Fundamental Defect Centers in Glass: The Peroxy Radical in Irradiated, High-Purity, Fused Silica

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A new fundamental radiation-induced defect in high-purity synthetic silica has been identified by electron-spin-resonance studies of ¹⁷O-enriched SiO₂ as a peroxy radical O_2^- bonded to one Si in the glass matrix. The precursors of these defects are envisioned to be \equiv Si=O-O-Si \equiv structures, some of which preexist in the silica, are formed in greater numbers during neutron bombardment, and which may release an electron either during irradiation or subsequent annealing.

We report a new and previously uncharacterized fundamental radiation-induced defect in silica—a peroxy radical O_2^- bonded to one Si in the glass matrix. Although several distinct paramagnetic resonance spectra were observed by Weeks¹ in irradiated α -quartz and fused silica in 1956, only recently have the E' center² and a singlenonbridging-oxygen hole center³ been fully characterized. Positive identification and characterization of a third intrinsic defect center—the peroxy radical—is presented here.

Recently, Stapelbroek and Griscom⁴ resolved a broad electron-spin-resonance (ESR) spectrum previously observed in neutron-irradiated samples¹ into two distinct components, whose relative intensities varied with the OH content of the γ -irradiated silicas. Based on positive g shifts and the form of the g tensors, these defects were postulated³⁻⁵ to be oxygen-associated hole centers (OHC's). The two centers were called "wet" OHC and "dry" OHC to distinguish the two variants according to their relative prevalence in fused silicas of high or low OH contents, respectively. Stapelbroek and co-workers^{3, 4} established by ¹⁷O enrichment of fused silica that the wet OHC comprises a hole trapped in a single nonbonding 2porbital of an oxygen. It was previously suggested on the basis of the g values^{3, 6} that the dry OHC might be a peroxy radical defect. Here we show conclusive proof of this postulate.

Details of the sample preparation and characterization have been published elsewhere.³ Since the dry OHC spectrum was observed when high-OH-content silica was neutron irradiated and annealed,¹ the enriched silica samples were neutron irradiated to a dose of $5 \times 10^{19} n/\text{cm}^2$. ESR measurements were carried out at 9.15 GHz on a Varian E-9 ESR spectrometer. Previous work^{3, 4} had shown the dry-OHC spectrum to be well resolved and free of motional effects or microwave saturation at 110 K.

The ESR spectrum of the sample enriched with 36% ¹⁷O following neutron irradiation is shown in Fig. 1. The hyperfine (hf) interactions of the paramagnetic centers with the ¹⁷O nuclei $(I = \frac{5}{2})$ give rise to six-line spectra corresponding to the wet³ and dry (vide infra) OHC's, as shown partially by the combs: the intensity of the hf spectra varied in proportion to the ¹⁷O enrichment. Although Stapelbroek and co-workers^{3, 4} observed the presence of the "A1" center⁷ at about half the intensity of the wet OHC when the enriched silicas were γ irradiated, there is no evidence of this center in heavily neutron-irradiated samples (Fig. 1). Likewise, there is no evidence of hf interactions with the other prevalent impurities such as Cl $(I=\frac{3}{2})$ or H $(I=\frac{1}{2})$. We conclude that the observed spectrum is due to oxygen-associated, radiation-



FIG. 1. ESR spectrum at 110 K of 36% ¹⁷O-enriched SiO₂ following neutron irradiation to $5 \times 10^{19} n / \text{cm}^2$.

induced centers that are intrinsic to the silica.

The (dry OHC): (wet OHC) ratio is maximized and the E' center is eliminated (at the expense of a considerable loss in overall intensity) by heating to 500 C.³ The spectrum of the enriched sample following the latter treatment is shown in Fig. 2(a). The number of lines is not unexpected for peroxy radicals containing ¹⁷O.⁸ The presence of more than one set of hf lines implies inequivalent sites for the two oxygens and is attributed to the bonding of one of the oxygens of the O_2 molecular ion to a Si. Thus, the peroxy radical has the form \equiv Si-O(1)-O(2)[•]. There are four different cases: site I, \equiv Si⁻¹⁷O(1)⁻¹⁶O(2)[•]; site II, \equiv Si⁻¹⁶O(1)⁻¹⁷O(2)[•]; site III (the dry OHC in unenriched silica), \equiv Si⁻¹⁶O(1)⁻¹⁶O(2)[•]; and site IV, \equiv Si⁻¹⁷O(1)⁻¹⁷O(2)[•]. In a sample enriched with 36% ¹⁷O, the relative concentrations of these sites will be 0.23:0.23:0.41:0.13. The spectrum observed in Fig. 2(a) is a weighted composite of these four spectra. It is the interaction of the hole with two inequivalent oxygen nuclei upon which confirmation of the peroxy radical is based.

