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γ-ray-induced bleaching in silica: Conversion from optical to paramagnetic defects

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We report experimental results on optical and ESR measurements performed in γ-irradiated natural silica samples having different content of OH groups. A partial bleaching of the optical absorption band $B_{2\beta}$ at 5.15 eV and the related photoluminescence emissions at 3.1 eV and 4.2 eV is observed together with the growth of an ESR doublet split by 11.8 mT. The kinetics of the two processes as a function of the γ dose are correlated and depend on the OH content. Our experiments indicate the occurrence of a γ-ray-induced conversion, from optically active centers to paramagnetic ones and vice versa, changing the relative concentration of the two defects until a steady state is reached. A conversion model is proposed in which γ-ray-activated H atoms either are trapped in optically active defects, giving rise to paramagnetic ones, or interact with the last ones, restoring the original optical centers. Our results are consistent with a structural model in which the optical active center is a twofold coordinated Ge and the 11.8 mT doublet originates from a O═Ge$^{\cdot}$—H center.

I. INTRODUCTION

The origin of the *B*-type activity in natural silica, optical absorption (OA) at 5.15 eV ($B_{2\beta}$ band), and the related emissions at 4.26 eV (α_E band) and 3.15 eV (β band),[1] is still matter of debate in the field of point defects in SiO_2, in spite of many experimental and theoretical studies reported in the literature from about four decades.[2] Some authors suggested that the defect responsible for this activity is an intrinsic oxygen deficient center (ODC) consisting in a twofold coordinated Si (O═Si$^{\cdot\cdot}$),[3,4] where the symbol (═) indicates the bonds of Si with two O atoms and (the double overdots) indicate two paired electrons in the same orbital. Alternatively, on the basis of the observation of an intense absorption at $\sim$5.1 eV in Ge doped silica, the $B_{2\beta}$ band was ascribed to a Ge-related ODC.[5–9] In particular, under the hypothesis that the Ge is substitutional to Si, structural models directly related to Ge, as the twofold coordinated[5] Ge (O═Ge$^{\cdot\cdot}$) or Ge-related oxygen vacancies, have been proposed.[6,7] Other authors, ascribing an indirect role to Ge impurities, have suggested that the *B* activity arises from a silicon based ODC perturbed by a neighboring Ge atom.[8,9]

Actually, the consideration of only the optical activity is not sufficient to identify the structure of the defect. At variance, valuable information on the structure both of the active center and of its neighborhood can be obtained by electron spin resonance (ESR) spectroscopy, provided the paramagnetic nature of the defect. Moreover, correlation between optical and ESR signals shows evidence of conversion mechanisms involving the corresponding point defects. In this respect, the bleaching of the OA in the spectral region around 5 eV and the simultaneous generation of ESR signals associated with Ge-related paramagnetic centers were observed in Ge-doped silica irradiated with UV light.[7,10–17] The conversion mechanisms proposed to explain those findings[7,10–12,14,15] support the direct role of substitutional Ge in the ODC defect creating the *B* activity, but they do not allow univocal determination of its structural model.

Recently, in a preliminary report[18] we found that the partial bleaching of the B activity, observed in a large number of natural silica types after exposure to a low dose of γ rays, is correlated to the growth of an ESR doublet with a split of 11.8 mT. In particular, as the observed structure can be ascribed to the hyperfine interaction of an electronic spin $S=1/2$ with a hydrogen nucleus,[19,20] we tentatively hypothesized that H atoms, activated by γ rays, induced a conversion between the optically active center and the paramagnetic one. In this paper, we investigate the γ-ray-induced bleaching of the B activity and the growth of the 11.8 mT doublet in natural silica samples having different OH content, aiming to clarify the effective role played by H atoms in the conversion mechanism.

II. SAMPLES AND METHODS

Optical and ESR measurements were performed at room temperature in four representative natural silica samples, before and after exposure to γ rays: two natural dry (type I),[21] Infrasil 301 (I301) and Silica EQ (EQ906), with nominal content of hydroxyl groups of 10–20 part per million (ppm) by weight ($\sim 10^{18}$ centers/cm^3); and two natural wet (type II),[21] Herasil 1 (H1) and Homosil (HM), with nominal OH content of 150 ppm ($\sim 10^{19}$ centers/cm^3).

