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# The double nature of the 3.1 eV emission in silica and in Ge-doped silica

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**Abstract.** The 3.1 eV photoluminescence emission ('beta' band) has been studied both in natural silica and in Ge-doped silica in the temperature range 80–475 K under UV and VUV excitation. A detailed analysis of the $\beta$ band, as a function of temperature and excitation energy in the 5 eV region, gives evidence for a double structure of this emission. A first component peaks at 3.05 eV at 300 K and increases its intensity as the temperature rises up to 380 K. A second one has a peak at 3.21 eV at room temperature and its emission intensity is constant up to 300 K.

The two $\beta$ bands may be due to two different modifications of a Ge-related centre. However the presence of the $\beta$ emission in silica obtained from fused quartz with low Ge content would indicate that other impurities could favour the presence of the $\beta$ band as well.

## 1. Introduction

The study of the optical properties of silica is finding continuous interest, mainly due to the technological importance of the material, and allows us to clarify the complex picture of the absorption and emission bands in variously prepared materials, both irradiated and 'as-grown'.

Among other features, the $B_2$ absorption band, present in natural silica and also in irradiated synthetic silica at around 5 eV, has received great attention and has been recognized as being due to several intrinsic and extrinsic components [1, 2]. Besides studying absorption, we think that better information can be achieved by studying the excitation spectra of the various emission bands excited in the $B_2$ absorption region: substantial differences are evidenced when the $B_{2\alpha}$ (5.0 eV) or the $B_{2\beta}$ (5.15 eV) are alternatively present. Specifically, two emissions at 2.7 eV ($\gamma$ band) and 4.4 eV (intrinsic $\alpha$ band) are excited within the $B_{2\alpha}$ absorption band, with excitation peaking at 4.85 eV and 5.0 eV respectively at room temperature (RT): the responsible centres are thought to be of intrinsic origin. At variance, emissions at 3.1 eV ($\beta$ band) and at 4.2 eV (extrinsic $\alpha$ band) are detected when the $B_{2\beta}$ absorption band is present: both their excitations peak at about 5.1 eV [2–4].

Recent works on Ge-doped silica have shown that two bands contribute to the $B_{2\beta}$ absorption: a 5.06 eV component, which has been proposed to be associated with the Ge–Ge ODC (oxygen deficient centre) [3] and a 5.16 eV component tentatively assigned to the Ge divacancy [5].

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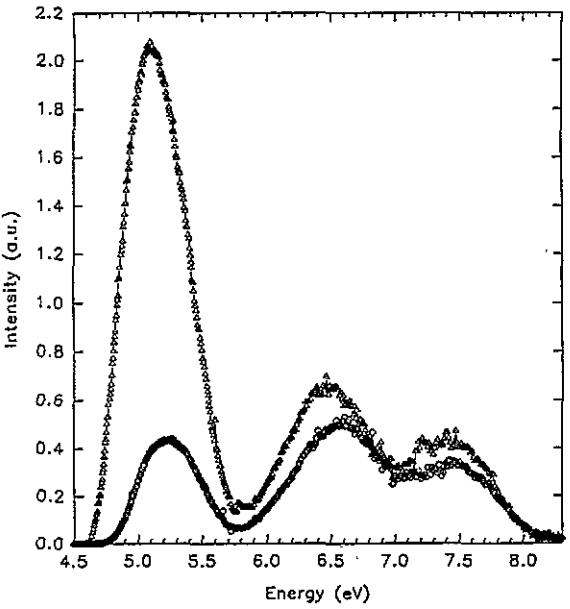


**Figure 1.** Excitation spectra of the emission at 3.2 eV in a Ge-doped silica (2% Ge) sample for different temperatures: O, 100 K; Δ, 295 K.

We have recently worked on the two $\alpha$ emissions [6] and on the $\gamma$ emission [7] excited in the 4.5–8.5 eV range; we have shown that the study as a function of temperature of the intensities has given results rather useful for the characterization of the optically active centres.In this paper we present new results on the $\beta$ emission in which the intensity and peak energy temperature dependence has allowed us to demonstrate that the $\beta$ luminescence is composed of two bands: a first one with a 'normal' behaviour as a function of $T$, peaking at 3.21 eV at RT, and a second band having an 'anomalous' behaviour similar to the gamma one [7], and peaking at 3.05 eV at RT.