The most prominent hf lines in the experimental spectrum [Fig. 2(a)] arise from sites I and II. A computer simulation of the experimental spectrum based on a properly weighted sum of these two sites is shown in Fig. 2(b); the component spectra are shown in Figs. 2(c) and 2(d). The position and shape of the prominent hf lines in the experimental and computed spectra | Figs. 2(a) and 2(b) are in good agreement. At much lower instrumental gain the underlying resonance between 3125 and 3250 G in the experimental spectrum that is not reproduced in the simulation was determined to be due to the unenriched dry OHC (site III), previously simulated in Ref. 3. The weak hf lines apparent in the experimental spectrum are attributable to the 36 lines of site IV. The tick marks in Fig. 2(a) show the position of the lines of site IV calculated from the parameters used to fit sites I and II. For clarity only those lines of site IV that are not obscured by sites I, II, or III are shown. It can be seen that there is good agreement between the tick marks and the weaker features of the experimental spectrum.

The g values used in the simulation were those derived from simulating the unenriched dry OHC under the following constraints³: The g_3 distribution was determined by best fit to the experimental spectrum, and the g_1 and g_2 distributions were calculated from the well-known theory for the g values of the O_2^- molecular ion.⁹ A similar distribution in *g* values has been previously observed for peroxy radicals in amorphous peroxyborates.^{10, 11}

The diagonal elements of the hf matrix, $A_{\parallel} = a + 2b$ and $A_{\perp} = a - b$, where a and b are the isotropic and anisotropic hf interactions, were determined by best fit to the spectrum in Fig. 2(a). Values of A_{\parallel} for both site I and site II could be measured directly (e.g., the comb in Fig. 1). It



FIG. 2. (a) ESR spectrum at 110 K of 36% 17 O-enriched SiO₂ following neutron irradiation and annealing at 500 C. (b) Computer simulation of the highly stuctured parts of (a) assuming a peroxy-radical model with one 17 O and one 16 O per defect. The two oxygen sites are inequivalent, so that (b) is the sum of component spectra (c) and (d). The tick marks in (a) are calculated line positions of the peroxy radical containing two 17 O per defect.

was determined that $|A_{\perp}| < 15$ G for site II and a value of 9 G was adopted. The value of $|A_{\perp}|$ for site I was fixed by requiring that 100% of the spin density reside on the two oxygen ions. For the single-nonbridging-oxygen hole centers in irradiated silicate glasses a superhyperfine splitting due to at most 1% of the atomic Si 3s-state value is observed, arising from core polarization effects.¹¹ We assume the degree of spin delocalization is not different in the case of nonbridging peroxy radical.

The parameters used in the simulation of sites I and II are shown in Table I. The sign of A_{\perp} could not be determined in this experiment; a negative sign was adopted to minimize the asymmetry in charge density between sites I and II. The anisotropic component of the ¹⁷O hf interaction, b_0 , for the free O⁻ ion was calculated by Stapelbroek *et al.*³ to be -42 G; this value was used to estimate the overlap $\beta^2 = b/b_0$ for site II shown in Table I. β^2 for site I was constrained by the requirement of 100% confinement on the two oxygens. The hf interactions and g values are typical of peroxy radicals.^{6,8-12} Although determination of which oxygen has the larger spin density cannot be made on the basis of the present data, previous experimental studies of peroxy radicals *R*-O-O' with inequivalent oxygens have led to the conclusion that the larger spin density is on the terminal oxygen (e.g., Ref. 12). This convention has been adopted in correlating sites I and II with the component spectra.

We believe that the precursor of the peroxyradical defect is a peroxy linkage =Si-O-O-Si=, which is envisioned to be half of a Frenkel pair, the other half being the oxygen vacancy =Si-Si=. Apparently, this peroxy linkage precursor readily

TABLE I. Spin-Hamiltonian parameters for peroxyradical defect (dry OHC) is fused silica. The unique axes of the ¹⁷O hyperfine tensors are parallel to the axis of g_1 .