The concentration of OH was verified by measuring the intensity of the absorption band at 3600 cm^{-1} (due to the OH stretching). Other impurities with concentration of few ppm are also present in our samples; in particular, the nominal content of Ge atoms is $\leqslant 1$ ppm.

The materials I301, H1, and HM were supplied by Heraeus Quartzglas[22] while EQ906 was supplied by Quartz and Silice.[23] The samples have dimensions $5\times5\times1$ mm^3 with the large surfaces optically polished.

The γ irradiation was performed at room temperature using a ^{60}Co source. Doses ranging from 5×10^{-4} to 1 Mrad

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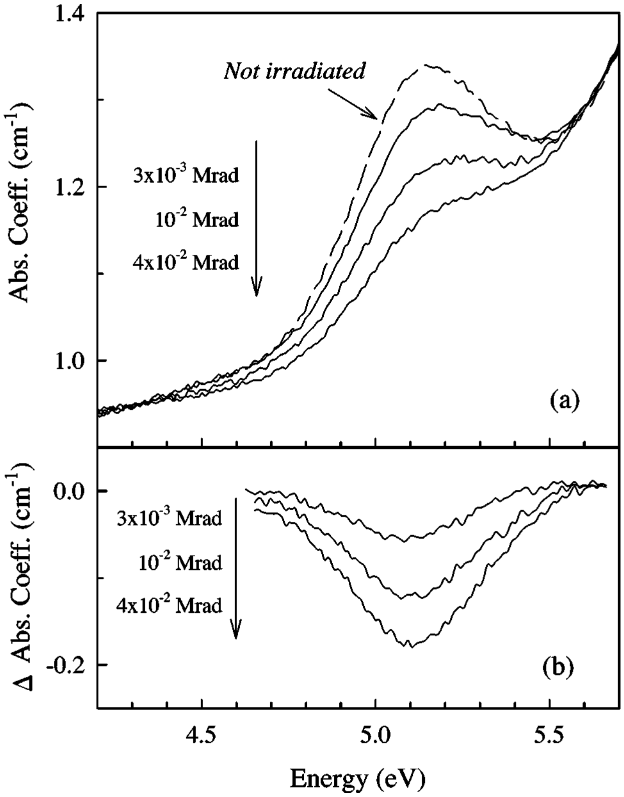

FIG. 1. (a) UV absorption spectra as detected in H1 sample: dashed curve, unirradiated; solid curves, irradiated with γ doses of 3×10^{-3}, 10^{-2}, and 4×10^{-2} Mrad. (b) Difference absorption spectra before and after γ irradiation with doses of 3×10^{-3}, 10^{-2}, and 4×10^{-2} Mrad.

(Si) were progressively accumulated in the same sample of each silica type.

OA measurements in the range 4.0–6.0 eV were carried out by a JASCO V-570 double beam spectrometer. Steady state photoluminescence (PL) spectra in the spectral region 2.5–5.0 eV under excitation by 5.0 eV light were investigated by a JASCO PF-770 spectrofluorometer, mounting a xenon lamp of 150 W and corrected for the energy dependence of the detection system. ESR spectra were detected by a Bruker EMX spectrometer at 9.8 GHz (X band) with microwave power $P=3.2$ mW and a modulation field having amplitude $B_m=0.4$ mT and frequency of 100 kHz. The concentration of paramagnetic centers that create the 11.8 mT doublet was evaluated by comparing the double-integrated ESR spectra with that of E' centers,[24] whose absolute density was determined by spin-echo measurements, carried out at $T=4.2$ K, using the instantaneous diffusion method.[25]

III. RESULTS

The effect of γ irradiation on the UV absorption of natural silica is shown in Fig. 1(a) as observed in our sample H1. The unirradiated sample exhibits a well-pronounced band $B_{2\beta}$ centered at 5.15 eV, whose intensity decreases on increasing the accumulated γ dose. The bleaching effect is evident in Fig. 1(b) where we report the difference between the spectra before and after each irradiation. As shown, the absorption coefficient at 5.15 eV decreases of $\sim$0.2 cm^{-1} after a dose of 4×10^{-2} Mrad. The decrease of the $B_{2\beta}$ band was observed in all the investigated samples, with a rate depending on the silica type. In particular, while the HM sample exhibited the same behavior as H1, the bleaching effect occurred at higher γ doses in dry samples I301 and EQ906.

