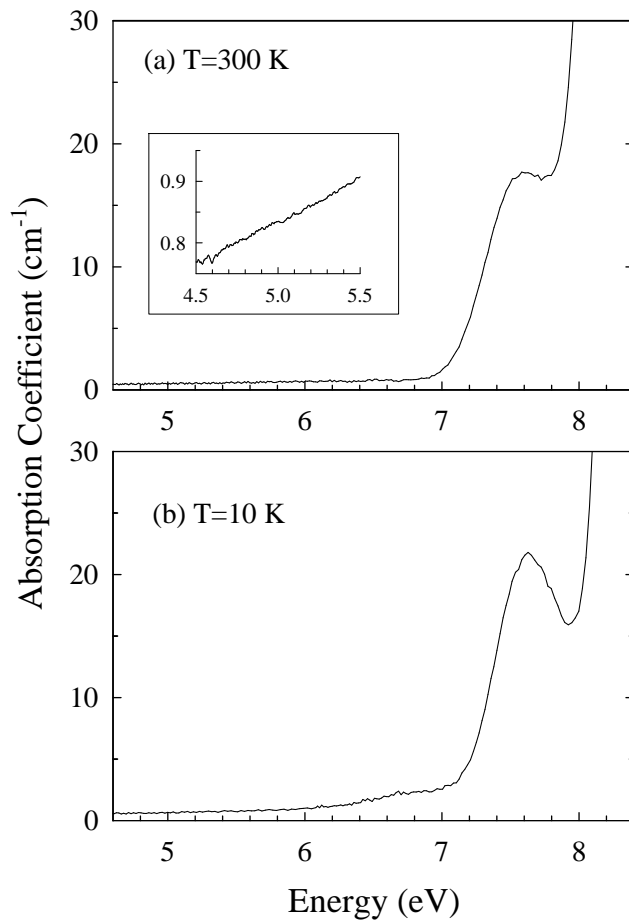
In this paper we report experimental results that isolate a further contribution to the PL activity at 4.4 eV in silica samples. The contribution considered below has spectral and kinetic characteristics which distinguish it both from  $\alpha_I$ - and from  $\alpha_R$ -emissions. Furthermore, it features a rapid decrease of intensity on increasing the temperature  $T$ , so it could only be observed at low temperatures. Hereafter, this contribution will be referred to as  $\alpha_T$ , where the subscript T indicates its strong dependence on the temperature. Finally, we show that it is just this contribution that is correlated with the OA band E.

The peculiarities of this PL band suggest to us that we ascribe it either to an alternative excitation channel or to a different emission centre with respect to the  $\alpha_I$ - and  $\alpha_R$ -bands. Moreover, we show that some aspects of the PL at 4.4 eV, not yet completely understood, can be explained by taking into account the different origins and roles of the isoenergetic emissions  $\alpha_T$ ,  $\alpha_I$  and  $\alpha_R$ .

## 2. Samples and methods

We report below the measurements performed on two representative samples of synthetic dry silica Suprasil 300 [16]. We denote by S300/0 a sample ( $5 \times 5 \times 1$  mm<sup>3</sup>) obtained from the ‘as-delivered’ slab and by S300/100 a sample of the same size and obtained from the same slab as the first one, but exposed to  $\gamma$ -irradiation with an integral dose of 100 Mrad (Si). The two samples can be considered as representative of two optical frames, well characterized by their PL activity in the vis–uv range (2.5–6.0 eV). In fact, at room temperature no PL emission could be detected from the unirradiated sample S300/0, whereas the sample S300/100 exhibits the band  $\alpha_R$  of the  $\gamma$ -generated ODC defects [9]. In the following we will use the former sample as evidence for the existence of the  $\alpha_T$ -band at low temperature in the absence of any other optical activity and the latter to investigate the effects of the its superposition with the  $\alpha_R$ -band.

The  $\gamma$ -irradiation was performed with a <sup>60</sup>Co source at room temperature at a dose rate of 0.75 Mrad (Si) h<sup>-1</sup>. The OA and the PL emission and excitation (PLE) spectra of our samples in the uv and vuv energy ranges were investigated using synchrotron radiation (SR) at the Superlumi experimental station on the I-beamline of HASYLAB at DESY (Hamburg, Germany), under multi-bunch operation. The intensities of the OA spectra were determined by normalizing them to a reference OA spectrum obtained with an empty sample holder. The PL decay times were measured under single-bunch operation, by scanning for 192 ns between adjacent SR pulses, 0.5 ns wide. Measurements were carried out both at 300 and at 10 K, by using a sample chamber with a helium-flow cryostat [17]. In addition, OA measurements at room temperature and in the range 4.5–5.5 eV were repeated using a JASCO V-570 double-beam spectrometer, to verify more accurately the presence of a  $B_{2\alpha}$  band.