It will be shown that the phenomenological model already used to fit $I(T)$ for the $\gamma$ band is again convenient in analysing $I(T)$ for the 'anomalous' component of the $\beta$ band as well. The double structure of the beta emission, as we will discuss in the following, is coherent with the recently reported evidence of a double nature of the $B_{2\beta}$ absorption band: the two excitation bands we found for the different $\beta$ emissions have energies (5.05 and 5.20 eV) very close to the $B_{2\beta}$ (5.06 and 5.16 eV) absorptions recently reported [3, 5].

Our results confirm the importance of Ge for the presence of optically active centres responsible for $\beta$ bands, particularly intense in Ge-doped silica. However, their presence in silica of natural origin ('fused quartz'), containing less than 1 ppm of Ge and about 100 ppm of other metals, gives an indication of a possible indirect role of various types of impurity, not only Ge, in favouring the formation of this type of defect.

## 2. Experimental procedure

The measurements we report have been performed mainly on Ge-doped silica (2% Ge), supplied by FOS (Fibre Ottiche Sud, Battipaglia, Italy) and on type II, Herasil, natural silica (fused quartz) supplied by Heraeus. The main impurities of Herasil, according to the producer's analysis, are Fe (80–200 ppm), Ti (~ 10 ppm), Zn (2–6 ppm) and Ge (~ 1 ppm).

All samples were discs (diameter 10 mm and thickness 1 mm) with optical grade polished surfaces.

Photoluminescence excitation in the 4.5–8.5 eV range was produced by a modified Hinteregger hydrogen discharge lamp (model 630, McPherson), followed by a grating monochromator (model 218, McPherson) operating in hydrogen atmosphere. The spectral band pass of the excitation was 2.65 nm, corresponding to 53 meV at 5 eV.

The photoluminescence in the 2.5–5.0 eV spectral range was analysed by a grating monochromator (model 82-410, Jarrel-Ash) followed by an EMI 9924QA photomultiplier (Bialkali photocathode). The spectral band pass was 13.2 nm, corresponding to 96 meV at 3.0 eV.

The measurements in the 80–370 K temperature range were performed on samples kept in high vacuum ($\sim 10^{-6}$ Torr). All PL spectra were corrected for the spectral response of the optical system. The PLE spectra were corrected for the spectral distribution of the excitation intensity.

## 3. Results and discussion

The $\beta$ emission band has been studied both in Ge-doped silica and in Herasil silica varying the excitation energy in the range 4.8–8.5 eV. The excitation spectra relative to the Ge-doped silica at two temperatures (295 and 100 K), reported in figure 1, show that the $\beta$ emission band has three excitation peaks: at 5.0–5.3 eV (in the $B_2$ region), at 6.5 eV and at 7.5 eV. Similar, but less intense, spectra have been obtained for Herasil silica samples. In this paper we do not discuss the two higher-energy excitations; we just mention that the 7.5 eV band is not modified passing from 100 K to RT, while the 6.5 eV excitation is slightly shifted.

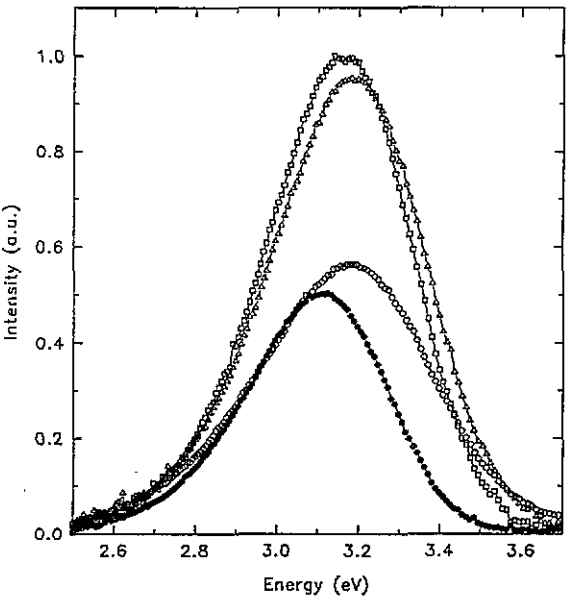


**Figure 2.** PL spectra of the $\beta$ band measured at 295 K of a Ge-doped silica (2% Ge) sample, excited by four different excitation energies: ○, 5.4 eV; △, 5.2 eV; □, 5.0 eV; ●, 4.8 eV.

