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Neutron irradiation effects in amorphous SiO_2: optical absorption and electron paramagnetic resonance

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Abstract. Optical absorption spectra of as-grown and neutron-irradiated amorphous SiO_2, both fused natural quartz and synthetic silica, have been analysed in the ultraviolet region below the fundamental edge. The description of the optical spectrum has been further clarified by a detailed study of the spectral components as a function of the neutron irradiation in different types of silica; we have verified known correlations between optical bands and between bands and paramagnetic centres. In 'as-grown' fused quartz samples, a previously unreported band at 6.2 eV has been detected. 'As-grown' synthetic silicas do not show any band, up to the intrinsic absorption edge. In the irradiated samples, the experimental results suggest a correlation between two bands at 5.8 and 7.1 eV, while previous attribution of the bands at 5.0 eV (B_2 band) and 7.6 eV (E band) to the same defect is discussed. The role of impurities in the optical absorption and in the radiation hardness is also considered.

1. Introduction

The optical absorption edge of amorphous SiO_2 is at approximately 8.1 eV [1]; at lower energies, several absorption bands have been detected, owing to the presence of point defects, both of intrinsic and of impurity origin. Most of these bands have a counterpart in the crystalline material, with nearly the same features; this is evidence that the responsible defects arise from very localized centres. These optically active centres appear to be created by exposure to ionizing radiations, even if some of them pre-exist in some kinds of as-grown material.

The attribution of these bands to specific electronic transitions, as well as the influence of the growth conditions on the spectrum, are important aspects in order to reach good control of the performances of the material. In fact, several methods of preparation are used, involving different types and contents of impurities, different oxygen stoichiometries, different densities and different OH concentrations. The resulting characteristics have a bearing on the possible applications. The intrinsic and extrinsic point defects have been mainly studied by electron paramagnetic resonance (EPR) [2–7] from which a satisfactory picture of a few paramagnetic centres has already been reached.

Many studies have been performed on ultraviolet (UV) optical absorption, but complete attribution of the bands to specific point defects is still lacking. In fact, the current description of the optical absorption spectrum mainly refers to early studies in which the material quality was less controlled than nowadays [8, 9], while successive studies mainly deal with the creation kinetics as a function of the type of irradiation (electrons, protons

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or heavy ions) [10, 11]; only recently have systematic studies been performed on variously prepared samples [12–17], leading to the correlation of some bands to undefined oxygen-surplus and oxygen-deficient defects or to impurities; some workers have proposed specific attributions, but different defect models are often associated with the same band by different workers. Furthermore, some generally accepted attributions in the analysis of the optical spectra seem to have to be reconsidered; early correlations with paramagnetic centres (E′ and peroxy radical) [18, 19] fail in recent observations [16, 20, 21], while correlations between bands assigned to the same defect [15, 21] by different experiments [12] are questionable.

The aim of the present work is to improve the general description of the UV absorption and to verify the association with paramagnetic and non-paramagnetic defects, checking also the already-proposed correlations between bands.

We have carried out a systematic study of the optical absorption properties of various commercial silicas, both 'as grown' and neutron irradiated. The data described here will be compared with those recently reported on crystalline quartz [20]. Neutron irradiations have been employed to induce optically active defects in concentrations suitable for investigating the absorption bands. Then, by using the neutron fluence as a parameter, we have compared the creation rates of these defects. The early association of the 5.8 eV absorption with the paramagnetic E′ centre is also discussed by comparing optical data with EPR measurements of the E′-centre density. Finally, the optical data evidenced the dependence of the overall intensity of the spectra on the impurity content of the material. The analysis of the effects of neutron irradiations showed different radiation hardnesses in amorphous SiO_2 characterized by different purities, this fact being of crucial importance for technological applications. The problem of matching the role of impurities with the intrinsic nature attributed to most defects responsible for the absorption bands is discussed; by means of EPR measurements of the intrinsic E′-centre density we verified that the creation yield of intrinsic defects may depend on the impurity content in different types of silica. The indirect role of impurities is thereby evidenced.