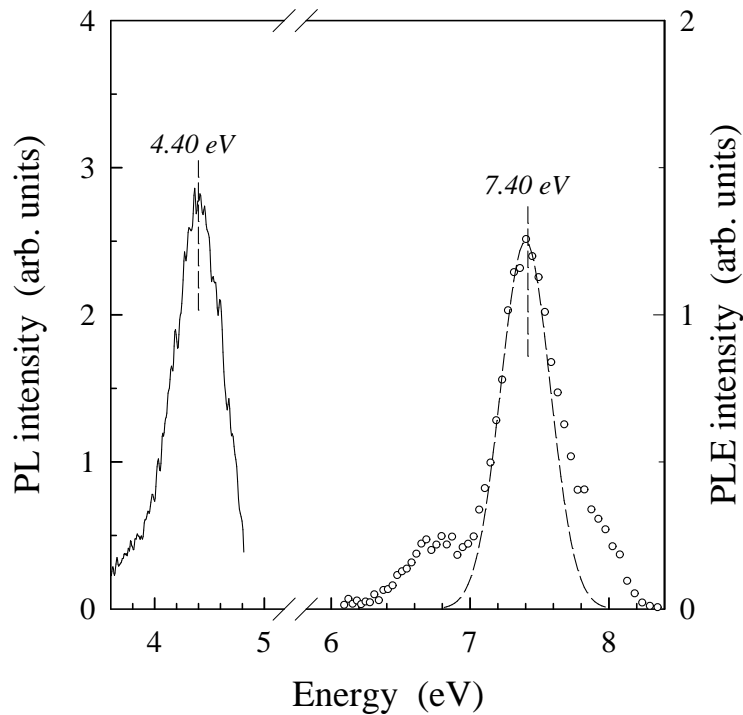


**Figure 1.** OA spectra of sample S300/0 at  $T = 300$  K (a) and  $T = 10$  K (b): in each spectrum, an OA band centred at 7.6 eV is present, whereas no OA band is observed near 5 eV. The lack of the  $B_{2\alpha}$  band is evident in the inset of (a), where an OA spectrum for the region 4.5–5.5 eV is reported.

### 3. Results

The OA spectrum of the unirradiated sample S300/0 over the range 4.6–8.4 eV is reported in figure 1, as measured at  $T = 300$  K (a) and at  $T = 10$  K (b). The E band is clearly evident in spite of its proximity to the edge at about 8.0 eV. By a best-fit procedure we found that this band shows a Gaussian profile; in particular, at room temperature it is peaked at  $7.54 \pm 0.02$  eV, where its absorption coefficient is  $\alpha = 15.5 \pm 0.4$  cm<sup>-1</sup>, and has a full width at half-maximum (FWHM) of  $0.53 \pm 0.02$  eV. At  $T = 10$  K, we note that the E band appears more pronounced because of the edge shift toward higher energies, but its shape and its intensity do not change very much, having a maximum at  $7.63 \pm 0.02$  eV with  $\alpha = 19.5 \pm 0.4$  cm<sup>-1</sup> and FWHM =  $0.53 \pm 0.02$  eV. No other band was found in the OA spectrum, not even near 5 eV where the  $B_{2\alpha}$  band, often found as a companion to the E band, is centred. On the basis of the spectra shown in figure 1, as the E band is expected to be more intense than the band  $B_{2\alpha}$  by at least three orders of magnitude [2, 5], one might suspect that the absence of the  $B_{2\alpha}$  band

is due to the limited sensitivity of the detection apparatus. Actually, we cannot rule out this possibility, even when a more accurate OA spectrum of the same sample was obtained using the double-beam JASCO spectrometer (see the inset of figure 1) and no experimental evidence of the  $B_{2\alpha}$  band was found, within the limit of  $\sim 10^{-3}$  of the E-band intensity. Also the PLE spectrum at 4.4 eV, where no structure at  $\sim 5$  eV is present, confirm that in sample S300/0 the optical activity related to the OA band  $B_{2\alpha}$  and the PL band  $\alpha_1$  is below the detection limit of our experimental set-up. Anyway, regardless of whether the  $B_{2\alpha}$  band is present or not, its very small intensity means that in sample S300/0 conditions are favourable for isolating the PL emission excited at  $\sim 7.6$  eV, owing to the absence of significant maxima at  $\sim 5.0$  and  $\sim 6.9$  eV in the PLE profile.



