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Radiation Centres in Various Silica Modifications

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Abstract

The paper studies low-temperature (77 K) radiolysis of various modifications of silica, such as macroporous glass (MPG) with a pore diameter of 2000 and 1500 Å, regular sodium glass, and fused quartz by the electron paramagnetic resonance (EPR) method. Paramagnetic centres in various modifications of SiO_2 may vary significantly, depending on origin, the presence of impurities, treatment conditions, and radiation activation of samples, as demonstrated. Hole centres in oxygen and silicon atoms and electron centres in silicon atoms and alkaline metal ions are the main paramagnetic centres in γ-irradiated SiO_2; their contribution in glasses and quartz is 90–95 and ~70 %, respectively. The number of radical centres in all silicas ($H^{\bullet}$, $\geqslant Si^{\bullet}$, $>Si^{\bullet}-H$) does not exceed 3–4 %. The radiation yield of atomic hydrogen G_H = 0.02–0.4 per 100 eV. Spectra of $HO_2^{\bullet}$ radicals and $\geqslant SiO_2^{\bullet}$ macroradicals are recorded during heating of irradiated samples in the oxygen atmosphere. According to the data of quantum chemical calculations, the doublet with the splitting α^H = 12.5 mT registered during heating of irradiated MPG and quartz belongs to formyl radicals that are formed from the self-hydrogenation reaction of natural impurities of CO in silicas. The doublet with $\alpha^H \approx$ 1.0 mT, g = 2.002 is referred to hole centres $-Si^{+}(OH)H$ in the surface silicon atoms containing hydroxyl groups and the H atom.

Key words: silica, radiolysis, paramagnetic centres

INTRODUCTION

Silica is widely used in the area of high technology, industry, and everyday life. In this regard, the composition and structure of SiO_2, the nature of matrix defects and inclusions, structural transformations caused by radiation are being intensively studied [1–4]. The compound is utilised as a catalyst or sorbent [5–8] in organic chemistry and technology; amorphous SiO_2 is a component of the composition and structure of $Si-SiO_2$ that is used in optical communication systems and microelectronics [9, 10]. Colloidal SiO_2 (aerosil) is applied in the production of pharmaceuticals and the food industry.

Silica is related to chemical sorption processes, heterogeneous catalysis, radical polymerisation, and the development of composites. Heterogeneous catalysis mechanism has not yet been identified. Catalytic processes proceed by a radical mechanism and the electron paramagnetic resonance (EPR) method is attracted to solving heterogeneous catalysis problems, as suggested. Consequently, certain information about the structure of catalyst intermediates is available, however, the issue of how paramagnetic centres are linked to increasing catalytic activity yet remains open. Adsorption plays a big part in catalysis. Papers [7, 8] detected high reactivities of sorbed monomers to graft polymerization over macroporous glass (MPG). Ion radical centres of the substrate initiate the process during radiation activation of the adsorbent-adsorbate system, as demonstrated, however, it needs to be seen how polymer chains are formed by a radical mechanism during ionic initiation. The heterogeneous $Si-SiO_2$ system is the basis of microelectronic and fibre-optic devices. It is being constantly improved as a composite with various ingredients; the EPR method is often used for its study [2, 9].

Thus, the study of radicals, ion radicals, paramagnetic ions, and elementary acts in the surface and in the volume of SiO_2 is relevant. Exploring is of interest for the theory of sorption and heterogeneous catalysis, graft polymerization, and obtaining composites. However, different paramagnetic centres (PMC) are able to become stabilized in different SiO_2 modifications with chemically homogeneous matrix composition and the same activation method. P- and E-type PMC are generally stabilized in the radiolysis of solids (oxides).

This work is devoted to the comparative X-range EPR-researches of different forms of SiO_2 (MPG of two types, regular sodium glass, fused quartz) generated at low-temperature (77 K) γ-irradiation, and also to the investigation of thermal and photochemical transformations of PMC. The radiation method of activation of SiO_2 allows obtaining sufficiently high concentrations of radical ions and radicals with resolved, intense EPR spectra.

EXPERIMENTAL

The paper studied MPG with a pore diameter of 2000 and 1500 E (MPG_{2000} and MPG_{1500}, specific surface is ~30 and ~45 m^2/g, respectively), regular sodium glass, and fused quartz. The samples were irradiated under vacuum in air and oxygen atmosphere at 77 К in the KU-150000 plant and Gammatok-100 gas analyzer (irradiation source is ^{60}Co, dose rates are 50 and 5 kGy/h) in SK-4 B glass vials not giving rise to EPR signals. Stepwise heating of the resulting samples to temperatures above 77 К was carried out in a thermostat cooled with liquid nitrogen vapours. After heating of irradiated samples at a specified temperature for 10−15 min, EPR spectra were recorded at 77 К. Silyl radicals $>Si^{\bullet}-$ (or $\geqslant Si^{\bullet}$) were generated (except for radiolysis) by grinding of SiO_2 samples in a porcelain mortar at room temperature. Photobleaching of the radiolyzed MPG samples was carried out in quartz vials by UV light of high-pressure mercury lamp DRSh-1000 (the intensity is ~10^{17} quantum/($cm^2 \cdot s$), $\lambda = 236{-}365$ nm). The EPR spectra were recorded using X band radiospectrometer at 77 and 300 K (microwave power was about 10^{-3} W). The concentration of MPG was determined by EPR spectra using a sample of stable nitroxyl radical with the known number of spins as a reference. A stable signal of Cr^{3+} ion ruby crystal built-in into the resonator was a side reference that monitored radio spectrometer parameters. The absolute error of the measurement of the PMC concentration was ±15 %. The values of g-factors of EPR signals were determined by the relative method taking a stable signal at $g = 2.001$ of the $\geqslant Si^{\bullet}$ radical in a quartz sample as g tap. Optical absorption spectra of irradiated sodium glass were removed using Specord UV-VIS spectrophotometer at 77 K. Quantum-chemical calculations of radical structures were performed by the density functional method B3Lyp/6-311++g(2d) using the GAUSSIAN 03 software package.