In figure 2 are reported the emission spectra at 295 K, for different excitation energies, of

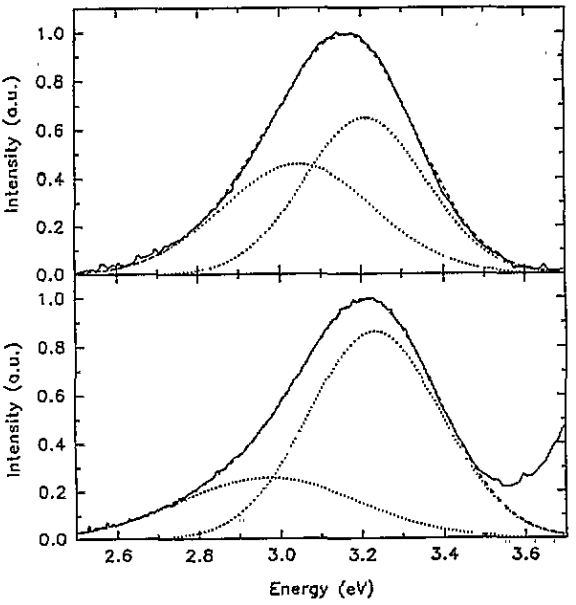


**Figure 3.** Deconvolution of the PL spectra of a Ge-doped silica (2% Ge) sample at different temperatures and excitation energies: (top) $T = 295$ K, $E_{exc} = 5.0$ eV; (bottom) $T = 100$ K, $E_{exc} = 5.4$ eV. Full line, experimental data; dashed line, fitting analysis; dotted line, Gaussian components.

a Ge-doped sample. Similar results, but two orders of magnitude less intense, were obtained on Herasil samples. From figure 2 it is evident that the emission energy varies together with the excitation energy: this would mean that more than one single emission band contributes to each of the observed curves. In fact, all spectra, in the temperature range 80–475 K, can be fitted using two components. To find out the exact energy of the two components, a Gaussian deconvolution has been successfully carried out, at RT, giving in both materials the same two values, 3.05 eV and 3.21 eV, and FWHM (full width at half maximum) of 0.42 eV and 0.38 eV, respectively. An example of such a deconvolution is reported in figure 3 (top), relative to Ge-doped silica. Less precise results have been obtained from the deconvolution of the low-temperature bands due to the overall lower intensity; in any case in figure 3 (bottom) an example of a deconvolution of an emission spectrum at 100 K is reported: there is evidence that the emission band with lower energy contributes less at low temperature. The presence of two bands in the $\beta$ emission, as evidenced varying the excitation energy, suggests searching for a correlation between the absorption–excitation and emission features.

A reasonably clear picture of the whole system of excitation and emission bands emerges from the analysis of figure 4, where the intensity of the emission bands (integrated between 2.5 eV and 3.7 eV) is reported as a function of temperature, using four different excitation energies. It is evident that the four sets of $I_i(T)$ data are quite different, but they can be well fitted as sums such as

$$I_\beta(E_i, T) = k_{1,E_i} I_{\beta_1}(T) + k_{2,E_i} I_{\beta_2}(T) \tag{1}$$

where $I_{\beta_1}(T)$ and $I_{\beta_2}(T)$ are the two curves reported in figure 4, having two completely different behaviours as a function of $T$.

It appears that two emission bands contribute to each $I_\beta(E_i, T)$ curve. Each band has its own behaviour as a function of $T$: the one excited at lower energy, $I_{\beta_1}(T)$, has

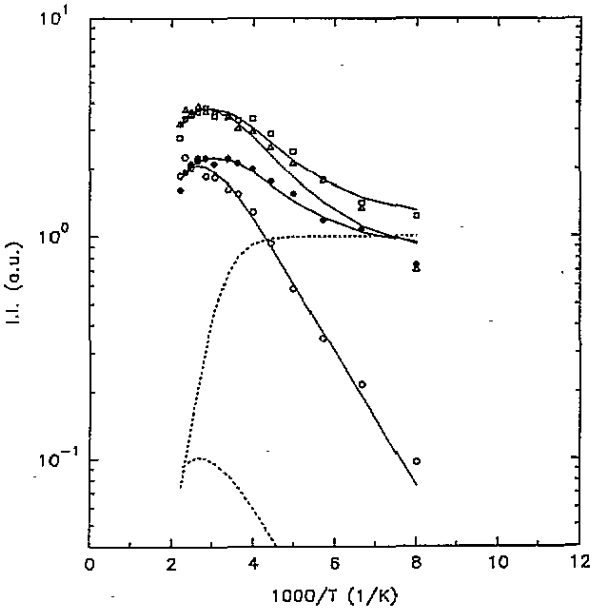


**Figure 4.** The temperature dependence of the integrated intensity of the $\beta$ band in a Ge-doped silica (2% Ge) sample excited by four different excitation energies: O, 4.8 eV; Δ, 5.0 eV; □, 5.2 eV; ●, 5.4 eV. The lines are fits to the experimental data, as obtained from linear combinations of $I_{\beta_1}(T)$ and $I_{\beta_2}(T)$.

an 'anomalous' behaviour, increasing its intensity with increasing temperature, similarly to what is already known for the 2.7 eV, gamma emission band and recently analysed [7]. The other band, $I_{\beta_2}(T)$, excited at higher energy, has a normal behaviour, constant in intensity until about RT, where a non-radiative recombination path is activated.