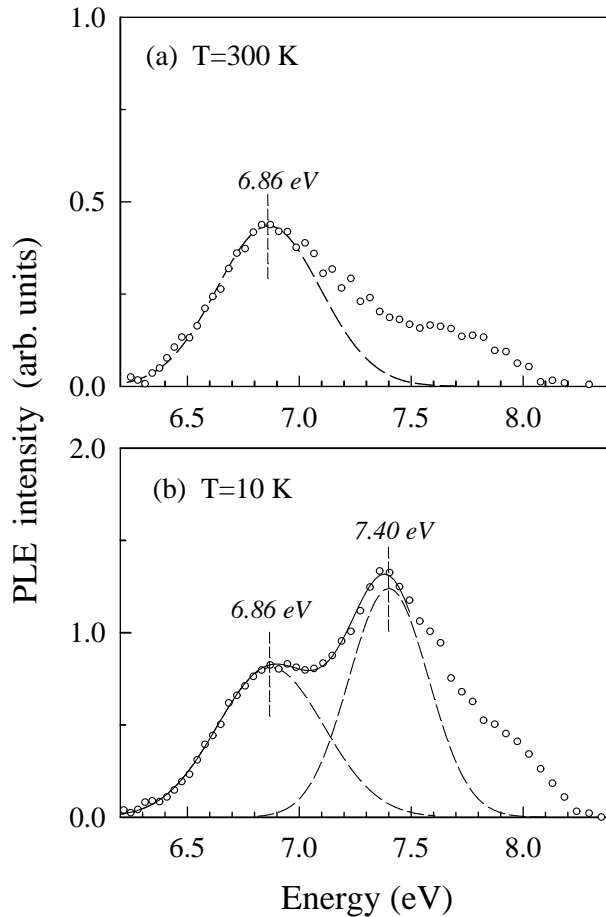
**Figure 2.** The PL activity of sample S300/0 at  $T = 10$  K. The PL emission spectrum excited at 7.4 eV is reported on the left; the corresponding PLE profile, monitored at 4.4 eV, is shown on the right-hand side. The dashed curve represents the Gaussian curve that best fits the experimental data in the range 7–7.6 eV.

On exciting within the E band, no PL activity could be detected in the sample S300/0 at  $T = 300$  K, whereas, at a temperature of  $T = 10$  K, an emission band ( $\alpha_T$ ), centred at  $4.40 \pm 0.03$  eV and having a FWHM =  $0.48 \pm 0.04$  eV, appeared in the PL spectrum as shown in figure 2.

We note that the emission spectrum of the  $\alpha_T$ -band has essentially the same properties as the  $\alpha_1$ - and  $\alpha_R$ -bands, peaked at  $4.42 \pm 0.1$  and  $4.37 \pm 0.1$  eV respectively and each having a FWHM =  $0.45 \pm 0.02$  [9]. However, in spite of the similarity of the emission spectra, the three isoenergetic bands can be distinguished by their PLE spectral features. In particular, the PLE profile of  $\alpha_T$ , reported in the same figure, figure 2, is characterized by a composite structure

extending over the range 6.2–8.4 eV. In this PLE spectrum, a band centred at  $7.40 \pm 0.02$  eV with  $\text{FWHM} = 0.42 \pm 0.02$  eV dominates over all of the other structures, as indicated by the dashed curve representing the Gaussian best-fit curve of the experimental points in the range 7.0–7.6 eV. The fit procedure is not reliable for the remaining part of the spectrum, since the signal-to-noise ratio is too low for excitation energy  $E_{\text{exc}} \leq 7.0$  eV and the PLE profile is distorted by the large absorption in the spectral region  $E_{\text{exc}} \geq 7.6$  eV [5]. However, we point out the unambiguous result that the PLE profile shown in figure 2 is quite different from the ones exhibited by the  $\alpha_{\text{T}}$ - and  $\alpha_{\text{R}}$ -emissions, both characterized by two bands centred at 5.0 and 6.9 eV [5, 9].

