ESR STUDIES OF IRRADIATED ^{17}O-ENRICHED SOL–GEL SILICAS
Organic impurity effects and the structure of the nonbridging-oxygen hole center

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ESR studies were carried out on ^{17}O-enriched sol–gel silicas subjected to 100-keV X irradiation at 77°K. Separate samples were given pre-irradiation heat treatments at 250, 600, and 800°C. A strong induced resonance due to ethyl alcohol radicals was found to decrease in intensity with increasing anneal temperature. Methyl radicals were also detected. The spectrum of the nonbridging-oxygen hole center, dominant only in the 600 and 800° samples, was identified and characterized by its ^{17}O hyperfine signature.

There have been a number of recently reported electron spin resonance (ESR) studies of radiation-induced defects in sol–gel-derived silicas [1–4]. Xerogels prepared by hydrolysis of tetraethoxysilane (TEOS) in ethanol have displayed ESR manifestations of a variety of organic radical species when irradiated prior to any drying or thermal treatment [1]. Annealing of these samples to temperatures ~ 600°C before irradiation resulted in substantially lower yields of organic species and revealed notable concentrations of peroxy radicals (O_2^--type defects). On the other hand, *vacuum-dried* gels prepared for various H_2O : TEOS ratios displayed mainly peroxy-radial spectra, irrespective of pre-irradiation heat treatments to temperatures up to ~ 500°C [2,3], and one glass hydrolized with 16 mol H_2O : 1 mol TEOS still exhibited radiation-induced peroxy components following heat treatment at 1000°C [2,3]. The only reported ESR study of an irradiated, fully densified gel (in this case an aerogel) also revealed a possible peroxy-radical species (although ref. [4] focussed mainly on several defects associated with minor chlorine and germanium impurities). The seeming ubiquity of the peroxy radical as a radiolysis product has been regarded as a possible indication that peroxy linkages, $\equiv$Si–O–O–Si$\equiv$, may form as condensation products in sol–gel silicas [1,5]. The present letter presents the results of the first of a series of experiments undertaken to characterize the ^{17}O hyperfine structure (hfs) of oxygen-associated hole centers, such as the peroxy radical, in gel-derived silicas.

The samples were prepared by mixing freshly distilled tetrahydrofuran (THF), TEOS, and 1M HCl in a volume ratio of 500 : 100 : 1 and exposing this mixture to a saturated atmosphere of ^{17}O-enriched water (56.4% ^{17}O) at 25°C. The HCl solution (and an NH_4OH solution for subsequent procedures) had been prepared using the isotopically enriched H_2O. THF, rather than one of the usual alcohols, was employed in the initial hydration stage for purposes of minimizing oxygen isotope exchange with the solvent. After 96 h, $\frac{1}{10}$ volume of the ^{17}O-enriched 0.5M NH_4OH was added, and the final mixture was transferred to 7.5-mm-ID teflon tubes where gellation occurred in about 30 min. Due to the anticipated shrinkage, the final samples were cylindrical slugs slightly less than 3 mm in diameter and $\sim$ 2 cm in length. Heat treatments were carried out in dry, flowing O_2 in a gradient furnace programmed to heat at 15°C/h to 200°C, hold for 10 h, heat at 15°C/h to 920°C, hold 2 h, and cool to room temperature at 600°C/h. Depending on their positions in the furnace, the heated samples experienced final hold temperatures of 250, 600, and 800°C. One of two "600°" samples" was re-exposed to $H_2^{17}O$ for 24 h and then reheated (same schedule) to 600°C in dry N_2. All samples were transferred under dry nitrogen to fused silica ESR sample tubes (3 mm ID) which were then sealed under rough vacuum and not reopened for the duration of the experiment. Based on previous experience producing ^{18}O-labeled samples by the same method [5], a final ^{17}O enrichment of $\sim$ 40% was expected.

Irradiations with 100-keV X-rays (doses $\sim$ 8–15 Mrad) were carried out with the tubed samples immersed in liquid nitrogen. Induced defects in the sample holders were destroyed by flaming with a hydrogen–oxygen torch while carefully maintaining the sample (at the opposite end of the tube) at 77 K. ESR spectra were acquired at 9.43 GHz on a Bruker ER-200 spectrometer with the sample temperature maintained at 105 K by a stream of cooled N_2 gas.