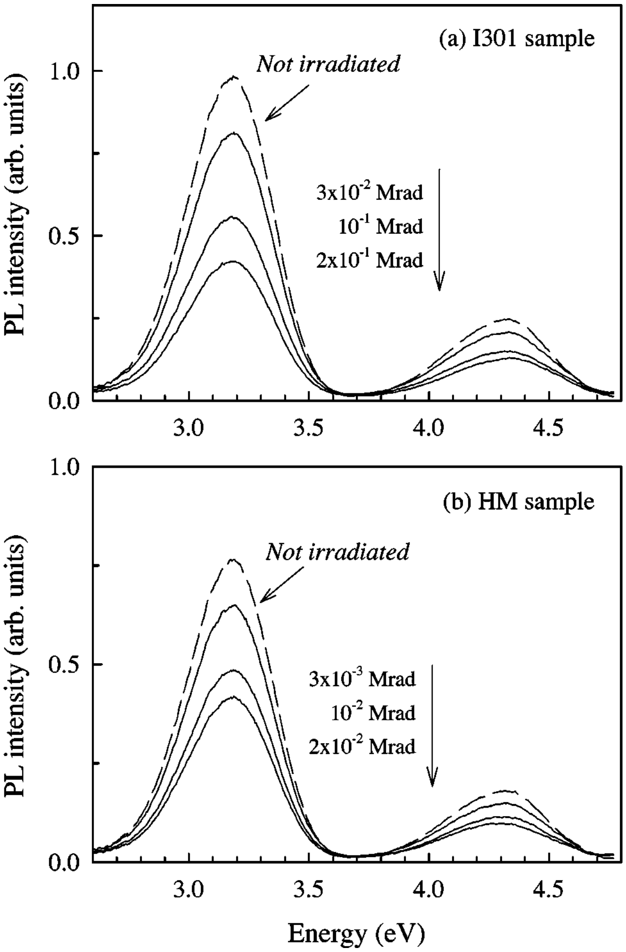

FIG. 2. Photoluminescence spectra excited at 5.0 eV in (a) I301 and (b) HM samples. Dashed curves are the spectra detected in unirradiated samples; solid curves are the spectra detected after various γ doses increasing up to 2×10^{-1} and 2×10^{-2} Mrad for I301 and HM, respectively.

The exposure to γ rays causes as well the growth of an OA band at 5.8 eV, associated with E' centers,[26] that partially superimposes to the $B_{2\beta}$ band. This circumstance makes unreliable the quantitative measurement of this band, so that the study of the B-activity bleaching is more conveniently carried out by detecting the PL emissions α_E and β. In fact, due to the low absorption at $\sim$5.1 eV, the emission intensities are proportional to the intensity of the $B_{2\beta}$ band and therefore to the concentration of optically active centers.

In Fig. 2 we report the PL spectra, excited at 5.0 eV, for the samples (a) I301 and (b) HM, before and after various γ doses. The intensity of the two emissions centered at $\sim$3.1 eV (β) and $\sim$4.2 eV (α_E) is maximum in the unirradiated samples (dashed curves) and it is partially reduced on increasing the γ dose. We observe that the decrease of these PL bands is effective up to an accumulated dose depending on the silica type: $\sim10^{-1}$ Mrad for sample I301 and $\sim10^{-2}$ Mrad for HM. At higher doses, the PL intensity remains constant, thus indicating the end of the bleaching process.