In order to stress this difference, we consider now the properties of the PLE spectra as detected for the irradiated sample S300/100, where both the native  $\alpha_{\text{T}}$ - and the  $\gamma$ -induced  $\alpha_{\text{R}}$ -emission bands are simultaneously present. In figure 3 we report the PLE profiles of the



**Figure 3.** PLE spectra detected for the  $\gamma$ -irradiated sample S300/100 monitored at the emission energy of 4.4 eV, at  $T = 300$  K (a) and  $T = 10$  K (b). In the spectrum (a), the points in the range 6.2–7 eV are best fitted by a Gaussian centred at 6.86 eV (dashed curve); in the spectrum (b), the best fit curve (solid curve) over the range 6.2–7.5 eV is the sum of two Gaussians (dashed curves) centred at 6.86 and 7.40 eV, respectively.

emission at 4.4 eV, as detected for sample S300/100 at  $T = 300$  K (a) and at  $T = 10$  K (b). The room temperature spectrum (a), extending from 6.3 up to 8.2 eV, is peaked at  $\sim 6.9$  eV, which is a peculiarity of the  $\alpha_R$ -emission [9]. As shown in figure, this PLE profile can be separated into a Gaussian band centred at  $6.86 \pm 0.02$  eV with  $\text{FWHM} = 0.55 \pm 0.02$  eV (dashed curve) and an asymmetric structure at higher energies that, as noted above, is strongly distorted by the large absorption activity characterizing this upper spectral region. The PLE spectral profile of the same PL emission at  $T = 10$  K (b) appears quite different. The difference between the two spectra can be explained in terms of a superposition of two contributions. In fact, the low-temperature spectrum (b) consists of a broad spectrum very similar to the spectrum (a), to be related to the  $\alpha_R$ -emission, and an additional structure, peaked at 7.4 eV, quite similar to the spectrum of figure 2, to be ascribed to the emission  $\alpha_T$ . More quantitatively, the data in figure 3(b), in the range 6.2–7.5 eV, are well fitted (solid curve) by two Gaussian profiles (dashed curves) having the same peak energies and FWHMs as the curves fitted to the PLE spectra in figure 3(a) and figure 2, where the bands peaked at 6.86 eV and 7.40 eV are separately present.

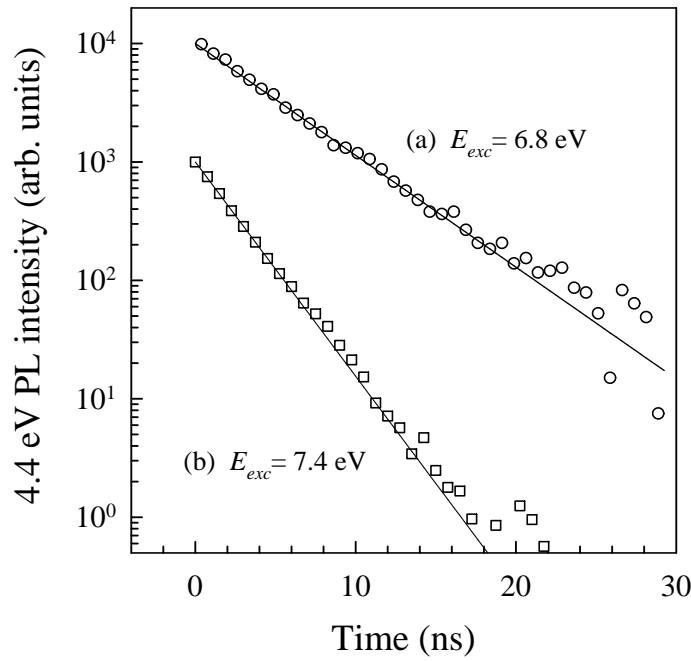
**Table 1.** Gaussian parameters (intensity  $I_0$ , peak energy  $E_0$  and FWHM) obtained by a best-fit procedure for the two PLE bands at 6.8 and 7.4 eV shown in figures 2 and 3; ‘n.d.’ stands for not detectable.

Samples	PLE bands					
	6.8 eV			7.4 eV		
	$I_0$ (arbitrary units)	$E_0$ (eV)	FWHM (eV)	$I_0$ (arbitrary units)	$E_0$ (eV)	FWHM (eV)
S300/0 (10 K) ( $\alpha_T$ )	n.d.	n.d.	n.d.	$1.23 \pm 0.04$	$7.40 \pm 0.02$	$0.42 \pm 0.02$
S300/100 (300 K) ( $\alpha_R$ )	$0.43 \pm 0.02$	$6.86 \pm 0.02$	$0.55 \pm 0.02$	n.d.	n.d.	n.d.
S300/100 (10 K) (both $\alpha_T$ and $\alpha_R$ )	$0.81 \pm 0.03$	$6.86 \pm 0.02$	$0.55 \pm 0.02$	$1.21 \pm 0.04$	$7.40 \pm 0.02$	$0.42 \pm 0.02$