2. Experimental details

The types of silica that we studied are the following [22]†: type I, a dry silica (OH content less than 20 ppm) produced from natural quartz (Pursil K (PK)); type II, a wet silica (OH content ranging from 130 to 180 ppm) produced from natural quartz (Herasil (HR)); type III, a synthetic wet silica with 1200 ppm of OH (Tetrasil B (TB)); type IV, a synthetic dry silica (Tetrasil SE (TS)) with OH content less than 20 ppm. Samples of type I and II are characterized by a relatively high content of metallic impurities, typically 100 ppm of aluminium ions and about 10 ppm of alkali ions. Other trace impurities (such as Fe and Ti) can also be present in quantities below 1 ppm‡. The density of metallic impurities in samples of type III and IV is lower than 1 ppm‡. By proton-induced x-ray emission (PIXE) analysis we checked for the presence of germanium ions, which could be easily introduced as silicon substitutionals; the resulting Ge content is less than 2 ppm in all types of silica.

Samples have been prepared in suitable shapes for both optical absorption and paramagnetic resonance measurements. Neutron irradiations were carried out with fluences ranging from 3×10^{15} to 3×10^{18} neutrons cm^{-2} obtained from a neutron beam of

† Pursil, Tetrasil B and Tetrasil SE are silica purchased from Quartz & Silice (Nemours, France), while Herasil was obtained from Heraeus (Orsay, France).

‡ All the data on impurities, included the information on the OH content, were supplied by the manufacturers.

10^{13} neutrons cm^{-2} s^{-1}. The sample temperature was 65 ± 2 °C. Reactor irradiations produce, together with neutron displacement damage, high levels of ionizing radiation (about 10^6 Gy γ-rays for a neutron fluence of 10^{16} neutrons cm^{-2}) and so the irradiation damage is produced both by neutrons and by γ-rays. Details of the sample preparation and irradiation treatments have already been reported [20].

Absorption spectra were measured at 300 K from 0.4 to 9 eV; in the 3.5–9 eV range a home-made double-beam vacuum-UV system was used, while the spectra between 0.4 and 6.2 eV were obtained with a Varian 2300 spectrophotometer [20]. Some measurements were also performed at 80 K; no variations in the peak position and half-width of the absorption bands, nor shifts in the edge position, were observed, as could be expected in the amorphous materials under investigation. The optical spectra were analysed in terms of Gaussian bands. The details of the numerical analysis have been described elsewhere [20]. We emphasize that we considered in the fits only those bands clearly evidenced in the spectra and those previously reported in literature, whose inclusion improved markedly the quality of the fit.

For the EPR measurements a spectrometer operating in the X band (about 9.13 GHz) was used. The measurements of the E′-centre signal were performed at room temperature, with the microwave power at about 10^{-6} W, and the field modulation amplitude lower than 10 μT. Measurements at higher power were also performed. The paramagnetic centre density was evaluated by comparison with the DPPH standard.

3. Results

3.1. Optical Absorption

3.1.1. Unirradiated samples. Synthetic samples (TB and TS silicas) do not show any absorption band below the fundamental edge prior to irradiation. On the contrary, the spectra of unirradiated PK and HR silicas (figure 1) show at approximately 7.6 eV an intense absorption (E band) with weak evidence of a shoulder on the low-energy side, at about 7 eV. A band at 6.2 eV is also present, which has not been observed up to now. At about 5 eV, a further band is detected; two different absorptions have already been recognized in this region, also by the aid of photoluminescence (PL) excitation [13]: the $B_2\alpha$ band (about 5.0 eV), with PL emissions at 4.35 eV (α_A), and the $B_2\beta$ band (about 5.15 eV) with emissions at 4.25 eV (α_B). Other workers also correlate the 2.7 eV (γ) emission and the 3.1 eV (β) emission to the $B_2\alpha$ and $B_2\beta$ absorption bands, respectively [15]. Therefore, the B_2 absorption band represents the envelope of various bands of slightly different energies. Our unirradiated PK and HR samples show PL emission typical of the $B_2\beta$ band [23].

3.1.2. Irradiated samples. Representative spectra observed following irradiation in fused quartz and synthetic silicas are shown in figures 2 and 3, respectively. In the region above 6 eV, two bands induced by the neutron irradiation are present in the synthetic silicas at 7.1 eV (D band) and 7.6 eV (E band), while in PK and HR samples the neutron-induced optical density is over the instrument limit. At 5 and 5.8 eV, two bands increase in the spectra of the four types of silica; they are usually denoted as B_2 and E′, respectively.

In the lower-energy region (2–5 eV), the various types of SiO_2 show different radiation-induced absorptions; the D_0 (4.7 eV) band is observed in pure synthetic samples, while PK and HR silicas are characterized by the presence of the B_1 absorption at 4.1 eV. Only in PK is a weak A band [8], centred at approximately 2.4 eV, also detected.