RESULTS AND DISCUSSION

Paramagnetic centres in PMG_{2000}

Al^{+3} cation in natural silica isomorphically replaces silicon in silicon-oxygen tetrahedra generating mixed (defective) $>Al{-}O{-}Si\leqslant$ tetrahedra. A negative charge of mixed tetrahedra is mainly compensated by Li^+, K^+, and Na^+ cations located in the voids of the glassy grid. Structural irregularities in the normal tetrahedral structure, *e.g.* surface non-bridging oxygen atoms also refer to defective structures, such as $\geqslant Si{-}OH$ and $>Si{=}OH$ coordinated with sodium or potassium ions [11].

During the early stages of radiolysis of MPG_{2000} (up to 2 kGy) at room temperature, there is an asymmetric signal in EPR spectra with the following values of the g-factor: $g_1 = 2.002$, $g_2 = 2.010$ and $g_3 = 2.021$. The signal shape does not change in the 77−300 K temperature range (Fig. 1, spectrum *1*) and may be referred to the active centre in the structural fragment $[SiO^{-}...K^{+}]$ by the low-field component with $g_3 = 2.021$, typical only for potassium glasses. The above fragment is a hole in non-bridging oxygen ion coordinated to potassium ion [11]. At doses above 2 kGy, a broad signal appears, in which four lines of the superfine structure (SFS) are characterised by the values of the g-factor, such as $g_1 = 2.079$, $g_2 = 2.035$, $g_3 = 1.980$, and $g_4 = 1.920$, and also by the values of hyperfine splitting (HFS) $\alpha = 7.4{-}9.6$ MT (see Fig. 1, spectrum *2*). A similar signal remains in samples γ-irradiated by large doses (under vacuum) at their heating to 520 К, which indicates high thermal stability of PMC responsible for this spectrum. Four components in spectrum *2* may be related to potassium ion activation. The average value of splitting ($\alpha_{av} = 8.5$ mT) is almost equal to isotropic coupling constants with potassium nuclei (potassium nuclear spin is 3/2, isotropic interaction constant is 8.3 mT [12]). Entrapped electron localization in the external *s*-orbital of potassium ion transforms it to zero-va-