The parameters relevant to the Gaussian curves fitting the spectra of figure 2 and figure 3 are summarized in table 1. We note that the  $\alpha_R$ -contribution increases by nearly a factor of 2 on lowering the temperature from  $T = 300$  K to  $T = 10$  K, as expected [10], whereas the dependence of the  $\alpha_T$ -intensity on temperature is much more pronounced. In fact, as  $\alpha_T$  is below the noise level at  $T = 300$  K, we can estimate that its intensity increases by a factor  $\geq 30$  on cooling to  $T = 10$  K. Finally, on comparing the data reported in table 1 for the samples S300/0 and S300/100, we note also that the  $\alpha_T$ -emission is barely affected by the  $\gamma$ -irradiation. Moreover, as no significant variation in the intensity of the band E was observed for the irradiated sample, we infer that  $\gamma$ -rays do not affect the structure or the number of the defects responsible for the  $\alpha_T$ -emission.

To further characterize the  $\alpha_T$ -emission, we investigated its transient behaviour under pulsed excitation in the S300/0 sample. The typical decay curves of the PL signal, ensuing from an SR excitation pulse at  $E_{\text{exc}} = 7.4$  eV, were best fitted by a single-exponential law with a decay time  $\tau = 2.3 \pm 0.1$  ns. So, the  $\alpha_T$ -band has a lifetime considerably shorter than those of the  $\alpha_I$ - and  $\alpha_R$ -bands, which are characterized by a lifetime  $\tau = 4.6 \pm 0.1$  ns at  $T = 10$  K, when excited at 6.8 eV, near to their PLE maxima [9].

This difference emerges unambiguously when the transient behaviour of the PL emission



**Figure 4.** The time decay of the PL emission at 4.4 eV observed for sample S300/100 at  $T = 10$  K, excited at 6.8 eV (a) and at 7.4 eV (b). Both decay profiles are well fitted by single-exponential laws (solid curves) with characteristic times of  $\tau = 4.6 \pm 0.1$  ns and  $\tau = 2.4 \pm 0.1$  ns, respectively. In the interests of clarity, the initial values of the decay curves are arbitrarily scaled by decades.

is detected, as a function of the exciting energy, in sample S300/100, where the two emissions  $\alpha_T$  and  $\alpha_R$  are simultaneously present. Two experimental decay curves of the 4.4 eV PL emission, detected at  $T = 10$  K for sample S300/100, are reported in figure 4. The excitation energies for the curves (a) and (b) were 6.8 eV and 7.4 eV respectively. As shown, both decay curves are well fitted by a single-exponential law, but with different characteristic times:  $\tau = 4.6 \pm 0.1$  ns under excitation at 6.8 eV where the contribution  $\alpha_R$  prevails (figure 4(a)) and  $\tau = 2.4 \pm 0.1$  ns when the PL emission was excited at 7.4 eV where the contribution  $\alpha_T$  prevails (figure 4(b)).

Finally, we report that, at  $T = 300$  K, where  $\alpha_T$  is not detectable, no difference in the decay time of the 4.4 eV PL signal was observed on varying the excitation energy from 6.8 to 7.6 eV. In particular, the same lifetime of  $\tau = 3.6 \pm 0.1$  ns, characterizing the  $\alpha_R$ -emission [9], was determined from the experimental decay curves.

#### 4. Discussion

Our results provide evidence for a contribution to the PL emission at  $\sim 4.4$  eV, named  $\alpha_T$ , clearly distinguished from the already known  $\alpha_I$ - and  $\alpha_R$ -bands. We recall that the isoenergetic bands  $\alpha_I$  and  $\alpha_R$  are characterized by a PLE spectrum with two maxima at  $\sim 5.0$  and  $\sim 6.9$  eV and a decay time  $\tau = 4.6 \pm 0.1$  ns at  $T = 10$  K [5, 9]. On the other hand, the features of  $\alpha_T$  can be summarized as follows:

- (a) it is present in those types of silica that exhibit the OA band at  $\sim 7.6$  eV, including high-



purity synthetic as-grown silica where  $B_{2\alpha}$  is absent, or at least below the detectability threshold;

- (b) it shows a strong dependence on the temperature;
- (c) its excitation spectrum is peaked at 7.4 eV;
- (d) its lifetime is  $\tau = 2.3 \pm 0.1$  ns at  $T = 10$  K.