In TB and TS samples, all the bands show a monotonic increase as a function of neutron fluence, from 3×10^{15} to 3×10^{18} neutrons cm^{-2}; PK and HR samples show spectra generally

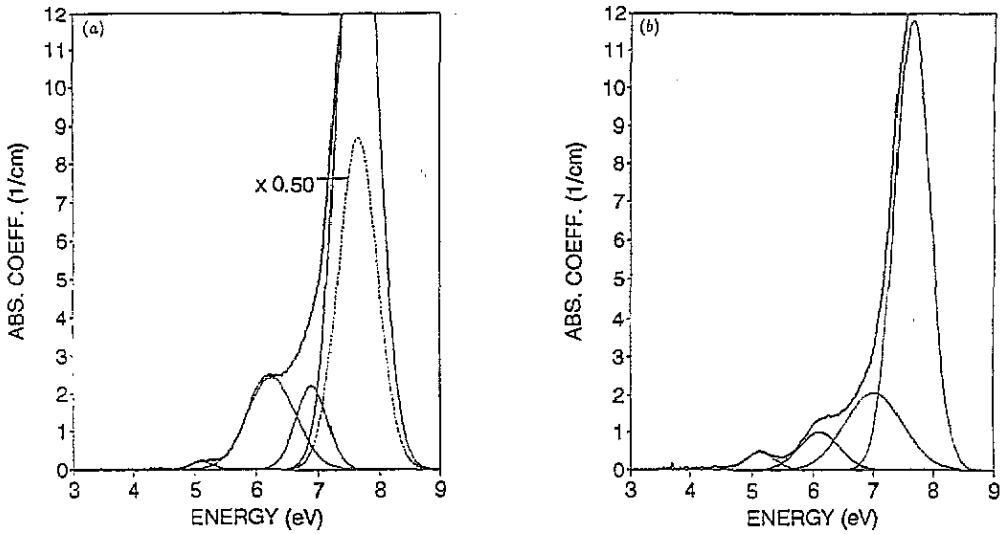

Figure 1. Optical absorption spectra measured at $T = 300$ K on unirradiated fused quartz: (*a*) PK; (*b*) HR. The decomposition into Gaussian components is also shown: ——, experimental data; ——, Gaussian components.

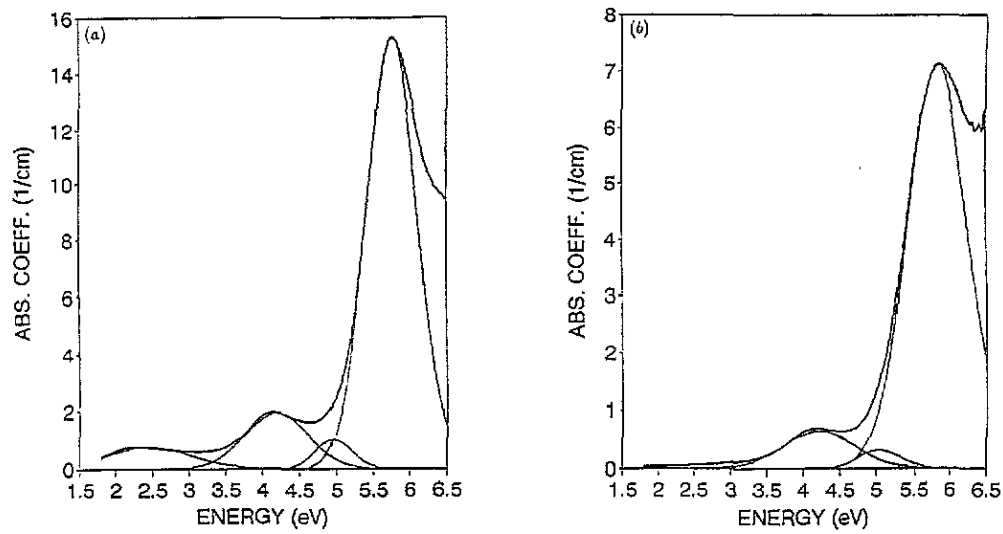

Figure 2. Optical absorption spectra measured at $T = 300$ K on irradiated fused quartz (neutron fluence, 3×10^{15} neutrons cm^{-2}): (*a*) PK; (*b*) HR. The decomposition into Gaussian components is also shown: ——, experimental data; ——, Gaussian components.

more intense but characterized by a weaker increase in the bands upon irradiation (namely by a factor of 2–3). An unusual behaviour characterizes the 4.1 eV (B_1) band which, after an increase at low doses, shows slight radiation bleaching. Tables 1 and 2 list the values of energies and half-widths of the bands.

