Luminescence of fused silica: Observation of the O_2^- emission band

M. Guzzi, M. Martini, M. Mattaini, F. Pio, and G. Spinolo

Dipartimento di Fisica, Università degli Studi di Milano, via Celoria 16, 20133 Milano, Italy

(Received 24 December 1986)

Phosphorescence (PP) and photoluminescence (PL) spectra on type-I and type-II fused silica have been measured. Comparison among them shows that the same bands are present in the PL and PP spectra; the only exception is the "resonant" emission excited in the B_2 absorption band (~ 5.1 eV) which is always absent in the PP spectrum. At low temperature in one of the PL emission bands, structures have been found whose energy spacing, ~ 1250 cm^{-1}, appears to identify the luminescent center as the O_2^- molecular ion.

INTRODUCTION

More than thirty years ago Garino Canina[1,2] studied the photoluminescence of fused silica and the influence on the absorption and emission spectra of thermal treatments in oxidizing or reducing atmospheres. Since then, a fairly large number of papers have been published on silica and quartz emission, differently excited and treated.

A dominant feature is the presence, in "reduced" silicas, of an absorption band at ~ 5.1 eV (also produced by heavy-particle irradiation[3] and called B_2) and of its "resonant" emission at ~ 4.2 eV. Other emissions, excited by the 253.7-nm line of a Hg lamp, are located at about 3.1 and 2.7 eV. Ge doping[4,5] was thought to have a role in the loss of oxygen and, even recently, several authors suggest that Ge impurities are responsible for some of the emission bands in silica.[6,7]

However, models of the emitting centers are still a matter of debate and, further, a certain confusion still remains due to the fact that emission bands probably related to the same process are cited in the literature with slightly different peak values. It is not always clear if the differences are real and induced by the different local situations present in the various types of silica or α-quartz, or if they are due to the difficulty in establishing the peak energy of broad emission bands.

Comparison with the emissions of analogous centers in α-quartz, silica, and thermally grown SiO_2 films[8] is certainly helpful but not conclusive in attributing the different emissions to specific centers and transitions. As an example, we may remember that the 4.28-eV photoluminescence emission in SiO_2 films increases its intensity upon reduction and goes to zero upon oxidation,[8] in agreement with old[4] and recent studies[6] on the 4.4-eV emission in silica. However, this fact does not help to propose a model for the responsible center, which is believed to be the same.

A discussion of all the available results could be useful but it is not yet timely in our opinion. Recently, in fact, in our laboratory,[9] earlier evidence[10] on the complexity of the excitation spectra in the 4.9–5.3-eV region has been confirmed. Further work is in progress along the lines mentioned above; here we are mainly concerned with the study of the 3.1-eV emission band, whose attribution appears conclusive.

In our study of the different types[11] of dry and wet silicas and of natural and synthetic quartz both as grown and variously irradiated and electrodiffused, the first step was that of studying photoluminescence in "as-received" silicas.

Among the different types examined only those of type I and type II (Ref. 11) exhibit the well-known B_2 band in the absorption spectrum and possess both photoluminescence and room-temperature (RT) phosphorescence: They will be the subject of our report.

EXPERIMENT AND RESULTS

A number of silica samples of different origin have been chosen and classified with reference to the accepted scheme:[11] All the types (I, II, III, and IV) were present among our available samples. By measuring optical absorption using a Cary 2300 spectrophotometer from 0.4 to 6 eV and a vacuum-ultraviolet apparatus from 4 to 8 eV we determined the type to which each sample belonged, essentially by comparison with the spectra given in Fig. 3 of Ref. 12. The characterizing features were the OH (~ 0.45 eV) and the B_2 (~ 5.1 eV) absorption bands. All the samples had optically polished surfaces and ranged in thickness from 0.5 to 2 mm.

Photoluminescence (PL) spectra from 300 down to 60 K were performed in a classical apparatus featuring two grating monochromators in crossed disposition for excitation and emission; the excitation source was a 200-W deuterium lamp; all the spectra were corrected for the spectral response of the optical system.

Phosphorescence (PP) spectra were taken at 300 K after excitation with an exposure of $\sim 7 \times 10^5$ roentgen by a Machlett OEG-50 x-ray tube operated at 35 kV and corrected for the decay occurring during the recording of the spectra which lasted about 10 min. As a matter of fact, the PP decay at 300 K is roughly exponential, with a time constant $\tau \sim 0.5$ h.