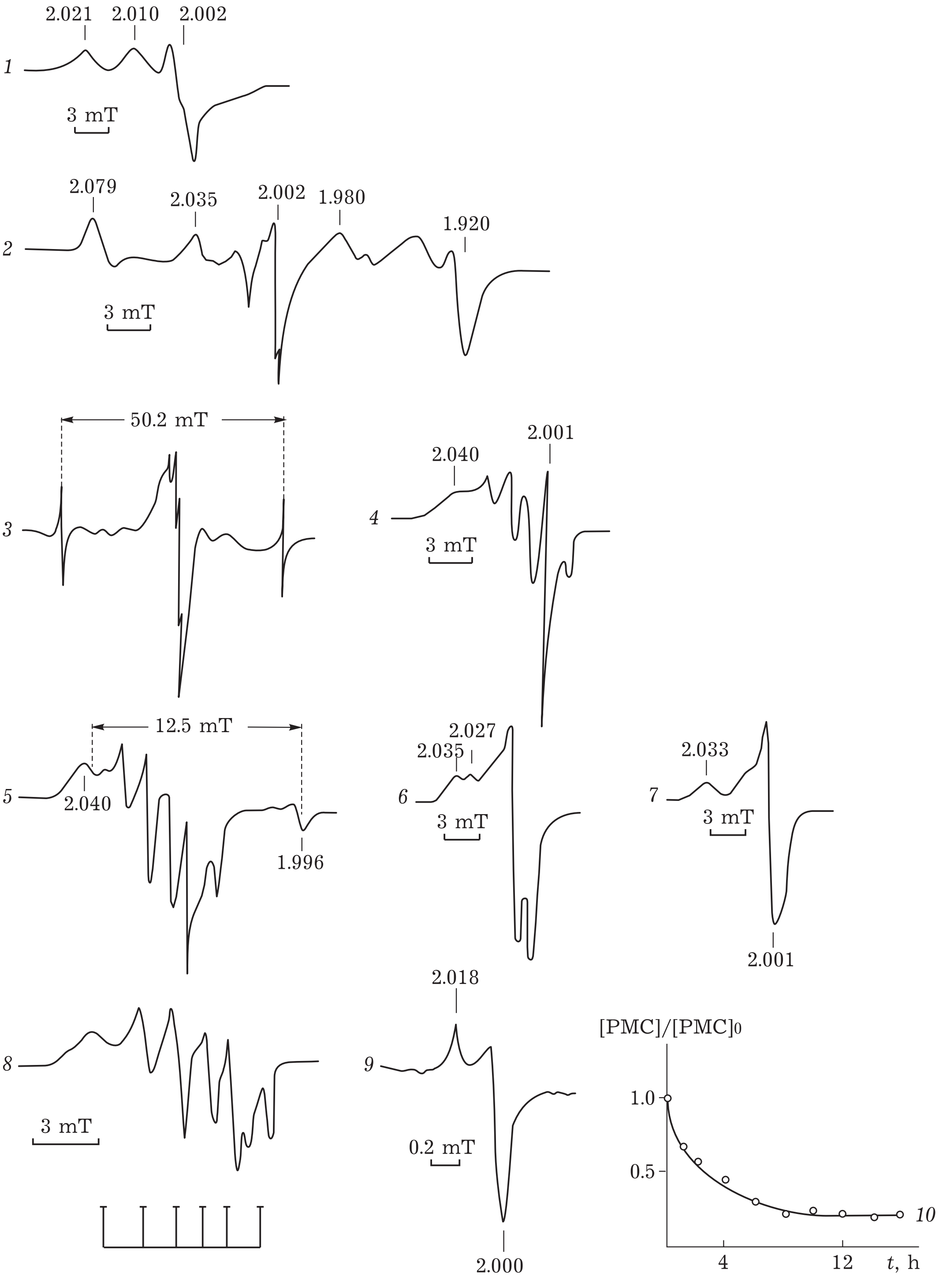


Fig. 1. EPR spectra of MPG_{2000} samples at low temperature radiolysis, kGy: 0.2 (*1*), 4 (*2*), 100 (*3*, *4*), 180 (*5*) at 77 K in vacuo; heating in sample 4 air atmosphere 350 (*6*), 370–400 (*7*) and 485 (*9*); sample 5 spectrum after photobleaching (*8*) and bleaching kinetics of γ-MPG_{2000} irradiated in vacuo at 77 K, $\gamma \geq 236$ nm (10). Spectral registration at 77 and 300 K (*9*).

lent paramagnetic K^0 atom. Thus, complex centres are accumulated in MPG_{2000} during the early stages of radiolysis that are a hole centre in nonbridging oxygen atoms in the structural fragment [SiO−...K^+] and zero-valent potassium K^0:

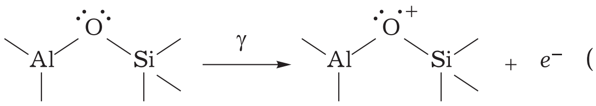
$$[\mathrm{SiO^-}\ldots\mathrm{K^+}] + \gamma \rightarrow [\mathrm{SiO^{\bullet}}\ldots\mathrm{K^+}] + e^-$$
$$\mathrm{K^+} + e^- \rightarrow \mathrm{K^0} \qquad (1)$$

Hole centres, such as [SiO−...K^+] have also been isolated during photochemical activation of an aerosil surface [13].

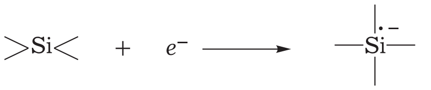
A multicomponent signal of MPG_{2000} involves lines of a hydrogen doublet (α = 50.2 mT) and a sextet with splitting α = 1.2–1.4 mT, g = 2.006 (see Fig. 1, spectra *3*, *4*) with liquid nitrogen temperature (77 K, doses $\geq$10 kGy). The radiation yield of hydrogen $G_H \approx 0.4$ per 100 eV; its contribution to the total concentration of PMC is ~15 %. Reactions with homolytic dissociation of surface O–H groups in water molecules are a source of atomic hydrogen. Radiolysis of H_2O also involves the capture of the electron by a proton [14]:

$$\geqslant SiOH + \gamma \rightarrow \geqslant SiO^{\bullet} + H^{\bullet}$$
$$H^+ + e^- \rightarrow H^0 \qquad (2)$$

A sextet similar to spectrum *4* was observed for the first time by O'Brien during X-ray irradiation of quartz. He linked it to ion activation of impurity aluminium that is part of mixed tetrahedra [15]. An active centre is formed resulting from the removal of one electron of a lone pair of electrons on the oxygen atom and represents a positive hole on the oxygen atom coupled with the aluminium atom according to equations:



(3)



(4)

The structure of the hole centre can be represented in a simplified way as >Al–O$^+$–Si$\leqslant$. It is noteworthy that similar spectra of hole centres near impurity aluminium in γ-irradiated silica gels were noted by the authors of [14]. The HFS constant of >Al–O$^+$–Si$\leqslant$ ion radicals in MPG_{2000} (α = 1.2–1.4 mT) is in line with unpaired electron delocalization to the aluminium atom by 2.8 %. The radiation yield (G) of ion radical is 4.5 and 6.5 spins per 100 eV at 77 and 300 K, respectively. The first component of the >Al–O$^+$–Si$\leqslant$ sextet is overlapped by the low-field component (at $g_{\|}$ = 2.040) of an asymmetric singlet of the >Al–O$^+$ hole centre, therefore, it is different by shape from other five lines. There is a small reversible shift ($g_{\|}$) depending on the spectrum recording time, which is typical for the signals of oxygen radicals and reflects some averaging of the g factor anisotropy.