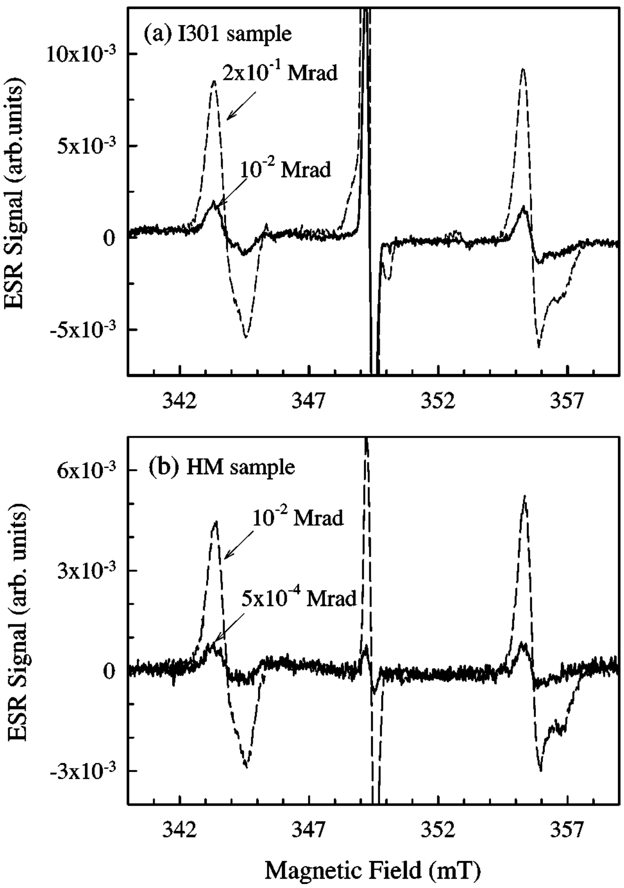

FIG. 3. ESR spectra detected in (a) I301 and (b) HM samples irradiated at different γ doses, increasing up to 2×10^{-1} and 10^{-2} Mrad, respectively.

Analogous effects were observed in samples EQ906 and H1, exhibiting the same dose kinetics of the samples I301 and HM, respectively.

The different behavior of the silica type I (I301, EQ906) and type II (H1, HM) is further pointed out by the ESR measurements. In Fig. 3, ESR spectra detected in (a) I301 and (b) HM, after various γ doses, are shown. For both samples, we observed a doublet with a split of 11.8 mT around the resonance line of E' center, which is strongly distorted by the high microwave power. In HM sample, the 11.8 mT doublet is detectable, in the limit of our experimental sensitivity, after a dose of 5×10^{-4} Mrad. On increasing the γ dose, its intensity grows and reaches a saturation value at $\sim10^{-2}$ Mrad. At variance, in I301 a minimum dose of $\sim10^{-2}$ Mrad is required to observe the doublet, whose intensity saturates after a dose of $\sim10^{-1}$ Mrad.

In Fig. 4 we compare the kinetics of bleaching of the β band and of growth of the 11.8 mT doublet for (a) I301 and (b) HM. In the I301 sample, the PL intensity decreases and the doublet signal grows until both reach a constant value after $\sim2\times10^{-1}$ Mrad. In HM, the same correlated behavior of PL and ESR signals is observed but the constant value is reached after $\sim10^{-2}$ Mrad, an order of magnitude less than that for I301. For the samples EQ906 and H1 we observed similar behaviors as I301 and HM, respectively. We note that the saturated concentration of paramagnetic centers for all investigated samples is estimated to be 10^{15}–10^{16} centers/cm^3.