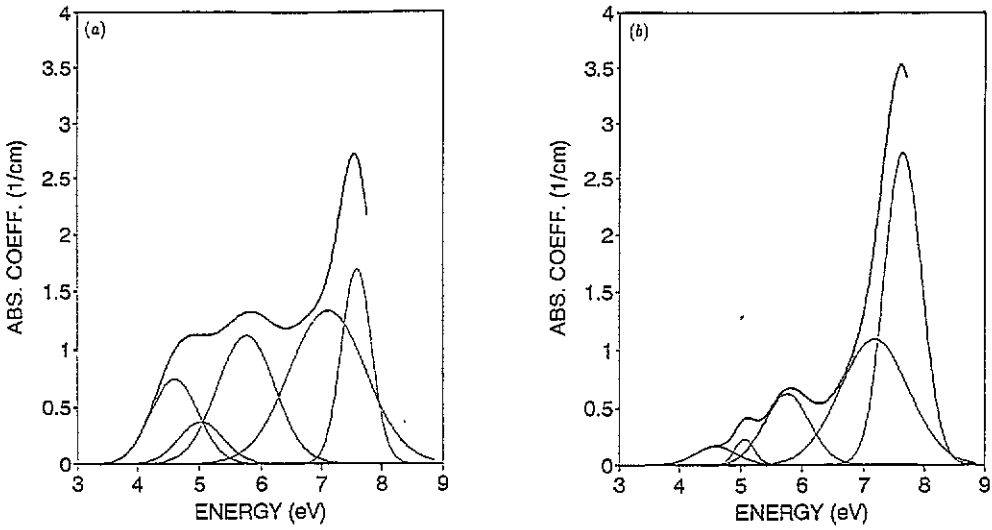

Figure 3. Optical absorption spectra measured at $T = 300$ K on irradiated synthetic silica (neutron fluence, 1×10^{16} neutrons cm^{-2}): (*a*) TB; (*b*) TS. The decomposition into spectral components is also shown: ——, experimental data; ——, Gaussian components.

Table 1. Peak energies E and half-widths ΔE of the components obtained from spectral decompositions for unirradiated and irradiated fused quartz. For irradiated quartz the parameters are mean values evaluated on all samples examined; the uncertainties, evaluated for the whole set of measurements, are 1% and 15% for the energies and half-widths, respectively. ND indicates not detected.

	Value for unirradiated fused quartz			
	B_2	6.2 eV	7 eV	E
PK E (eV)	5.45	6.24	6.90	7.62
PK ΔE (eV)	0.57	0.92	0.58	0.75
HR E (eV)	5.12	6.20	7.00	7.65
HR ΔE (eV)	0.57	0.94	0.99	0.66
	Value for irradiated fused quartz			
	A	B_1	B_2	5.8 eV
PK E (eV)	2.39	4.17	4.97	5.75
PK ΔE (eV)	1.48	1.34	0.60	0.80
HR E (eV)	ND	4.21	5.03	5.83
HR ΔE (eV)	ND	1.13	0.66	0.95

A few remarks should be made about some features of the radiation-induced bands and on their growth as a function of the neutron fluence.

(i) In the 5 eV region, a significant enhancement is observed upon irradiation. Although the resolution of the spectrum in the irradiated samples does not allow one to recognize shifts in the absorption peak with respect to the unirradiated samples, PL measurements of both

Table 2. Peak energies E and half-widths ΔE of the components obtained from spectral decompositions for irradiated synthetic silica. The parameters are mean values evaluated on all samples examined; the uncertainties, evaluated for the set of measurements, are 1% and 15% for the energies and half-widths, respectively.

	Value for irradiated synthetic silica				
	D_0	B_2	5.8 eV	D	E
TB E (eV)	4.65	5.04	5.75	7.14	7.65
TB ΔE (eV)	0.93	0.54	1.01	1.77	0.70
TS E (eV)	4.71	5.09	5.75	7.15	7.63
TS ΔE (eV)	1.05	0.51	0.73	1.82	0.77

synthetic silica and fused quartz suggest the attribution of the neutron-induced absorption to the $B_2\alpha$ band. The emission of the $B_2\beta$ band pre-existing in the unirradiated fused quartz is lowered by irradiation [23].