To complete the phenomenology on the $\beta$ emission we recall that the radiative lifetime is known to be substantially constant as a function of the temperature, of the order of 110 $\mu$s [9]. Recent experiments [11] have succeeded in showing that in the time decay of $\beta$ emission two slightly different components are present, one, excited at lower energy, of 80 $\mu$s and the other, excited at higher energy, of 120 $\mu$s.

The detailed analysis of our experimental results is rather complex, due to the contemporaneous presence, at all temperatures, of two components, both in excitation and in emission. All the spectra of figure 2 can be fitted as sums of two Gaussian components. The deconvolutions of the spectra measured at temperatures below RT are rather less precise; however, a few important observations can be made looking at the shift of the maximum energy as a function of both temperature and exciting energy, as reported in table 1.

The data of table 1, if read looking also at figure 4, allow us to reach a satisfying picture of the two components of the $\beta$ emission.

(i) Under 4.8 eV excitation the lower-energy emission band is mainly excited; it undergoes an increase both in intensity and in emission energy (blue shift) when raising the temperature. The analogy of this 'anomalous' $\beta$ component with the gamma band recently studied [7] is evident.

(ii) Under excitation between 5.0 and 5.4 eV the picture is much more complex: in the temperature range 100–300 K the higher-energy component is mainly excited its intensity is constant, its peak energy shifting to lower values, when raising the temperature (red shift).

**Table 1.** Peak energy and halfwidth of the $\beta$ band in a Ge-doped silica (2% Ge) sample as a function of the energy and temperature.

| | $E_{exc} = 4.8$ eV | | $E_{exc} = 5.0$ eV | | $E_{exc} = 5.2$ eV | | $E_{exc} = 5.4$ eV | |
|---|---|---|---|---|---|---|---|---|
| $T$ (K) | $E_{max}$ | FWHM | $E_{max}$ | FWHM | $E_{max}$ | FWHM | $E_{max}$ | FWHM |
| 100 | 2.97 | 0.58 | 3.18 | 0.30 | 3.22 | 0.36 | 3.21 | 0.40 |
| 125 | 3.06 | 0.46 | 3.19 | 0.33 | 3.22 | 0.36 | 3.20 | 0.43 |
| 150 | 3.08 | 0.36 | 3.16 | 0.36 | 3.20 | 0.37 | 3.20 | 0.44 |
| 175 | 3.09 | 0.38 | 3.15 | 0.37 | 3.19 | 0.38 | 3.20 | 0.43 |
| 200 | 3.06 | 0.39 | 3.15 | 0.38 | 3.18 | 0.40 | 3.19 | 0.44 |
| 225 | 3.08 | 0.39 | 3.14 | 0.39 | 3.18 | 0.41 | 3.17 | 0.46 |
| 250 | 3.09 | 0.40 | 3.15 | 0.39 | 3.18 | 0.43 | 3.18 | 0.47 |
| 275 | 3.10 | 0.40 | 3.14 | 0.40 | 3.18 | 0.43 | 3.17 | 0.49 |
| 295 | 3.10 | 0.40 | 3.15 | 0.42 | 3.17 | 0.44 | 3.18 | 0.50 |
| 325 | 3.11 | 0.41 | 3.16 | 0.42 | 3.18 | 0.44 | 3.18 | 0.51 |
| 350 | 3.10 | 0.41 | 3.16 | 0.43 | 3.17 | 0.47 | 3.17 | 0.50 |
| 375 | 3.12 | 0.42 | 3.16 | 0.44 | 3.18 | 0.47 | 3.18 | 0.51 |
| 400 | 3.13 | 0.43 | 3.16 | 0.45 | 3.18 | 0.47 | 3.19 | 0.51 |
| 425 | 3.12 | 0.43 | 3.17 | 0.45 | 3.19 | 0.49 | 3.19 | 0.51 |
| 450 | 3.13 | 0.45 | 3.17 | 0.46 | 3.20 | 0.48 | 3.20 | 0.51 |
| 475 | 3.14 | 0.45 | 3.18 | 0.46 | 3.20 | 0.49 | 3.20 | 0.51 |

(iii) Under excitation between 5.0 and 5.4 eV, in the temperature range 300–475 K, the growth in intensity of the low-energy emission is evident both in figure 4 and in table 1, in which the maximum emission energy shifts again towards the blue, following the temperature increase, due to the prevailing of the lower-energy emission.