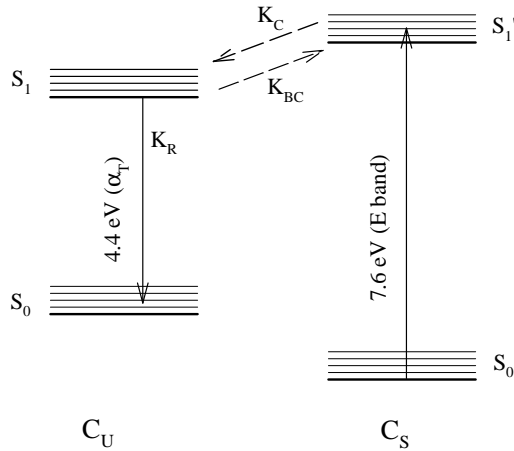
So, whereas the  $\alpha_I$ - and  $\alpha_R$ -emissions are ascribed to the direct inverse transition of the OA band  $B_{2\alpha}$ , the same excitation mechanism does not seem to be effective for the  $\alpha_T$ -band. Moreover, the short decay time of  $\alpha_T$  speaks for a transition from a singlet state and its PLE profile suggests that we should relate it to the OA band E ( $\sim 7.6$  eV).

In the light of the  $\alpha_T$ -contribution evident here, we wish to reconsider the results on the decay times of the PL activity at 4.4 eV in oxygen-deficient silica reported in reference [10]. In those experiments, the same decay time for the 4.4 eV PL was measured at  $T = 300$  K, independently of the excitation energy ( $\tau = 4.1 \pm 0.1$  ns with excitation at 5.0 eV, 6.8 eV and 7.6 eV). By contrast, at  $T = 10$  K a shorter lifetime was detected for excitation energy of 7.6 eV with respect to the excitation at 5.0 eV and 6.8 eV. The new results reported here suggest that at room temperature only the contribution  $\alpha_I$  was detected even under excitation at 7.6 eV, since this energy is within the broad excitation band centred at 6.8 eV. On the other hand, at  $T = 10$  K, when the PL emission was excited at 7.6 eV, the contribution coming from  $\alpha_T$  was superimposed on the  $\alpha_I$ -emission, and the PL signal was observed to decay with an intermediate lifetime ( $\tau = 3.1 \pm 0.1$  ns) compared with the characteristic lifetimes of  $\alpha_I$  ( $\tau = 4.6 \pm 0.1$  ns) and  $\alpha_T$  ( $\tau = 2.3 \pm 0.1$  ns). Moreover, we recall that a strong temperature dependence of the 4.4 eV PL emission excited at 7.6 eV in an oxygen-deficient silica sample was reported by Nishikawa *et al* [5, 15]. These authors measured the decay time of the 4.4 eV PL at  $T = 100$  K by varying the excitation energy from 5.0 eV to 8 eV, finding nearly the same value ( $\tau = 4.2 \pm 0.1$  ns) over the whole energy range, except for the region near to 7.6 eV where they measured  $\tau = 2.1$  ns. However, they did not put forward an explanation of their results in terms of two distinct emissions, while this is clearly supported by our experimental data.

Now we wish to address the problem of the structure of the centre responsible for the  $\alpha_T$ -emission. In this regard, Pacchioni and Ieranò [18] have recently proposed a model, based on ‘*ab initio*’ calculations, where the E band is due to a singlet–singlet transition ( $S_0 \rightarrow S_1$ ) of a neutral oxygen vacancy  $\equiv\text{Si}-\text{Si}\equiv$  and the radiative  $S_1 \rightarrow S_0$  decay gives rise to a 4.4 eV PL emission. In the framework of that model, the peculiar temperature dependence exhibited by  $\alpha_T$  could be ascribed to non-radiative relaxation processes from  $S_1$  to  $S_0$ : in fact, the  $\alpha_T$ -emission detected at  $T = 10$  K could be quenched at room temperature, as non-radiative mechanisms are expected to become more and more effective as the temperature is increased.

The attribution of the  $\alpha_T$ -activity to a neutral oxygen vacancy, on the basis of the above model, implies that this defect has a structure intrinsically different from the one responsible for the  $\alpha_I$ - and  $\alpha_R$ -emissions that is supposed to be a twofold-coordinated silicon. On the other hand, the strong similarity of the emission spectrum of  $\alpha_T$  with the corresponding spectra of  $\alpha_I$  and  $\alpha_R$ , in spite of the different excitation energies and lifetimes, leads us to consider an alternative explanation of our results. In fact, the characteristics of the emission  $\alpha_T$  and its connection with the E band can also be accounted for by a two-configuration (TC) model, as already proposed in the literature [5, 13], representing an ODC undergoing structural changes under vuv excitation.