(ii) Irradiation also gives rise to a band centred at 5.8 eV, recognizable as the E′ band. In fact, the creation rate of this band does not strictly agree with that of the EPR E′ density (see figure 4 for a TB sample). Furthermore, the ratios of EPR E′ densities in different silicas are not simply related to the corresponding ratios between the intensities of the 5.8 eV band (see table 3 for neutron fluences of 3×10^{15} neutrons cm^{-2}). This has already been remarked on in the case of crystalline quartz samples irradiated in the same conditions [20].

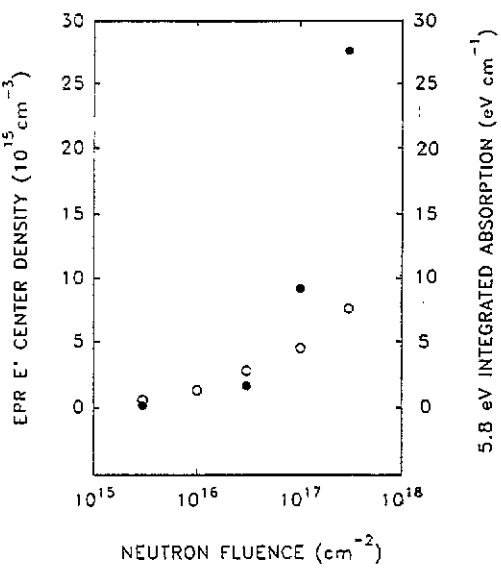

Figure 4. EPR E′-centre density (●) and integrated optical absorption (○) of the 5.8 eV band versus neutron fluence in the case of TB samples.

(iii) The intensity of the 6.2 eV band, which is present in unirradiated PK and HR silicas, cannot be correctly evaluated in irradiated samples (compare figures 1(*a*) and 2(*a*)) owing to the high intensity of the overlapping 5.8 eV band; it is not possible to determine whether the 6.2 eV band has been bleached by irradiation or simply overlaps the 5.8 eV band.

(iv) Absorption measurements as a function of neutron fluence also provides information on possible correlations between optical transitions; different electronic transitions at the same defect are expected to give rise to absorptions with linearly related intensities. In

figure 5(*a*) the absorption coefficient of the 7.6 eV (E) versus the 5.0 eV ($B_2\alpha$) bands in type III silica with the neutron fluence as a parameter is reported; the deviation from linearity means that the proposed correlation between these two bands is questionable [15]. In figure 5(*b*), analogous data on the 7.1 eV (D) band versus the 5.8 eV band are shown; a linear relationship is evidenced by the slope of the interpolating line. This result has been found to be a common feature of all kinds of silica in which the study of this spectral region has been performed, and it has also been observed for crystalline quartz [20].

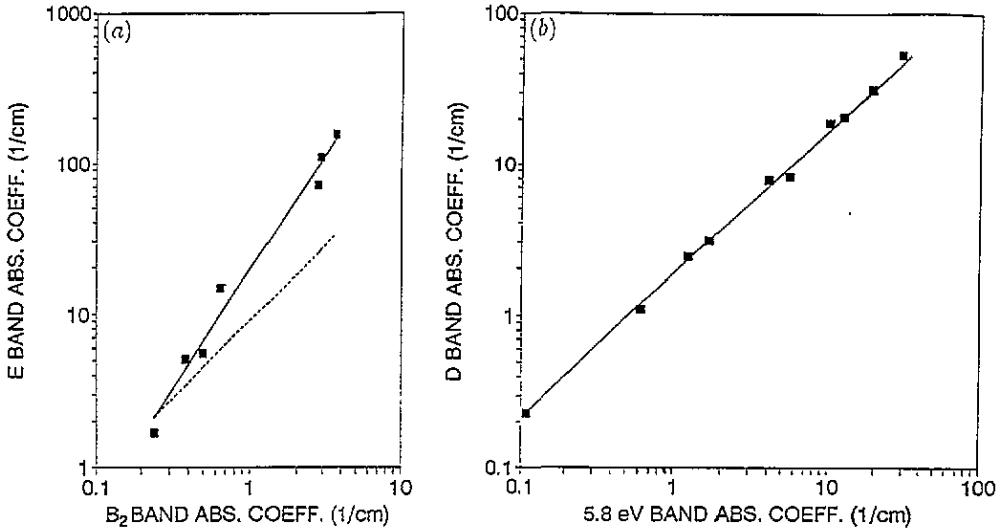

Figure 5. (*a*) 7.6 eV (E) band versus 5.0 ($B_2\alpha$) band peak absorption coefficient with the neutron fluence as parameter, in the case of TS. The least-squares fit (——) is compared with the slope expected in the case of a linear relation (- - - -). (*b*) 7.1 eV (D) band versus 5.8 eV peak absorption coefficient with the neutron fluence as parameter, in the case of TB. The least-squares fit is also shown.