The fifth component of a sextet of the >Al–O$^+$–Si$\leqslant$ hole centre is overlapped by a narrow singlet spectrum with a width $\Delta H \approx$ 0.3 mT, g = 2.001 to >Si$^{-\bullet}$< electrons stabilized on silicon atoms, as referred to in paper [12]. Electron spectra can be represented in a simplified way as $\geqslant$Si$^-$. Their formation may proceed by equation (4) (see Scheme 1). The contribution of electron spectra with a dose of 300 kGy is ~3 %. An EPR signal of the ($\geqslant$Si$^-$) centre is readily saturated, and it is bleached under the action of the UV light with $\lambda \geq$ 236 nm. A spectrum of hole centres >Al–O$^+$–Si$\leqslant$ decreases synchronically with the loss of electrons proving the ion radical nature of these particles. The concentration of PMC decreased approximately by 80 % (see Fig. 1, spectrum *10*) during 10 h of photolysis, and a signal of electron centres completely disappeared. An EPR spectrum after photobleaching of γ-irradiated MPG_{2000} (77 K) is presented in Fig. 1 (spectrum *8*). The sensitivity of hole and >Al–O$^+$–Si$\leqslant$ and $\geqslant$Si$^-$ electron centres to the light of shorter than 300 nm testifies deep electron traps, the energetic level of which corresponds to the energies of about 4–5 eV. Synchronous bleaching of >Al–O$^+$–Si$\leqslant$ centres and electrons stabilised in silicon may point at the formation (and destruction under the light) of [Al–O+...Si–] hole and electron centres.

The doublet with splitting α =12.8 mT, g = 2.001, the first line of which is overlapped in a low field with the first (at $g_{\|}$ = 2.040) component of the >Al–O$^+$–Si$\leqslant$ sextet (see Fig. 1, spectrum *5*) is registered in EPR spectra of MPG_{2000} irradiated in vacuo at doses above 100 kGy. In paper [16], the doublet is referred to H–C$^{\bullet}$=O formyl radicals as to radiation centres that arise resulting from the interaction of carbon oxide physically dissolved in a SiO_2, matrix with atomic hydrogen:

$$H^{\bullet} + CO \rightarrow H{-}C^{\bullet}{=}O \qquad (5)$$

However, one may assume that the formation and accumulation of the SiO_2 – radical that may be a product of a heterogeneous self-hydration reaction of own surface defects of silica, *e.g.* silylene structures [17] containing a silicon atom with two free valences of (>Si:) happen during radiolysis of SiO_2. However, as quantum chemical calculations have demonstrated, isotropic HFS constants of hydrogen for H–C$^{\bullet}$=O and H–Si$^{\bullet}$=O radicals are very different: α^H = 13.5 mT for HC$^{\bullet}$O and α^H = 15.1 mT for HSi$^{\bullet}$O). The experimental data obtained by us are almost the same (12.2 and 12.8 mT, respectively). This has proven the accumulation of only formyl radicals formed by the hydrogenation reaction of natural (existing in many rocks) CO impurities in silicas. Silica is formed under natural conditions (in the crust) resulting from incomplete combustion of organic carbon compounds (wood, coal, natural gas, *etc.*), which is driven by the carbonization process of vegetable raw materials and bitumens into coal. Carbon monoxide (CO) is one of the gas products.

Thermal transformations of PMC of radiolyzed PMG_{2000}

The doublet of atomic hydrogen disappears in the 134–140 K range, a sextet of $>\mathrm{Al{-}O^{+}{-}Si}\leqslant$ ion radicals remains up to ~520 K during heating of MPG_{2000} irradiated in vacuo. After the loss of ion radicals, a low-intensity signal of hole centres in the structural [SiO−...K^{+}] fragment remains in EPR spectra (the signal is similar to spectrum *1*, see Fig. 1). The loss of PMC in the presence of O_2 is more intense and accompanied by oxidation reactions. An asymmetric doublet with splitting α = 1.3 mT and g-factor components g_1 = 2.035 and g_2 = 2.027 belonging to $HO_2^{\bullet}$ hydroxyl radicals [12] appears in EPR spectra at 273 K (see Fig. 1, spectrum 6). An oxidation reaction of atomic hydrogen with oxygen dissolved in the matrix is the most likely $HO_2^{\bullet}$ formation mechanism. The concentration $HO_2^{\bullet}$ was ~10 % of the initial concentration of PMC, which adequately corresponded to the amount of atomic hydrogen (~15 %) released during radiolysis of MPG_{2000}. Species ($HO_2^{\bullet}$) sorbed by silica surface are characterised by high thermos abilities and remain right up to 350 K. According to the data of [18], there might be one more channel of generation through recombination and transformation of hydroxyl radicals $HO^{\bullet}$ formed during radiation destruction of molecules of water that is a part of natural silicas. However, hydroxyl radicals were not detected in MPG_{2000}. An asymmetric singlet with $g_{\parallel}$ = 2.033 and $g\perp$ = 2.001 was registered in EPR spectra of radicalised MPG2000; its parameters corresponded to the data of signals of peroxide organic radicals (see Fig. 1, spectrum 7).