The energy levels and transitions of a TC defect are schematically reported in figure 5 for the sake of clarity. In this scheme, our results could be interpreted as follows: the absorption of energy at 7.6 eV causes the conversion of the  $\alpha_T$ -centre from its stable configuration ( $C_S$ ) to an



**Figure 5.** Schematic diagrams of the energy levels and transitions of a two-configuration defect to which the whole observed optical activity could be ascribed. Solid and dashed arrows represent radiative and non-radiative transitions, respectively.

unstable one ( $C_U$ ), via their excited states, at a rate  $K_C$ . The relaxation from the excited state of the  $C_U$  configuration can take place either by PL emission at 4.4 eV toward the ground state of  $C_U$  at a rate  $K_R$ , or, as also proposed in references [5, 15], by a non-radiative back-conversion (BC) process to the excited state of  $C_S$ , at a rate  $K_{BC}$ . We note that, in this model, the  $C_U$  configuration, from which the  $\alpha_T$ -emission originates, coincides with the ODC responsible for the isoenergetic bands  $\alpha_I$  and  $\alpha_R$ , and all of the observed peculiarities of  $\alpha_T$  are due to the different excitation process of this PL band.

The occurrence of the BC process can affect the time decay and the temperature dependence of  $\alpha_T$ . In fact, in the framework of the TC model, the short lifetime of  $\alpha_T$  can be explained by considering that the BC mechanism from  $C_U$  to  $C_S$  offers a relaxation path alternative to the PL emission from the excited state of  $C_U$ . If one neglects any other non-radiative process, the decay rate of  $\alpha_T$  is  $\tau^{-1} = K_R + K_{BC}$  and, deriving the value  $K_R \sim 2.2 \times 10^8 \text{ s}^{-1}$  from reference [9], we can estimate a rough value of  $K_{BC} \sim 2.2 \times 10^8 \text{ s}^{-1}$  at  $T = 10 \text{ K}$ . Moreover, the BC process is expected to be enhanced in effectiveness on increasing the temperature and this dependence may account for the lack of PL emission at room temperature. In fact,  $K_{BC}$ , of the same order as  $K_R$  at  $T = 10 \text{ K}$ , is expected to increase by at least a few orders of magnitude when the temperature is increased to  $T = 300 \text{ K}$ . As a consequence, at room temperature, the condition  $K_R \ll K_{BC}$  could make the PL emission undetectable.

As regards the structure of the point defect which a TC model is based on, Nishikawa *et al* [5] propose oxygen vacancies in relaxed and unrelaxed configurations; this was also suggested in reference [19]. In contrast, Trukhin *et al* [13] present a structural model consisting of a complex defect containing a twofold-coordinated silicon and a mobile impurity (H or Cl atoms), whose relative distance increases under vuv excitation and resumes its equilibrium value after PL emission.

On the basis of the reported results, we are not able to establish unequivocally whether the  $\alpha_T$ -emission comes from a distinct point defect or from the same ODC as is responsible for  $\alpha_I$  and  $\alpha_R$ , but in an unstable configuration. This question is crucial and implies, in the

former case, that the  $\alpha_T$ -emission and its excitation take place in the same defect, consisting of a neutral oxygen vacancy, as suggested by Pacchioni and Ieranò [18]. On the other hand, in the TC model, the twofold-coordinated silicon could be the luminescent defect, but the occurrence of the OA transition at 7.6 eV in such a defect seems to be not sufficiently well justified. In fact, a structural process suggested recently by Skuja [20] could remove some of the inconsistencies between the two models discussed above. In order to explain the connection between the OA band E and the PL emission at 4.4 eV, Skuja hypothesized an interconversion mechanism from a neutral oxygen vacancy to a twofold-coordinated silicon defect, under excitation at 7.6 eV, assisted by structural rearrangements of the surrounding amorphous network. This model is consistent in particular with the experimental results obtained for the irradiated sample S300/100. In fact, as shown in figures 2 and 3,  $\gamma$ -rays give rise to the PLE band at 6.9 eV, whereas they do not affect at all the intensity of the PLE band at 7.4 eV, compared to that of the 'as-grown' sample S300/0. This result indicates that the two PLE bands have to be ascribed to distinct structural defects, and this condition fits the model proposed in [20]. Nevertheless, in our opinion, Skuja's hypothesis, which could account for most experimental results as regards the optical activity of the ODCs, needs further experimental support to be considered not merely 'ad hoc'.