Table 3. Ratios of the EPR E′ densities in the four types of silica compared with the corresponding ratios between the intensities of the 5.8 eV optical absorption band (neutron fluence 3×10^{15} neutrons cm^{-2}).

	TS/TB	PK/HR	PK/TS	HR/TB	PK/TB	HR/TS
EPR	24	3	8	66	204	3
Optical absorption	6	2	5	14	31	2

3.2. Electron paramagnetic resonance

Unirradiated samples did not show any paramagnetic signal. This should be taken into account in the discussion of the optical bands detected for some kinds of unirradiated silica; attributions to structural models which imply paramagnetic activity are to be ruled out.

Neutron irradiation gives rise to several paramagnetic centres whose EPR signals are mainly due to holes trapped at oxygen orbitals (oxygen hole centres, peroxy radicals,

fourfold-coordinated aluminium centres, etc) or to electrons trapped at impurity sites [24]. However, the main EPR defect is the E′ centre resulting from an unpaired electron spin highly localized in an sp^3 hybrid orbital of a single threefold-coordinated silicon atom [25, 26]. This paramagnetic centre, the best characterized intrinsic defect in SiO_2, exhibits a long spin lattice relaxation time; this feature makes the E′ centre detectable at very low microwave powers (figure 6, curve (a)), differently from other types of defect whose EPR spectra observed at high microwave powers generally result in a complex overlapping signal (figure 6, curve (b)). In order to study the creation rate of intrinsic defects as a function of the impurity content, we monitored the E′ EPR centre signal, clearly defined in the low-power spectra.

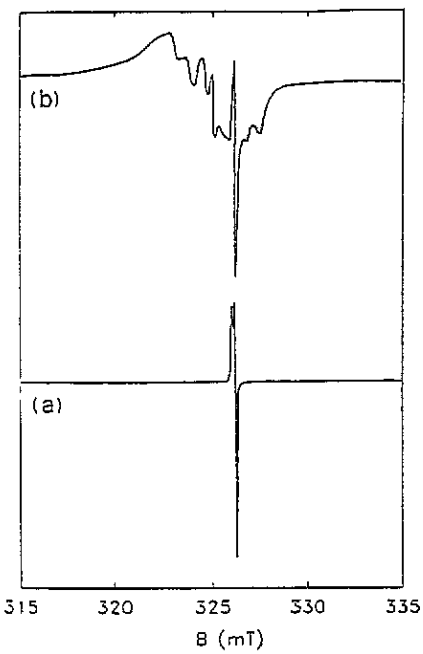

Figure 6. Representative EPR derivative signals of irradiated HR (neutron fluence, 1×10^{17} neutrons cm^{-2}) detected at (*a*) a high microwave power (10^2 mW) and (*b*) a low microwave power (10 μW).

In figure 7 the E′-centre densities, as computed from double integration of the first derivative EPR spectra, are reported for the four types of silica as functions of neutron fluence. The E′ defect concentration induced by irradiation is higher in the less pure materials (type I and type II silica). In these types of silica, the higher OH content corresponds to a lower induced E′ density. In the pure wet synthetic silica irradiated at the lowest neutron fluence, the E′ density is two orders of magnitude lower than in PK and HR samples, while this difference is reduced to a factor of 5 in the more strongly irradiated samples. At high neutron fluences, for TS samples the induced E′ density is substantially similar to that for TB samples but somewhat dependent on the different batches.

4. Discussion

4.1. General remarks

There are several similarities in the features of the optical absorption spectra of crystalline

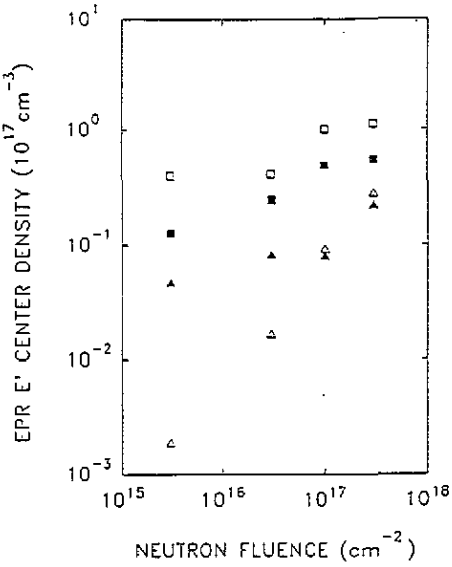

Figure 7. EPR E′-centre densities of the four types of silica examined as a function of neutron fluence: □, PK; ■, HR; △, TB; ▲, TS.

quartz and amorphous silica; this agrees with the presence of a short-range order common to the SiO_4 tetrahedra in both forms of SiO_2. However, some features of the optical spectra are peculiar to the amorphous form, which may stabilize specific defects; further, the low local symmetry of the glass may allow transitions not allowed in the crystalline material.