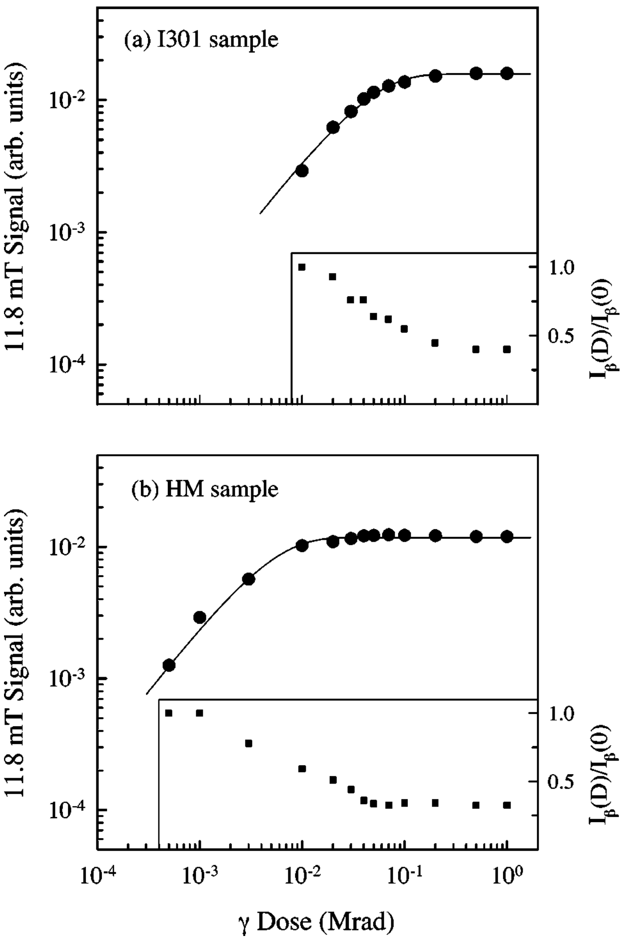

FIG. 4. Kinetics of the 11.8 mT doublet as a function of the γ dose, detected in (a) I301 and (b) HM samples. The solid lines result from a fit of Eqs. (5) to the experimental data. In the insets of both figures we report the intensity of the photoluminescence β band (3.15 eV) as a function of the γ dose, normalized to the value obtained in the unirradiated sample.

IV. DISCUSSION

The correlation of the variation of the OA at 5.15 eV and the two PL emissions at 3.15 and 4.26 eV with the growth of the 11.8 mT doublet signal, already shown in Ref. 18, is confirmed by the extended data reported here. Such a correlation leads one to interpret the bleaching effect in terms of a conversion mechanism, activated by γ rays, from an optically active center responsible for the B activity to a paramagnetic one originating the 11.8 mT doublet. As the ESR signal originates from the hyperfine interaction between an electron spin and a H nucleus,[19,20] H atoms are expected to play a crucial role in this conversion process.

Our experimental results point out two main features.

(a) The bleaching of the optical B activity is only partial in all the investigated samples, as the luminescence intensity decreases from the initial value (before irradiation) by a factor ranging from 2 to 3 (see insets in Fig. 4).

(b) The conversion rate depends on the OH content of the silica samples, as for type II silica (H1, HM) the conversion is completed within $\sim10^{-2}$ Mrad whereas for type I (I301, EQ906) it occurs more slowly and stops at $\sim10^{-1}$ Mrad.

The partial bleaching effect of the B activity indicates that a back-conversion occurs from ESR to B optically active centers, which counteracts the conversion until equilibrium is reached, according to the following reaction scheme:

$$N^{OPT} \mathrel{\substack{k_c \\ \longrightarrow \\ k_{bc} \\ \longleftarrow}} N^{ESR}, \tag{1}$$

where N^{OPT} (N^{ESR}) is the concentration of B-active (ESR-active) centers, and k_c (k_{bc}) is the rate of the γ-induced conversion (back-conversion) process.

To take into account the observed dependence on the OH content (Fig. 4), we assume that the H atoms involved in the above process are generated by a γ-activated breaking of O—H bonds. A simple law connecting the incremental number of γ-activated H atoms to the incremental γ dose dD is

$$dN^{\mathrm{H}} = (N^{\mathrm{OH}} - N^{\mathrm{H}}) P_\gamma dD, \tag{2}$$

where N^{OH} and N^{H} are the concentrations of OH groups and H atoms, respectively, and P_γ is the H generation probability per unitary dose. Assuming that all the H atoms generated are involved in the reaction (1) and on the basis of the measured concentration of paramagnetic centers (10^{15}–10^{16} centers/cm^3), we infer that N^{H} is much less than N^{OH}, by two orders of magnitude, at least. So, Eq. (2) can be rewritten as

$$dN^{\mathrm{H}} \cong N^{\mathrm{OH}} P_\gamma dD. \tag{3}$$

On the basis of Eq. (3) and under the condition $N^{OPT}(\mathrm{D}) + N^{ESR}(\mathrm{D}) = \mathrm{const} = N^{OPT}(0)$, the rate equations for N^{OPT} and N^{ESR} can be written as