Peroxide radicals $\geqslant\mathrm{Si{-}O{-}O^{\bullet}}$ are formed resulting from the interaction of active silyl radicals $\mathrm{Si}^{\bullet}$ with oxygen dissolved in the matrix. The amount of $\mathrm{SiOO}^{\bullet}$ did not exceed ~4 % of the initial concentration of all paramagnetic particles. It is noteworthy that a clear signal of the $\geqslant\mathrm{SiOO}^{\bullet}$ radical, magnetic resonance parameters of which entirely match signals of organic radicals $\mathrm{ROO}^{\bullet}$, were obtained in silica for the first time due to a highly dispersed state of MPG, in which oxygen was able to move freely. Peroxide radicals were not formed in rigid matrixes of quartz and sodium glass when heating the resulting samples in the presence of O_2.

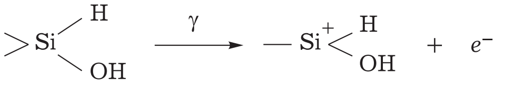
The formation of $\geqslant\mathrm{SiOO}^{\bullet}$ evidences homolytic splitting of the main siloxane bonds of a $\geqslant\mathrm{Si{-}O{-}Si}\leqslant$ matrix accompanied by generation of $\geqslant\mathrm{Si}^{\bullet}$ and $\geqslant\mathrm{SiO}^{\bullet}$ radicals. However, the latter were not possible to observe by EPR spectra due to line broadening caused by a degenerate orbital state [19]. The signal of peroxide radicals $\geqslant\mathrm{SiOO}^{\bullet}$ disappears at 485 K when heating γ-irradiated MPG_{2000}. EPR spectra demonstrate the presence of a low-intensity asymmetric singlet with anisotropic g-factor: $g_{\parallel}$ = 2.0018, g⊥ = 2.0007 (Fig. 1, spectrum *9*), the parameters of which correspond to the spectrum of the silyl radical ($\geqslant\mathrm{Si}^{\bullet}$) [20]. Spectrum registration above 485 K evidences high thermal stability of $\geqslant\mathrm{Si}^{\bullet}$ radical centres that are not oxidised apparently because of the fact that they are located in rigid sites of the matrix unavailable for oxygen. These centres are presumably not related to radiolysis and relate to own defects of silicas that exist in all forms of SiO_2. Singlet lines of $\geqslant\mathrm{Si}^{\bullet}$ radicals with g = 2.001 are often used in EPR spectroscopy as a tap when determining the g-factor.

As already noted, the first sextet component of the $>\mathrm{Al{-}O^{+}{-}Si}\leqslant$ ion radical centre is overlapped with the low field component (at $g_{\parallel}$ = 2.040) of the asymmetric $>\mathrm{Al{-}O^{+}}$ singlet. An asymmetric singlet of $>\mathrm{Si}^{\bullet}$ radicals and a line of electrons stabilised on $\geqslant\mathrm{Si}^{-}$. These two singlets of active centres on silicon (radical $\geqslant\mathrm{Si}^{\bullet}$ and electron $\geqslant\mathrm{Si}^{-}$) are registered with the identical value of the g-factor (g = 2.001) but have different shapes. This may be related to the nature of orbitals occupied by an unpaired electron. It occupies in the 3_{Pz}- orbital of the $\geqslant\mathrm{Si}^{\bullet}$ radical has a visible spin-spin bond, which determines the anisotropy of the g-factor and an EPR spectrum is recorded as an asymmetric singlet with the anisotropic g-factor. The entrapped electron in the $\geqslant\mathrm{Si}^{-}$ ion radical is stabilised on the external hybrid sp^2-orbital that has the space symmetry. The EPR spectrum of this centre is a symmetrical singlet with the isotropic g-factor. $\geqslant\mathrm{Si}^{\bullet}$ and $\geqslant\mathrm{Si}^{-}$ particles have different photochemical properties. $\geqslant\mathrm{Si}^{-}$ ion radicals are completely bleached during UV radiation, and their singlet in EPR spectra disappears. The intensity of the asymmetric $\geqslant\mathrm{Si}^{\bullet}$ singlet is not changed, and at $\lambda \leq 280$ nm increases due to the generation of $\geqslant\mathrm{Si}^{\bullet}$. $\geqslant\mathrm{Si}^{\bullet}$ radicals are also accumulated upon mechanical impact on silica [21]. These centres were obtained by us in direct grinding of the studied silicas. NMR spectra for all samples contained identical asymmetric singlets of $\geqslant\mathrm{Si}^{\bullet}$ radicals similar to spectrum *9* in Fig. 1.