Figure 1 illustrates the basic types of ESR spectra observed immediately following irradiation for samples taken from the three positions in the gradient furnace. The spectrum of fig. 1 (a) was recorded using an overall spectrometer gain roughly 30 times lower than was required for the spectra of figs. 1 (b, c) and is essentially identical in shape with the spectrum of ethyl alcohol radicals in an unheated sol–gel silica, as described by Wolf et al. [1]. Because of its mean g value ($\sim$ 2.007) and nearly-structureless asymmetric shape, the spectrum of fig. 1(b) is reasonably ascribed to oxygen-associated hole centers (OHCs) [6]; this attribution will be confirmed below by detection (on a wider field scan) of the associated ^{17}O hyperfine structure. As verified by annealing experiments to be described, the weak structure superimposed on the spectrum of fig. 1(b) is due to minor organic radical components. Similarly, fig. 1(c) appears to consist mainly of contributions due to OHCs and methyl radicals (the spectrum of $\overset{\cdot}{C}H_3$ in silica is fully discussed by Friebele et al. [7]). The 505-Gauss doublet spectrum of atomic hydrogen was observed (also on a broader field scan than illustrated in fig. 1) in all three samples, although its
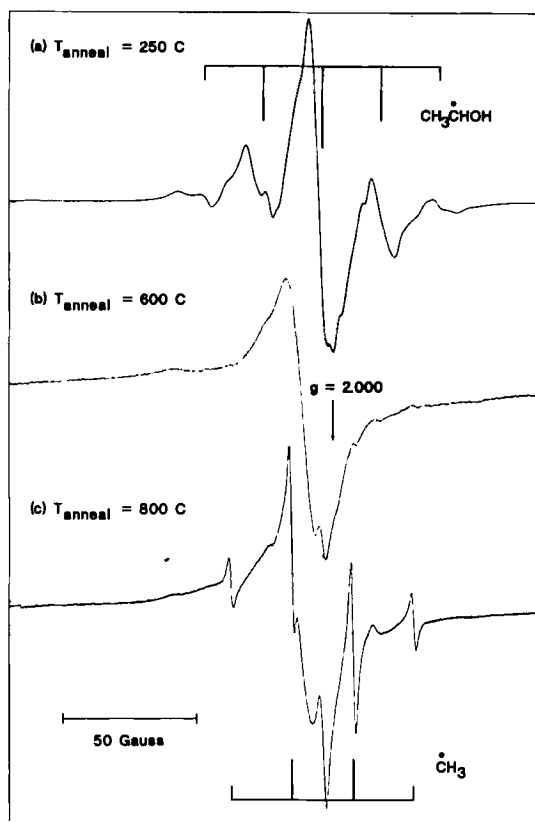
Fig. 1. Narrow-field-scan ESR spectra of ^{17}O-enriched sol–gel silica samples as a function of preirradiation heat treatment. (a) $T_{anneal} = 250\,^{\circ}C$; (b) $T_{anneal} = 600\,^{\circ}C$; (c) $T_{anneal} = 800\,^{\circ}C$. Samples were exposed to 100-keV X-rays to a dose of ~ 8 Mrad at 77°K and spectra were recorded at 105°K without warming to higher temperatures. Combs indicate the proton hyperfine spectra of $CH_3\dot{C}HOH$ and $\dot{C}H_3$ radicals.

intensity was much weaker in the 250° sample. Presumably, much of this H^0 arises from radiolysis of silanol groups:

$$\equiv Si-OH \rightarrow \equiv Si-O \cdot + H^0, \tag{1}$$

where the notation "$\equiv$" denotes three bonds to network oxygens and $\equiv Si-O \cdot$ is a nonbridging oxygen hole center (NBOHC). The well-known E' center ($\equiv Si \cdot$) [8,9] is not manifest in the spectra of fig. 1 (the sharp "central" line being due to $CH_3\dot{C}HOH$ radicals) and was only detected with great difficulty at lower microwave power settings.