$$\frac{dN^{OPT}}{dD} = -\frac{dN^{ESR}}{dD} \cong P_\gamma N^{\mathrm{OH}}(-k_1 N^{OPT} + k_2 N^{ESR}), \tag{4}$$

where k_1 and k_2 are the probabilities of conversion of an optical center and of a paramagnetic one, respectively. The solutions of Eq. (4) are given by

$$N^{OPT}(D) = N^{OPT}(0)\frac{1}{k_1+k_2}(k_2 + k_1 e^{-P_\gamma(k_1+k_2)N^{\mathrm{OH}}D}),$$
$$N^{ESR}(D) = N^{OPT}(0)\frac{k_1}{k_1+k_2}(1 - e^{-P_\gamma(k_1+k_2)N^{\mathrm{OH}}D}). \tag{5}$$

The solutions (5) fit the process (1), provided $k_c = P_\gamma k_1 \ N^{\mathrm{OH}}$ and $k_{bc} = P_\gamma k_2 N^{\mathrm{OH}}$ and agree with our experimental results in the following respects.

(i) The bleaching of the optical activity and the growth of the paramagnetic ones occur with the same dose rate, proportional to the OH content.

(ii) The saturated value of $N^{OPT}(\infty)$ is reduced by a factor $k_2/(k_1+k_2)$ with respect to its initial value $N^{OPT}(0)$. As a consequence, the experimental values of this ratio (from 0.3 to 0.5) indicate that the conversion and the back-conversion processes have probabilities of the same order of magnitude, $k_1 \approx (1\text{–}2)k_2$.

(iii) The high-dose saturated value of N^{ESR} is proportional to the initial value $N^{OPT}(0)$ (see Fig. 5 of Ref. 18) and is independent of OH content.

TABLE I. Sample list: absorption coefficient α at 5.15 eV ($B_{2\beta}$ band), OH content and best-fit parameters of 11.8 mT kinetics with the function $I_{ESR} = a(1 - e^{-bD})$ where D is the accumulated γ-ray dose and I_{ESR} is the intensity of the hyperfine structure.

Sample name	α at 5.15 eV (cm^{-1})	[OH] (ppm by weight)	a (arb. units)	b (Mrad^{-1})
I301	0.46±0.02	10	0.016±0.001	24±1
EQ906	0.39±0.02	20	0.012±0.001	30±1
H1	0.41±0.02	150	0.011±0.001	280±10
HM	0.36±0.02	150	0.012±0.001	220±10

Additionally, the points (ii) and (iii) allow us to estimate the concentration of the defects responsible for the B activity to be within the range 5×10^{15}–10^{16} cm^{-3} and to determine roughly that the absorption cross section at 5.15 eV (peak energy of the $B_{2\beta}$ band) lies in the range 5×10^{-17}–10^{-16} cm^2.

Finally, we report in Table I the parameters obtained by a best-fit procedure of Eqs. (5) to the experimental curves of the ESR intensity as a function of the γ dose (Fig. 4), for the investigated samples. The quantitative analysis makes evident the strict correlation between the rate of the conversion process and the OH content in the samples; on the other hand, the number of converted centers does not depend on the OH concentration, rather it is proportional to the concentration of the B-active defects in our samples before γ irradiation.

We discuss now the possible structure of diamagnetic and paramagnetic centers and the conversion mechanisms acting on them. The paramagnetic one is commonly identified[19,20] as the structure (O═Ge$^{\cdot}$—H) known as H(II) center, where the 11.8 mT doublet originates from the hyperfine interaction between the unpaired electron and the H nuclear spin. Since the H(II) saturated concentration does not depend on the OH content, it is reasonable that the precursor B-active center is OH free. Moreover, as the rate of creation of H(II) centers depends on OH content, we can assume that the γ rays break OH groups and the activated H atoms react with the optical centers. These evidences support the hypothesis that the optically active center is a twofold coordinated[5] Ge (O═Ge$^{\cdot\cdot}$) and the γ-induced reaction is

$$\underbrace{\mathrm{O=Ge}}_{B\text{-active center}}{}^{\cdot\cdot} + \mathrm{H}^0 \Longrightarrow \underbrace{\mathrm{O=Ge^{\cdot}-H}}_{\mathrm{H(II)\ center}} \tag{6}$$