Thus, a number of various PMC were identified in low-temperature (77 K) radiolysis of PMG_{2000} followed by thermal and photochemical reactions of the irradiated sample. Hole and electron PMC make the main contribution (~90 %). Hole centres on oxygen atoms in $\geqslant\mathrm{SiO}^{+}$ and $>\mathrm{AlO}^{+}$ are characterised by asymmetric signals with the low field component of the anisotropic g-factor at 2.021 and 2.040, respectively. An asymmetric singlet of $>AlO^+$ has an additional six-component structure due to partial delocalization (by ~2.8 %) of the spin density on the aluminium nucleus. Electron PMC are stabilised on silicon atoms and alkaline metal cations. Among radical particles, $H^•$, $HO_2^•$, $\geqslant Si^•$, $\geqslant SiO_2^•$ were detected; their number did not exceed 10 %. The radiation yield of the accumulation of PMC in vacuo GPMC = 4.5 per 100 eV. A doublet of formyl radicals formed through the self-hydrogenation reaction of natural impurities of CO with atomic hydrogen in silicas is recorded in EPR spectra with doses above 100 kGy.

Radiolysis of MPG$_{1500}$

The accumulation of PMG at low-temperature (77 K) radiolysis of MPG$_{1500}$ proceeds with the radiation yield $G_{PMC} \approx 2.0$; the yield of atomic hydrogen $G_H \approx 0.1$ per 100 eV. Figure 2 presents the EPR spectrum of γ-irradiated MPG$_{1500}$ that includes two lines of atomic hydrogen and a broad component in the high field at g = 1.920 (spectrum *1*). As can be seen, spectrum *1* in the region $g \approx 2$ is similar by shape to the spectrum of irradiated MPC$_{2000}$, though MPS have different pore sizes and surface values. Several signals are recorded in the region $g \approx 2$. An intense doublet with splitting $\alpha \approx 1.0$ mT, g = 2.0059 unknown from the literature prevails in the total spectrum (spectrum *2*). The doublet is readily bleached by the visible light, which may testify the non-radical nature of PMC. According to quantum chemical calculations, the experimental constant of SFS doublet ($\alpha \approx 1.0$ mT) corresponds to the structure of the $-Si^+H(OH)$ hole centre on surface silicon atoms connected with a hydroxyl group and the H atom. A singlet spectrum on the second doublet component (indicated by *e* letter) characterises the electron stabilised on the $\geqslant Si^-$ atom. A scheme for the formation of hole and electron centres in MPC$_{1500}$ may be represented as follows:



$$>\mathrm{Si}\langle^{\mathrm{H}}_{\mathrm{OH}} \xrightarrow{\gamma} -\mathrm{Si}^{+}\langle^{\mathrm{H}}_{\mathrm{OH}} + e^- \qquad (6)$$

The signal of $\geqslant Si^•$ radicals, the asymmetric singlet of which is highlighted during heating of photobleached MPC$_{1500}$ to room temperature (see Fig. 2, spectrum 7) is overlapped with a singlet of stabilised electrons. According to the data of [22], the broad doublet with splitting α = 8.3 mT is driven by $>Si^•-H$ radicals (its lines in spectrum *3* are marked with an asterisk). The doublet with splitting α = 12.5 MT (lines are marked with a cross) is the signal of formyl radicals $O=C^•-H$ formed, as already noted, in the hydrogenation process with atomic hydrogen of CO impurities in MPG$_{1500}$.

The number of reactive radicals in γ-irradiated-MPG$_{1500}$ was determined by the quantity of peroxide radicals $\geqslant SiOO^•$. formed during heating of samples in the presence of oxygen. At 310 K, the typical asymmetric singlet with $g_\parallel$ = 2.030 and $g\perp$= 2.001 of peroxide radicals is recorded in ESR spectra (see Figure 2, spectrum *4*). A small part of