Figure 2 illustrates the influences of a succession of 5-min isochronal anneals on the intensities of the spectra of fig. 1. Here spectral amplitudes of
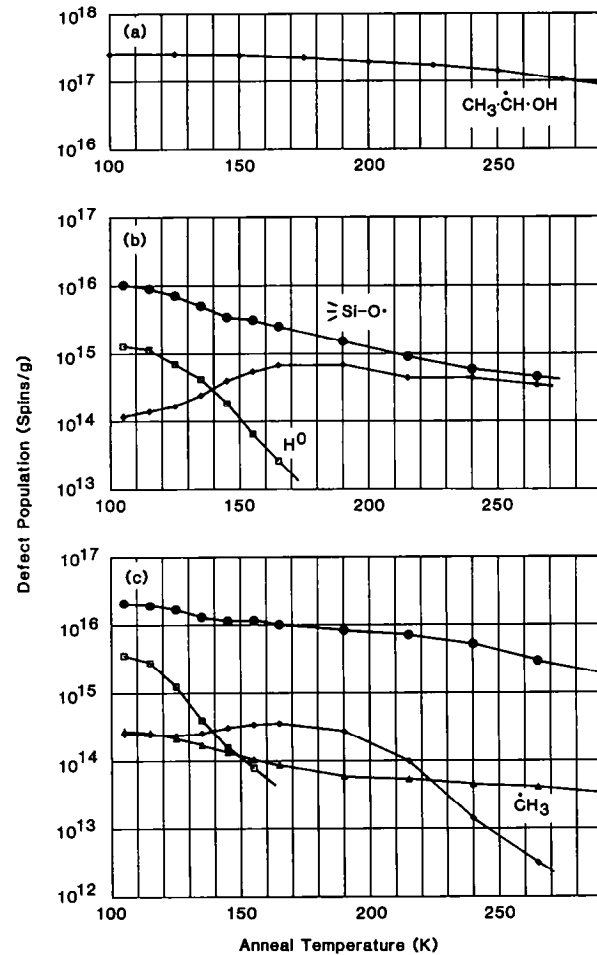
Fig. 2. Isochronal anneal curves (5 min at temperature) for various X-ray-induced defect centers in
^{17}O-enriched sol–gel silicas heat-treated at (a) 250°C, (b) 600°C and (c) 800°C. Experimental
conditions were as described in the caption to fig. 1. Circles = nonbridging oxygen hole center;
squares = atomic hydrogen; diamonds = ethyl alcohol radical; triangles = methyl radical.

the individual resonance components have been converted to absolute spin
concentrations by double numerical integration of at least one specimen of
each spectral type and comparison of the results to those obtained for a
standard sample of known spin density (see, e.g., [10] for details). Due to
measurement problems imposed by the strong overlapping of the weaker
organic spectral components with the OHC line, the relative positionings of
the $CH_3 \cdot \dot{C}H \cdot OH$ and $\dot{C}H_3$ curves in fig. 2(a, and b) may be inaccurate by as

much as a factor of 3. In spite of this limitation, the trends in fig. 2 are quite clear: for the sample annealed to 800°C, the OHCs (filled circles) outnumber the organic radicals by nearly two orders of magnitude; for the 600° sample, the OHC and organic–radical spin counts are comparable; and for the 250° sample, the ethyl–alcohol radical (whose spectrum totally obscures that of the OHC in fig. 1(a)) presumably outnumbers the OHC by more than an order of magnitude.

In fig. 2, the initial atomic hydrogen spin counts are notably lower than those for the OHCs, an outcome which contrasts with the case for flame hydrolyzed (type III) fused silica where the radiolytic H^0 yields are found to outnumber the OHCs by as much as a factor of 4 [10]. The concomitant decays of the H^0 and OHC species in fig. 2(b, c) are consistent with the supposition that some of the OHCs in the present gel-derived silicas are NBOHCs which are destroyed in the reverse reaction of eq. (1). In fig. 2(b), the increases in ethyl–alcohol radical concentrations above ~ 130°K are seen to occur in approximately one-to-one correlation with *decreases* in the concentration of H^0. The post-irradiation growth in the ethyl–alcohol radical population is therefore attributed to the reaction:

$$CH_3 \cdot CH_2 \cdot OH + H^0 \rightarrow CH_3 \cdot \dot{C}H \cdot OH + H_2. \tag{2}$$
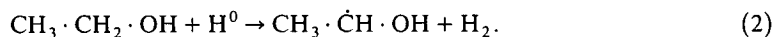
Detailed balancing of eqs. (1) and (2) would require more atomic hydrogen than has been measured. This suggests either that the concentrations of H^0 have been underestimated in the present case or else that some of it has been consumed, e.g., by dimerization [10], even at temperatures as low as 105 K.