First of all, we observed that type-III and type-IV silicas (no B_2 band in absorption) show neither PP nor PL. On the contrary, the PL spectrum (excited at 4.96 eV) in all the type-I and -II silicas we studied, shows three emission bands that for ease of identification we call α (~ 4.2 eV), β (~ 3.1 eV), and γ (~ 2.7 eV); these bands have
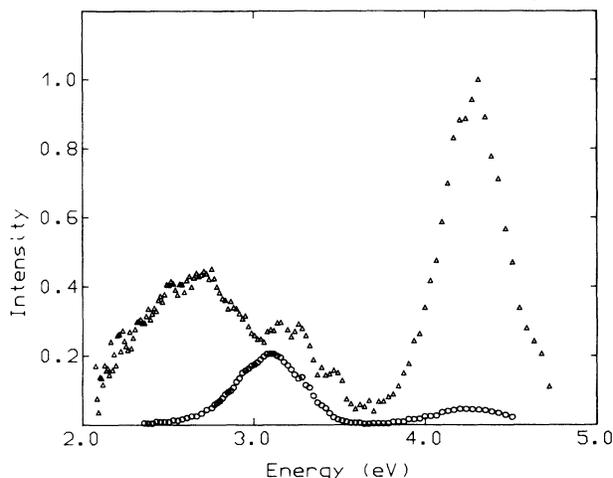
FIG. 1. RT (O) and LNT (△) photoluminescence spectra of a type-I silica sample; all the spectra are normalized to the maximum intensity of the 4.2-eV emission band at LNT.

been discussed several times in the literature.

At 300 K the α and β PL bands are easily distinguishable while the γ band is very weak; at liquid-nitrogen temperature (LNT) α and γ increase their intensity: Typical spectra are shown in Fig. 1. To complete the picture, we give in Fig. 2 the room-temperature PL spectra of two other samples; it appears that the ratios of the intensities among the three PL bands differ from sample to sample: For this reason one is compelled to attribute them to different emission centers.

In Fig. 2 are also shown the PP spectra taken at 300 K. Two points are worth noting: (i) the α emission is always absent in the PP spectra; (ii) the intensity of the γ component in the PP spectrum increases with the intensity of the α component in the 300-K PL spectrum.

It should be remarked that at 300 K the peak position of the α PL band is 4.15 eV in some of our silicas and 4.30 eV in others. This fact, generally corresponding to differences in the peak energy of the B_2 absorption band, has not yet been discussed in sufficient detail in the literature;[7,10] the eventual role of Ge impurities, proposed by some authors,[4,7] needs more experimental evidence.

The α-band excitation spectrum superposes well on the B_2 absorption while β and γ emissions are excited in the B_2 band and at different energies as well.[10]

The main new result we want to show, however, is that of Fig. 3, in which a portion of the emission spectrum at 60 K is reported with an enlarged energy scale as compared to Figs. 1 and 2. In the spectrum it is quite evident that the β band (which at 300 K has a substantially Gaussian shape) appears to be quite structured at low temperature; a deconvolution is proposed by subtracting the contributions of the γ emission band (supposedly Gaussian in shape); the β band appears to be made out of subbands spaced about 1250 cm^{-1} apart. Both the shape and the spacing among the subbands are quite reminiscent of the O_2^- emission in alkali halides;[13] further, the measured energy value of the spacing agrees with that calcu-
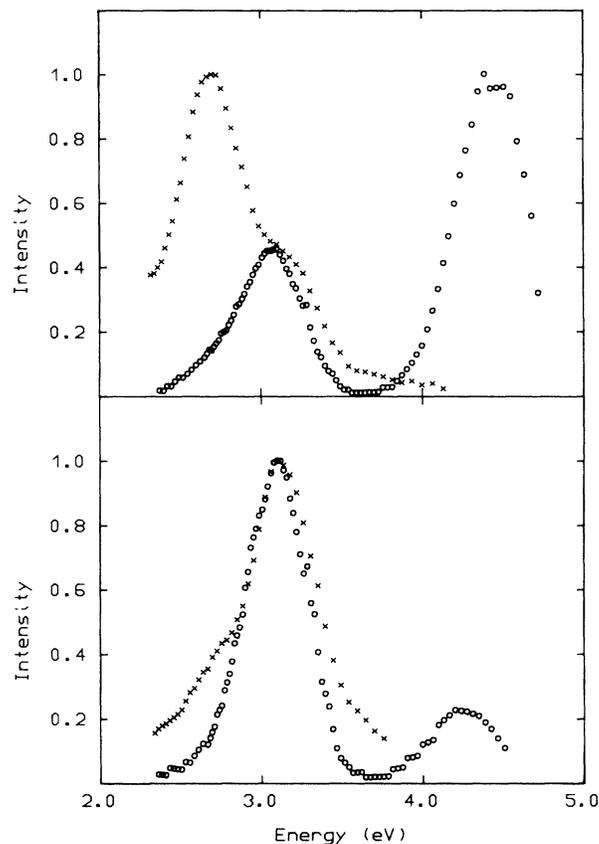