Parameter	Site I ¹⁷ O(1) ¹⁶ O(2)	Site II ¹⁶ O(1) ¹⁷ O(2)
A_{\parallel}	- 43.2 ±0.5 G	- 101.7 ±0.5 G
A_{\perp}	- 9.5 G	-9 G
a	– 21 G	- 40 G
b	– 11 G	- 31 G
β^2	0.26	0.74
g_1	2.0014	
g_2	2.0074	
$\langle g_{3} \rangle$	2.067	

sheds an electron to form a peroxy radical since its ESR spectrum has been observed to grow in not only by irradiation but also when certain compounds known to contain peroxy linkages are heated,¹⁰ when low-OH-content silica is drawn into fibers, and when these fibers are thermally annealed.^{3, 13} The lower concentration of the peroxy radical (dry OHC) observed in the γ -irradiated high-OH-content silicas^{3,14} is ascribed to the reaction in the melt of water with the Frenkel defects, e.g., $(\equiv Si - O - O - Si \equiv) + (\equiv Si - Si \equiv) + 2H_2O$ \rightarrow 4(\equiv Si-OH). Neutron irradiation enhances the number of peroxy linkages in both low- and high-OH-content silica by providing enough energy to break oxygens loose from the glass matrix and drive them away to form additional Si-Si and Si-O-O-Si groupings. For example, the peroxyradical concentration in γ -irradiated dry silica is measured by ESR to be ${\sim}10^{16}/{\rm g}$ after a dose of 10⁸ radicals,³ whereas a neutron irradiation of 2×10^{19} /cm² produces ~ 10^{19} radicals/g in wet silica.¹ The concentration of peroxy-linkage precursors cannot be measured directly in this experiment. However, noting that the E' center and peroxy-radical concentrations are approximately equal in γ -irradiated low-OH-content silica,¹⁴ the peroxy-linkage content can be inferred to be at least $10^{16}/g$ in these materials.

The correlation between the peroxy-radical concentration in γ -irradiated dry silica and a 7.6-eV radiation-induced optical band is well established.³ We also suggest that peroxy linkages and/or radicals may be responsible for the Raman band observed¹⁵⁻¹⁷ at 610 cm⁻¹ on the basis of similar increases in both band height and the intensity of the ESR spectrum of the peroxy radical following neutron irradiation^{15, 17} or fiber pulling of low-OHcontent silica.^{3, 13, 17} In any event, the present work establishes that the peroxy radical is an intrinsic defect in amorphous SiO₂; it is only the third fundamental center in this material to be clearly identified.

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Symmetry in Low-Energy-Polarized-Electron Diffraction

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The first low-energy-electron-diffraction measurements using a polarized incident electron beam are reported and compared to measurements where an unpolarized incident beam is analyzed after scattering. Whereas, because of multiple scattering, equivalence of the two measurements is not expected in general, excellent agreement is obtained for specular scattering in the (010) plane from W(100). A theoretical argument is presented for the case where the scattering plane is a mirror-symmetry plane of the crystal.

Electron scattering from both free atoms and surfaces is a spin-dependent process; i.e., the cross section for scattering an electron at a given energy and angle will in general be different for electrons with spins aligned up or down relative to the scattering-plane normal. This comes as a consequence of the interaction between the incident electron's spin, s, and its orbital angular momentum, L, as it scatters from the atom core. This spin-orbit interaction energy is proportional to $(1/r)(dV/dr)\mathbf{\bar{s}}\cdot\mathbf{L}$, where V is the scattering potential. As a consequence of the different cross sections, an unpolarized beam (made up of equal number of spin-up and -down electrons) will be polarized after scattering, and an initially polarized beam will scatter with different intensity when its spin direction is changed from up to down.

The purpose of this paper is to report the first use of a beam of polarized electrons as a surface

probe and to demonstrate that under certain symmetry conditions measurement of the dependence of the scattered intensity on incident-beam polarization, and the measurement of the polarization of an initially unpolarized beam after scattering, are equivalent. In recent polarized low-energyelectron-diffraction (PLEED) studies.¹⁻⁵ an unpolarized incident beam was scattered from a crystal, and the polarization $P(E, \theta)$ induced by the crystal in the scattered beam was measured with respect to the scattering plane normal \hat{n} $=(\bar{k}\times\bar{k}')/|\bar{k}\times\bar{k}'|$, where \bar{k} and \bar{k}' are the electron wave vectors before and after scattering.⁶ In contrast, we use a polarized incident beam to determine the strength of the spin dependence of the scattering,

$$S(E,\theta) = \frac{1}{P_0} \frac{I(P_0) - I(-P_0)}{I(P_0) + I(-P_0)},$$
(1)