Two fundamental types of OHC are known in amorphous fused silicas, namely, the NBOHC and the peroxy radical. A means of discriminating between these two centers on the basis of their principal g values was developed by Griscom [11] and further demonstrated by Stapelbroek et al. [6], who also characterized the ^{17}O hfs of the NBOHC. Friebele et al. [12] employed computer lineshape simulation methods to analyze the ^{17}O hfs of the peroxy radical in neutron-irradiated, ^{17}O-enriched silica.

On the basis of the g values reported by Kordas et al. [2,3] and similarly noted by the authors [13] in a number of irradiated silica xerogels, it was anticipated that the peroxy radical would dominate the ESR spectra of the present sol–gel silicas. But contrary to this expectation, the spectrum of fig. 3, which typifies the OHC line shapes observed for the ^{17}O-enriched samples annealed at 600 and 800°C, was computer simulated (dashed curve) using only the spin-Hamiltonian parameters for the *NBOHC*. It is to be recognized that under some circumstances it may be difficult to distinguish an NBOHC from a peroxy radical on the basis of g values alone, since their g matrices are quite similar [6,11]. However, the simple 6-line ^{17}O hyperfine spectrum of fig. 3 with $A_{\parallel} = 110$ Gauss is characteristic of the NBOHC [6] and differs substantially from the more complex ^{17}O hyperfine signature of the peroxy radical [12]. It is concluded therefore that the spectrum of fig. 3 arises almost wholly ($\geqslant 90\%$) from NBOHCs.
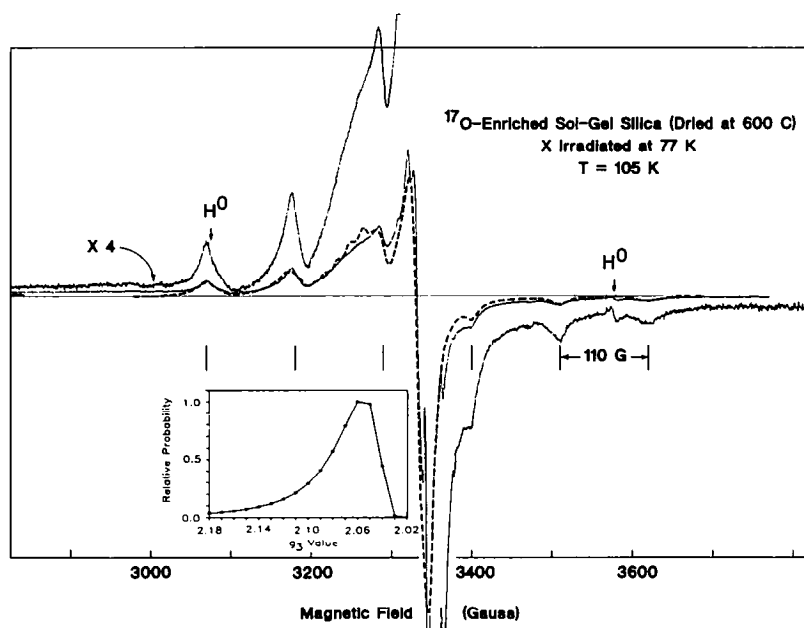
Fig. 3. Broad-field-scan ESR spectrum of an [17]O-enriched sol–gel silica heat-treated at 600°C in flowing N_2 prior to 100-keV X-irradiation. Sample received a total dose of ~15 Mrad at 77°K and was thermally bleached for 5 min at 130°K prior to measurement at 105°K. The dashed curve is a computer line-shape simulation employing spin Hamiltonian parameters typical of the nonbridging-oxygen hole center [6,11] ($A_{\parallel}$([17]O) = 110 G, $A_{\perp}$([17]O) = 16 G, g_1 = 1.9999, g_2 = 2.0095, the g_3 distribution is shown in inset). The computed [16]O and [17]O spectra were added together in a 60:40 ratio.