We recall that to ascribe the optical B activity to a twofold coordinated Ge is consistent with recent *ab initio* theoretical calculations.[27,28]

As regards the back-conversion process from H(II) to the twofold coordinated Ge, since k_{bc} is of the same order of magnitude as k_c and both parameters are related to the OH concentration, we infer that free H atoms produced by γ rays are involved as well in the process in which the break of a Ge—H bond in the H(II) defect occurs and the twofold coordinated Ge structure is restored. In this scheme, the conversion and back-conversion processes reach a stationary state, when the concentrations of diamagnetic and paramagnetic centers are of the same order of magnitude and the free H atom has equal probability to be trapped in a diamagnetic defect or to interact with a H(II) center, detaching the bonded H atom and, probably, forming H_2 molecules. According to this mechanism, both optical and ESR intensities do not change for a γ dose $D \gg (k_c + k_{bc})^{-1}$, as experimentally observed.

A final remark concerns the comparison of our results with the previously reported data[7,10–17] on the bleaching of the OA band $B_{2\beta}$ induced by UV irradiation in Ge-doped silica. In those samples, it was observed that the decrease of the absorption at 5.15 eV induced by UV photons is correlated to the growth of ESR signals. In particular, it was hypothesized a different conversion mechanism, in which a twofold coordinated Ge $(\mathrm{O{=}Ge}^{\cdot\cdot})$ originates two paramagnetic centers, the positively charged $(\mathrm{O{=}Ge}^{\cdot})^{+}$ and the $(\mathrm{GeO_4})^{-}$, via an electron transfer.[12,14]

In the conditions considered in the present paper, the situation appears to be different. In fact, the γ-ray-induced bleaching of the OA at 5.15 eV is related only to the growth of the ESR doublet at 11.8 mT and no signal ascribable to the above Ge-related paramagnetic centers could be observed. The absence of these defects in our samples can be explained by considering the different Ge concentration in Ge-doped silica of Refs. 12 and 14 and in ours. In fact, the process proposed in Refs. 12 and 14 implies a correspondence of each twofold coordinated Ge with a relatively large number of substitutional fourfold-coordinated Ge. This condition can be easily fulfilled in samples where the ratio $\mathrm{GeO_2/SiO_2}$ reaches a few percent but it is not expected in our samples, where the estimated concentration of B-active defects $(\mathrm{O{=}Ge}^{\cdot\cdot})$ is of the same order of the nominal Ge concentration, namely, less than 1 ppm. We conclude that the conversion mechanism proposed here is the most effective in natural silica but our results do not rule out that other processes can be effective in heavily Ge-doped silica. In our opinion the interplay between different bleaching mechanisms is controlled by the content of Ge impurities and OH groups.

V. CONCLUSION

The results here reported show that γ rays induce two correlated effects in natural silica samples: the partial bleaching of the optical B activity (OA band $B_{2\beta}$ at 5.15 eV and PL emissions at 3.15 eV and 4.26 eV) and the simultaneous growth of an ESR doublet split by 11.8 mT. The kinetics of the two processes as a function of the γ dose strongly depends on the silica type: in type I (OH content $\sim$10 ppm) they tend to saturate at $\sim 10^{-1}$ Mrad, whereas in type II (OH content $\sim$150 ppm) they have a faster rate and saturate at doses $\geqslant 10^{-2}$ Mrad. At variance, the saturated intensity of the 11.8 mT doublet does not depend on the silica type and it is well correlated to the initial intensity of the absorption band $B_{2\beta}$. These experimental findings clearly indicate the occurrence of γ-ray-induced conversion and back-conversion processes from optically active centers to paramagnetic ones whose rates are proportional to the OH content. Our results can be explained using a model in which a free H atom, produced by γ-rays via the breaking of a O—H bond, either is trapped in a twofold coordinated Ge $(\mathrm{O{=}Ge}^{\cdot\cdot})$ giving rise to the H(II) center $(\mathrm{O{=}Ge}^{\cdot}\mathrm{{-}H})$ or reacts with the latter, restoring the original structure of the optical center.

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