FIG. 2. Phosphorescence (×) and photoluminescence (O) spectra recorded at RT for two different samples. Each spectrum is normalized to its maximum.
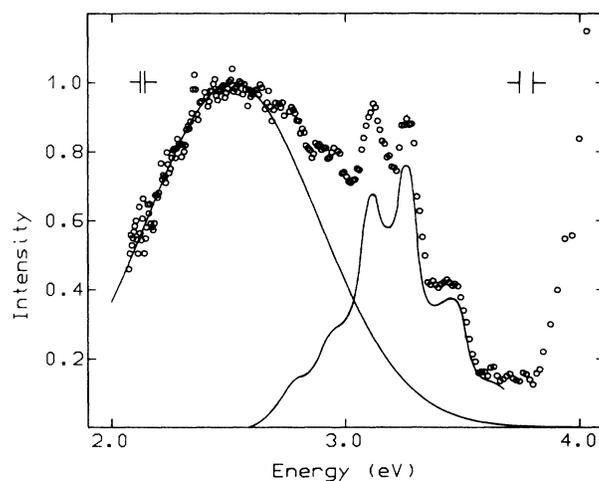

FIG. 3. Photoluminescence spectrum of a type-I silica sample recorded at 60 K under 4.96-eV excitation. Only the spectral region of the β and γ emission bands (see text) is shown; the spectrum is normalized to its maximum. The solid lines give the proposed deconvolution of the β and γ bands; on the high-energy side of the spectrum the tail of the α band is present.

lated in Ref. 13. Due to the weakness of the PL intensity it has not been possible to record spectra with higher resolution and, therefore, the presence of the fine structure typical of the O_2^- emission in alkali halides[13] could not be investigated. An emission band with analogous structures has been recently observed in quartz and attributed to O_2^- as well.[14]

DISCUSSION AND CONCLUSIONS

In this paper phosphorescence spectra of fused silica are reported and, in a broad sense, they agree with former radio- and thermoluminescence spectra.[15] It is evident that the often reported "blue" luminescence[15] is due to a mixture of what we call the β and γ bands; it has been shown here that the relative intensity of these bands and therefore the concentration of the responsible centers, is very much dependent on the sample.

The α emission is always absent in the PP spectra: therefore the "α-center" excited state should have a capture cross section for the free carriers much smaller than that of β- and γ-center excited states. The excellent matching between the B_2 absorption and the excitation of the α emission[9] supports the identification of the α band as the emission of the B_2 center. The rather small Stokes shift ($\sim$0.9 eV) between B_2 absorption and α emission speaks for a rather localized center.

To go further into these aspects one needs to know at least the distance from the conduction band of the excited relaxed levels from which α, β, and γ emissions take origin; a check of the old data[1] is needed.

The α, β, and γ emissions are present in all the forms of SiO_2 (quartz, silica, thermally grown films)[8] and so we believe the responsible defects are of intrinsic origin.

As a matter of fact, the attribution of the 3.1- and 4.2-eV photoluminescence bands to triplet-to-singlet and singlet-to-singlet transitions of a Ge impurity[7] seems contradicted by the experimental results reported here.

In this paper, very strong experimental support is given to the proposal that the 3.1-eV (β) emission band is, in reality, due to the O_2^- intrinsic defect. The structures on the β emission band are present in all the untreated samples we studied; however, when the 3.1-eV band is studied in irradiated samples the structures are much less defined. Among the possible environments of the O_2^- defect, is there one favored during growth or post-growth annealing? Do there exist different possible locations (and, as a consequence, a smearing out of the structures) when the defect is produced by irradiation?

As a final comment, we believe that the identification of the O_2^- emission band is an important step in deepening our knowledge of the intrinsic defects in the various forms of SiO_2. Optical data now appear to be more useful than heretofore in building up a model for a localized center in SiO_2; up to now only ESR seemed to be able to do that.

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