The main differences are found in the region below 5.5 eV where the B_1 (4.1 eV) and B_2 (about 5 eV) bands are typically detected in the amorphous form. The 4.1 eV absorption is present only in irradiated fused quartz samples and it does not show any marked increase on increasing the neutron fluence; for these reasons, an impurity-related defect is likely to be responsible for this band. Also the 5 eV absorption is characteristic of amorphous SiO_2; the problem of its attribution is discussed in section 4.3.

The 4.7 eV (D_0) and the 2.4 eV (A) bands are also present in quartz [20, 27]. The 2.4 eV band has usually been associated with aluminium impurities [27]. The 4.7 eV band is probably of intrinsic origin; our results demonstrate its existence only in highly pure materials and support the previous intrinsic attribution [28].

'As-grown' fused quartz samples show the so far unreported 6.2 eV band, which is either bleached by irradiation or simply hidden by the increasing 5.8 eV band. It may be attributed to an impurity-related defect or to a diamagnetic intrinsic defect.

At energies higher than 5 eV, the spectra of irradiated silica and quartz show the same bands; at 5.8 eV, 7 eV (D band) and 7.6 eV (E band). In fact, the complex structure evidenced in quartz in the 5–6 eV region [20] is not observed in silica, even though inhomogeneous broadening may hide possible structures. However, we do not observe any correspondence between the relative intensities and the neutron fluence dependence of the 5.8 eV band in different silicas and the EPR E′-centre densities; therefore, we question their association. Our results are consistent with similar evidence previously observed both for silica and for quartz; after early observations of a correlation between the optical band and the EPR defect in quartz [29], other studies failed to confirm this [20, 30]; furthermore, in some types of silica the band at 5.8 eV is seen to increase for decreasing oxygen partial pressure during synthesis without any detectable paramagnetic activity [16], while *significant*

absorption in the 5–6 eV region is observed after annealing the EPR E′ centres [31]. In fact, the analysis of this spectral region must be completely revised. A spectral component at 5.8 eV not related to the E′ centre is necessary to explain all the available experimental data. Two different possibilities should be taken into account; either firstly more than one band is present at the same energy, at least one of which arises from a diamagnetic defect, or secondly the 5.8 eV absorption is characterized by a single band associated with a diamagnetic centre.

Little attention has been paid in the literature to the D band at 7.1 eV, in spite of the fact that we found indications of its presence in every type of SiO_2, included crystalline quartz [20]. This evidence suggests that the 7.1 eV band of irradiated samples can be attributed to an intrinsic defect. The linear relationship between this absorption and the 5.8 eV band, in all types of silica as well as in crystalline material [20], may suggest their correlation, which could constitute a valuable constraint in the determination of its origin. On the contrary, the shoulder at approximately 7 eV observed in unirradiated fused quartz is not associated with the 5.8 eV absorption and definitely appears to be of different origin with respect to the 7.1 eV (D) band.

4.2. Role of impurities

Figures 2 and 3 show the dependences, at a fixed neutron fluence, of the intensities of most bands upon the impurity content, the less pure material showing UV absorptions generally more intense. This phenomenology might suggest an extrinsic origin of the absorption spectrum, contrary to the intrinsic nature attributed to most of the spectral components. On the other hand, one should also consider the possible indirect role of impurities in the creation processes of intrinsic defects. In this regard, the well defined E′ centre may be an interesting probe of the influence of impurities on the radiation-induced growth rate and absolute density of a surely intrinsic centre. Our EPR results, shown in figure 7, give the independent evidence that we are looking for of the indirect role of metallic impurities and OH groups on the creation of structurally intrinsic defects; this evidence suggests that an analogous mechanism may operate in the case of those optical bands up to now attributed to intrinsic defects. This observation may also give some insight into the damage processes induced by neutron irradiations in SiO_2; by taking into account the possible role of impurities suggested by the EPR measurements, simple defect creation mechanisms may be described as follows.