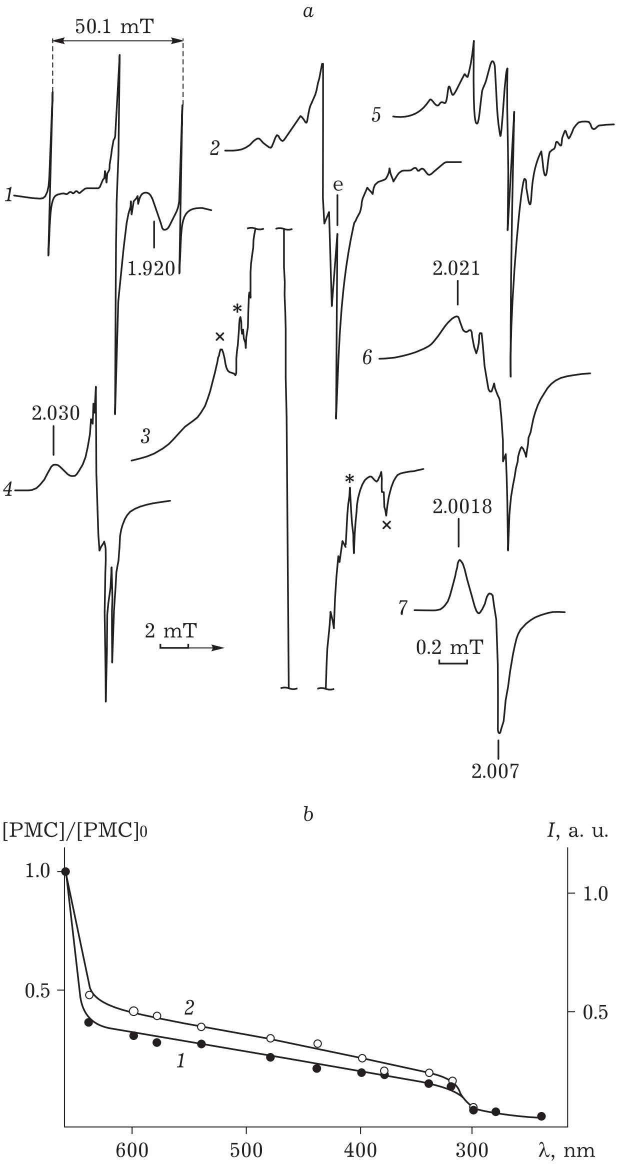


Fig. 2. EPR spectra of γ-irradiated MПG$_{1500}$ (*a*: *1* − radiolysis (100 kGy) in vacuo at 77 K; 2, *3* − central part of spectrum *1* at a gain of 1 and 5, respectively; *4* −sample *1* heating to 310 K in the presence of O$_2$; *5*–*7* − photobleaching of radiolized samples at 77 K, $\gamma \geq 365$ (*5*), $\gamma \geq 236$ nm (*6*) and the heating of the sample 6 to 300 K (*7*); the spectra at 77 K); *b*: changes in PMC concentration (*1*) and line intensities of $\geqslant Si^-$ electron centres (*2*) during bleaching of γ-irradiated MPG$_{1500}$ by light with different γ-values at 77 K ($[PMC]_0 \approx 10^{18}$ g^{-1}).

PMC (~3 % of the initial concentration) were oxidised, however, the oxidation process confirms the presence of radical particles; all paramagnetic centres disappeared in O_2 atmosphere at ~420 K.

The quantity of ion radical centres in radiolized MPG$_{1500}$ was defined by optical bleaching techniques. Figure 2, *b* presents the total concentration of PMC and line intensities of electron centres ($\geqslant Si^-$) versus the γ value. The effect of the longwave light with $\lambda \geq 640-600$ nm leads to a decrease in the concentration of PMC by 70 % (curve *1*), and the doublet of ion centres $-Si^+H(OH)$ with $\alpha^H \approx 1.0$ mT disappears in EPR spectra. The line intensity of stabilised electrons (curve *2*) decreased synchronically with the disappearance of the doublet. The sextet ($\alpha = 0.8-1.0$ mT, $g = 2.004$) of cation radicals $>Al-O^+-Si\leqslant$ (see Fig. 2, spectrum *5*) appeared at $\lambda \geq 360$ nm (prior to bleaching, the sextet is shielded by the intense doublet of hole centres $-Si^+H(OH)$. The total concentration of PMC at $\lambda \geq 236$ nm decreased to ~4 %, and the EPR spectrum transformed into a superposition of the singlet of the structural fragment $[SiO^-...K^+]$ with $g_{\parallel} = 2.021$ PMC and the residual signal of cation radicals (spectrum *6*). The singlet of $\geqslant Si^\bullet$ radicals (spectrum 7) remained in EPR spectra of the bleached MPG1500 at room temperature.

Thus, PMC of MPG$_{1500}$ γ-irradiated at 77 K differ from PMC in similarly generated MPG$_{2000}$, which is testified by the initial EPR spectra. The bulk of active centres of MPG$_{1500}$ are ion radical centres, the amount of which reaches approximately 96 %. The majority of them are hole centres $-Si^+H(OH)$ with shallow traps (1.9−2.0 eV). The proportion of ion radicals $>Al-O^+-Si\leqslant$ is almost 25% of PMC. The number of electron centres in $\geqslant Si^-$ and $[SiO^-...K^+]$ fragments is 1−1.5 %; the contribution of radicals $\geqslant Si^\bullet$, $Si^\bullet H$, $O=C^\bullet-C$ does not exceed 3 %.

Ion radicals in MPG as initiators for graft polymerization

Silica-based MPG that have large specific surfaces efficiently sorb monomers and can be used as sorbent substrates in the synthesis of filled polymers. Filled silica-based polymers are widely used in chromatography, biology, medicine (especially effective in cleansing the blood). Post-irradiation graft polymerization of tetrafluoroethylene (TFE) and methyl methacrylate sorbed into pores of MΠG$_{2000}$ and MΠG$_{1500}$ was studied by the EPR method and low-temperature calorimetry [7, 8]. The monomers in the sorbed state showed high abilities towards polymerization reactions. The monomer conversion in the 160−240 K range with doses of preliminary radiation of ~10 kGy reached 100 % (Fig. 3, *c*). The formation of a covalent bond during grafting of polymer chains to support surface has been proven by IR spectroscopy method.