While qualitatively similar to previously published [17]O hyperfine spectra of the NBOHC [6], the spectrum of fig. 3 is decidedly superior from the standpoints of overall signal-to-noise ratio, the effective degree of isotopic enrichment (the present simulation assumed 40%), and the absence of interfering impurity spectra (a substantial aluminum–oxygen hole center component was present in the spectra of [6]). For these reasons, it was possible to perform a more exacting computer simulation analysis in the present case. In order to achieve the fit illustrated in fig. 3 it proved necessary to incorporate a distribution of [17]O parallel hyperfine coupling constants ($\Delta A_{\parallel}$ ~ 5%, uncorrelated with the g_3 distribution). The optimized g_3 distribution illustrated in the inset of fig. 3 differs little from that employed in refs. [6] and [11]. As before, the value of $A_{\perp}$ could not be measured directly but the simulation was again achieved by assuming the semi-empirical value of 16 Gauss calculated by Stapelbroek et al. [6]. However, the slight discrepancy between the experimental and computed amplitudes of the innermost hfs peaks in fig. 3 may be a

clue that this canonical value of $A_\perp$ might ultimately require minor readjustment. In any event, the measured and estimated [17]O hfs parameters continue to indicate the unpaired spin to be localized in an essentially pure 2p orbital of a single oxygen, as expected for a structure of the type $\equiv$Si–O $\cdot$.

The surprising absence of any noticeable peroxy-radical contribution to the spectra of the present samples is very tentatively ascribed to a different condensation pathway arising from the use of an aprotic solvent (THF) in place of alcohol in the primary hydrolysis step. While no clear chemical justification can be offered for this conclusion, it might be noted that other possible influences (e.g., H_2O : TEOS ratios during hydrolysis, methods of drying, exposures to ambient atmospheres, and temperatures of heat treatment) were widely varied in earlier studies with no apparent effect on the radiation yield of peroxy radicals [1–3,13]. Certainly, the use of a different solvent conceivably might affect the pore structures of the gels, which could in turn account for the apparently higher retention of hydrocarbons in the present glasses relative to those of previous studies [1–3,13]. Additional samples are being prepared to test these suggestions. In the meantime, the [17]O-enriched samples already in hand will be reinvestigated following further heat treatment at progressively higher temperatures. Whereas many of the OHCs characterized in the present study are reasonably attributed to the radiolysis of silanol groups (eq. (1)), it is hoped in the future to obtain OH-free samples suitable for use in the search for the self-trapped hole in amorphous SiO_2.

References

[1] A.A. Wolf, E.J. Friebele and D.C. Tran, J. Non-Cryst. Solids 71 (1985) 345.

[2] G. Kordas and R.A. Weeks, J. Non-Cryst. Solids 71 (1985) 327.

[3] G. Kordas, in: Defects in Glasses, MRS Vol. 61, eds. F.L. Galeener, D.L. Griscom, and M.J. Weber (Mat. Res. Soc., Pittsburgh, PA, 1986), p. 419.

[4] D.L. Griscom, E.J. Friebele and S.P. Mukherjee, Crystal Lattice Defects and Amorphous Materials (Gordon and Breach, New York, in press, 1987).

[5] C.J. Brinker, D.R. Tallant, E.P. Roth and C.S. Ashley, ibid., ref. [3], p. 387.

[6] M. Stapelbroek, D.L. Griscom, E.J. Friebele and G.H. Sigel, Jr., J. Non-Cryst. Solids 32 (1979) 313.

[7] E.J. Friebele, D.L. Griscom and K. Rau, J. Non-Cryst. Solids 57 (1983) 167.

[8] R.A. Weeks, J. Appl. Phys. 27 (1956) 1376.

[9] D.L. Griscom, Phys. Rev. B20 (1979) 1823.

[10] D.L. Griscom, M. Stapelbroek and E.J. Friebele, J. Chem. Phys. 78 (1981) 1638.

[11] D.L. Griscom, J. Non-Cryst. Solids 31 (1978) 241.

[12] E.J. Friebele, D.L. Griscom, M. Stapelbroek and R.A. Weeks, Phys. Rev. Lett. 42 (1979) 1346.

[13] D.L. Griscom and C.J. Brinker, unpublished.