(i) The elementary neutron damage event produces a Frenkel pair.

(ii) In pure synthetic silica the recombination of the Frenkel pair, which restores the local structure, is the most probable event; this justifies the high 'radiation hardness' of these materials.

(iii) In less pure silica the impurities stabilize one of the two centres, promoting a mechanism competing against the recombination mechanism.

(iv) Lower effectiveness of impurities is observed in wet material and is probably due to the role of hydrogen as a compensator of substitutional impurities.

Actually, one should also consider the possible presence of defect precursors which may give rise to optical and paramagnetic defects by ionization processes; figure 7 shows for PK, HR, and TS samples a much higher concentration of E′ defects than for TB samples, particularly at low doses; this demonstrates the effectiveness of ionization processes in the PK, HR and TS samples, arising from their high defect precursor density. The different behaviour of TB brings us to the conclusion that, in this case, neutron displacement constitutes the main mechanism of defect creation, because of its high purity and the presence of hydrogen as a compensator.

4.3. Considerations on 5 eV (B_2) and 7.6 eV (E) bands

Our optical measurements, and the accurate PL characterization of [13, 23], show that neutron irradiations allow us to discriminate between the two different contributions to the 5 eV absorption; the $B_2\alpha$ band increases on irradiation and at the same time the $B_2\beta$ band bleaches; these results enable us to operate a selective comparison of the $B_2\alpha$ growth with respect to other bands, and to solve the problem of the controversial association of the 5 and 7.6 eV absorptions [14, 15] to transitions at the same defect. In fact, Tohmon *et al* [15] observed the systematic contemporary presence of these two bands ($B_2\alpha$ and E) in as-grown silicas produced by different manufacturing methods, and they proposed a strict correlation attributing them to the same defect. A one-to-one correlation of the intensities of the $B_2\alpha$ and E bands was not observed [15], but the presence of other absorptions at 5 eV were suggested to be a possible cause of this failure. The same kind of difficulty affects the opposite proposal of a different origin of the two absorptions [14]. In this case these workers drew this conclusion observing that, in oxygen-deficient silica, exposure to a 6.4 eV laser beam caused the partial bleaching of the 5 eV band without any effect on the 7.6 eV band. This study, however, did not take into account the double nature of the B_2 absorption, and the presence of the $B_2\beta$ component (probably bleached by the 6.4 eV light) may affect their conclusions. On the contrary, our experimental results, i.e. the creation upon irradiation of the $B_2\alpha$ band and the lack of a linear correlation between its creation yield and that of the E band in synthetic silica (where the $B_2\beta$ band is not detected) demonstrate without any ambiguity that the $B_2\alpha$ and E bands arise from distinct defects.

5. Summary

The optical study of neutron-irradiated samples of different types of silica has allowed us to reach a general assessment of the phenomenological description of the near-UV absorption features; we planned this work in the belief that this must constitute a necessary step before any detailed attribution of the optical spectral components, owing to some controversial interpretation of the previously observed features. In particular we have found and verified the following.

(i) In unirradiated fused quartz samples a previously unobserved 6.2 eV band is detected, which is possibly bleached by neutron irradiation.

(ii) The 4.1 eV (B_1) and 5.15 eV ($B_2\beta$) bands are probably impurity related; they are observable only in type I and II silicas and saturate or decrease, respectively, on increasing neutron fluence.

(iii) The 4.7 eV (D_0) band is detected only for irradiated high-purity silicas, confirming the attribution to an intrinsic defect.

(iv) The neutron-induced 5.0 eV ($B_2\alpha$), 5.8 eV, 7.1 eV (D) and 7.6 eV (E) bands are observed in all types of silica and increase as a function of increasing neutron fluence, supporting an intrinsic attribution.

(v) The creation rate of the 5.8 eV band and a comparison of its intensity in different silicas do not agree with those of the E′-centre EPR signal.

(vi) EPR measurements of the density of the intrinsic paramagnetic E′ centres as a function of neutron fluence evidence the indirect role of impurities as stabilizers of intrinsic defects and may clarify the origin of the impurity content dependence of most optical bands tentatively attributed to intrinsic centres.

(vii) The analysis of the optical band growth rates shows a linear correlation between the 5.8 eV and the 7.1 eV (D) bands, possibly arising from transitions at the same defect.

(viii) Lack of linear relation between the growth rates of the 7.6 eV (E) and 5.0 eV ($B_2\alpha$) bands makes the previous attribution of these absorption to different transitions at the same defect unlikely.

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