## 5. Conclusions

We have reported experimental evidence of a new contribution to the PL emission at 4.4 eV in silica. The related PL band, here named  $\alpha_T$ , can be easily distinguished from the already known bands  $\alpha_I$  and  $\alpha_R$ , on the basis of its peculiar temperature dependence, excitation profile and lifetime. We also detected the simultaneous presence of  $\alpha_T$  and  $\alpha_R$  in a  $\gamma$ -irradiated silica sample, indicating that the decay time of the 4.4 eV emission strongly depends on the excitation energy, because of the superposition of the two contributions. This superposition can also account for previously reported results [9, 10], showing that the decay time of the PL at 4.4 eV, excited at 7.6 eV, is shorter than that obtained under excitation at lower energies, i.e. 5.0 eV and 6.8 eV. In fact, the different excitation spectra show that the  $\alpha_T$ -emission is mainly excited at 7.6 eV, with a shorter lifetime, whereas at 5.0 and at 6.8 eV only  $\alpha_R$  (or analogously  $\alpha_I$  for oxygen-deficient samples) is excited and contributes to the PL emission at 4.4 eV.

Our results show that two distinct excitation processes are responsible for the luminescence at 4.4 eV and probably originate from two distinct defects: the first one occurs via optical absorption at 5.0 eV ( $S_0 \rightarrow S_1$  transitions) and 6.8 eV ( $S_0 \rightarrow S_2$  transitions); the second one involves the absorption transition at 7.6 eV. In the latter case under excitation at  $\sim 7.6$  eV the occurrence of a mechanism able to change the absorbing defect to a luminescent one, and vice versa, could account for our results.

## Acknowledgments

We wish to thank Professor E Calderaro (Dipartimento di Ingegneria Nucleare, University of Palermo) for dealing with the  $\gamma$ -irradiation in the irradiator IGS-2. Stimulating discussions with G Pacchioni are also acknowledged. The SR experiments were carried out at HASYLAB (DESY, Hamburg) (Project No I-96-08 EC, Project Leader Professor G Spinolo). This work is a part of a research project supported by EU (Progetto Sud, INFN, Genova, Italy) and by the Italian Ministry of University and Research, Rome, Italy.

**References**

- [1] Griscom D L 1985 *J. Non-Cryst. Solids* **73** 51
- [2] Tohmon R, Mizuno H, Ohki Y, Sasagane K, Nagasawa K and Hama Y 1989 *Phys. Rev. B* **39** 1337
- [3] Zhang B L and Raghavachari K 1997 *Phys. Rev. B* **55** R15 993
- [4] Skuja L N 1992 *J. Non-Cryst. Solids* **167** 77
- [5] Nishikawa H, Watanabe E, Ito D and Ohki Y 1994 *Phys. Rev. Lett.* **72** 2101
- [6] Hayashi S, Awazu K and Kawazoe H 1994 *J. Non-Cryst. Solids* **179** 235
- [7] Anedda A, Congiu F, Raga F, Corazza F, Martini M and Spinolo G 1994 *Nucl. Instrum. Methods Phys. Res. B* **91** 405
- [8] Bagratashvili V N, Tsypina S I, Radstig V A, Rybaltovsky A O, Chernov P V, Alimpiev S S and Simanovskii Y O 1995 *J. Non-Cryst. Solids* **180** 221
- [9] Boscaino R, Cannas M, Gelardi F M and Leone M 1996 *Phys. Rev. B* **54** 6194
- [10] Boscaino R, Cannas M, Gelardi F M and Leone M 1996 *J. Phys.: Condens. Matter* **8** L545
- [11] Boscaino R, Cannas M, Gelardi F M and Leone M 1996 *Nucl. Instrum. Methods Phys. Res. B* **116** 373
- [12] Cannas M, Boscaino R, Gelardi F M and Leone M 1997 *J. Non-Cryst. Solids* **216** 99
- [13] Trukhin A N, Skuja L N, Boganov L C and Rudenko V S 1992 *J. Non-Cryst. Solids* **149** 96
- [14] Nishikawa H, Shiroyama T, Nakamura R, Ohki Y, Nagasawa K and Hama Y 1992 *Phys. Rev. B* **45** 586
- [15] Nishikawa H, Miyake Y, Watanabe E, Ito D, Seol K S, Ohki Y, Ishii K, Sakurai Y and Nagasawa K 1997 *J. Non-Cryst. Solids* **222** 221
- [16] Heraeus Quartzglas, Hanau, Germany, catalogue No POL-0/102/E.
- [17] Zimmerer G 1992 *Nucl. Instrum. Methods Phys. Res. A* **308** 178
- [18] Pacchioni G and Ierano G 1997 *Phys. Rev. Lett.* **79** 753
- [19] Imai H, Arai K, Imagawa H, Hosono H and Abe Y 1988 *Phys. Rev. B* **38** 12 772
- [20] Skuja L N 1998 *J. Non-Cryst. Solids* **239** 16