For the sake of clarity we will refer to the two $\beta$ components as $\beta_1$ (the lower-energy band) and $\beta_2$ (the higher-energy band). To summarize their characteristics we observe that the $\beta_1$ emission band shifts from $\sim 3.0$ eV to 3.14 eV passing from 100 K to 473 K, while in the same temperature range the $\beta_2$ emission band shifts from 3.22 eV (at 100 K) to 3.20 eV (at 473 K).

Considering the behaviour of the $\beta$ band components as a function of temperature we have seen that all the curves of figure 4 can be well fitted using equation (1). We now consider the analytical form of $I_{\beta_1}(T)$ and $I_{\beta_2}(T)$: they are reported as dashed lines in figure 4. $I_{\beta_1}(T)$ has been obtained using the same model we recently proposed to fit $I(T)$ for the gamma emission at 2.7 eV in silica [7]. We just mention here the basic features of the model of [7] and the resulting parameters: to account for a curve increasing in intensity, but not in lifetime, when the temperature rises, we used an energy level scheme (see figure 5 of [7]) consisting of two relaxed excited states: a metastable state (M), reached by the $\sim 5$ eV excitation and from which radiative recombination is not allowed, and a radiative state (R) at a higher energy, that can be populated by electrons thermally excited from level M.

Calling the energy difference between levels M and R, $\Delta E_R$, the number of electrons that reach R is

$$n_{0R} = n_{0\beta} \exp(-\Delta E_R / kT) \tag{2}$$

where $n_{0\beta}$ is the number of electrons in the state M. The complex mechanism of the intensity increase and of the quenching of the emission at higher temperatures can be described by the following equation in which the emission efficiency $\eta_R$ is expressed as a function of the

temperature:

$$\eta_R(T) = \exp(-\Delta E_R/kT)/[1 + (\tau_R/\tau_0)\exp(-\Delta E/kT)] \quad (3)$$

where $\Delta E$ is the energy difference between the level R and the level responsible for the quenching of the emission.

By the use of equation (3) we have obtained $I_{\beta_1}(T)$ with the following parameters:

$$\Delta E_R = 0.06 \text{ eV} \qquad \Delta E = 0.19 \text{ eV} \qquad \tau_R/\tau_0 = 165$$

$I_{\beta_2}(T)$ is described by a simpler scheme that takes into account a non-radiative path that causes a quenching at $T > 250$ K. The calculated value of $\Delta E$ is 0.24 eV.

From the reported analysis of the excitation and emission features and of $I(T)$, relative to the $\beta$ emission band, we conclude that two emissions contribute, with different weights as a function of temperature, to the total emission in both silica and Ge-doped silica. The two bands have slightly different excitations whose energies are in good agreement with the two components, recently evidenced in the $B_{2\beta}$ absorption band: at RT the excitation bands are at 5.05 and 5.20 eV; the two components of the absorption band are reported [3] at 5.06 eV and 5.16 eV.

A few considerations can now be made as regards the centres responsible for the $\beta$ emissions. Many authors have evidenced the correlation of impurities with the $B_{2\beta}$ absorption band and the corresponding $\beta$ emission [8–10]. They have been found only in silica of natural origin ('fused quartz'), containing a high concentration of impurities, and are not produced by irradiation. There is also agreement [3, 5] that the $B_{2\beta}$ absorptions are due to Ge-related ODCs. The $\beta$ emission has also been proposed to be due to specific Ge centres [8]. The high intensity of the $\beta$ emissions we have found (as others did) in Ge-doped silica would confirm a role of Ge. However the presence of the $\beta$ emissions in Herasil silica, that contains a high concentration of various impurities, but less than 1 ppm of Ge (producer's analysis), could possibly indicate that, besides Ge, other impurities contribute to inducing the ODC responsible for the $B_{2\beta}$ absorptions and the $\beta$ emissions.

The presence of the two $\beta$ components in absorption, excitation and luminescence with slightly different emissions and lifetimes points to two modifications of the same centre, maybe two different relaxations of the surrounding vitreous network.

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