The EPR spectrum of the [MPC$_{2000}$ + TFE] system jointly irradiated at 77 K is presented in Fig. 3, *a* (spectrum *1*) and practically does not differ from the signal of pure irradiated MPG (see Fig. 1, spectrum *4*). As it follows from the above

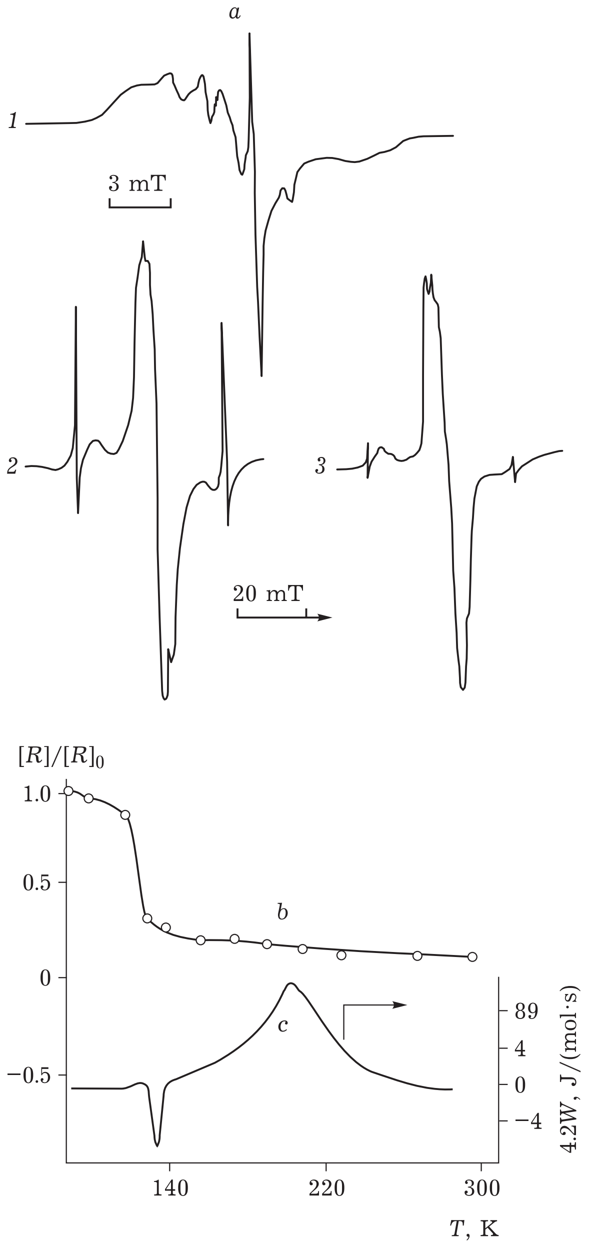


Fig. 3. Radiolysis of MΠG$_{2000}$ + TFE: *a* − EPR spectra of jointly irradiated MPG + TFE system at 77 (*1*), 105 (*2*) and 120 K (*3*); *b* − PMC concentration versus temperature during heating of MPC+TFE irradiated system; *c* − calorimetric curve of heat release during heating of MPC +TFE irradiated system (pre-irradiation dose is 180 kGy at 77 K, $[R]_0 = 2.5 \cdot 10^{18}$ g^{-1}, spectral registration at 77 K).

data, PMC of the jointly irradiated system are of radical and ion nature. As experimentally established, ion particles (most likely, the hole centres of the substrate) initiate polymerization of sorbed monomers and the growth of polymer chains proceeds via a radical mechanism. Apparently, the first step of initiation involves the interaction of an ion-radical particle of silica with monomer species and the formation of neutral terminal radical $R^{\bullet}$ that generates the polymer chain.

Addition of monomer species to the active centre of the substrate begins with the appearance of the molecular mobility with increasing temperature. Apparently, monomers are polarized in a strong electric field; charge shift of $CF_2{=}CF_2$ species contributes to double bond expansion, the formation of a biradical and its addition to the hole centre. The second free valence (or spin state) migrates upon the addition of TFE species, forming a polymer chain:

$$\text{МПС} + \gamma \rightarrow (R+)^{\bullet} \tag{7}$$

$$(R+)^{\bullet} + {>}CF_2{=}CF_2{<} \rightarrow (R{-}CF_2{-}C^{\bullet}F_2) \tag{8}$$

The signal of $(R{-}CF_2{-}C^{\bullet}F_2)$ radicals of a growing polymer chain is registered in EPR spectra even before polymer melting at 105–120 K as a typical trilinear spectrum with a distance between side cycles of ~40 mT (see Fig. 3, *a*, and spectra *2*, *3*). During a further increase of temperature in the presence of monomers, the concentration of PMC is sharply decreased, and it reduces to ~25 % (see Fig. 3, *b*) during TFE melting (~130 K).

The reactions of monomers, olefines, and CO and N_2O gases with radiolized silica can also be used for obtaining free radicals in specified structures on silica surface [21].

Radiolysis of glass

The accumulation of PMC at low-temperature (77 K) γ-irradiation of glass proceeds with the radiation yield $G_{PMC} = 4.5$. The yield of atomic hydrogen $G_H = 0.02$ per 100 eV. The transformation of the total EPR spectra of glass radiolized at 77 K and a change in the concentration of PMC resulting from bleaching and heating are presented in Fig. 4.

Six lines of SFS with splitting $\alpha = 1.1{-}1.4$ MT ($g = 2.004$) and the first component at $g = 2.040$ in spectrum *1* indicate the signal of the ${>}Al{-}O^{+}{-}Si{\leqslant}$ hole centres. Unlike the spectrum of this centre for MPC having the form of "saw", the central component of EPR spectra of glass (obtained both in vacuum and air) has an inflection determined by the small contribution of the line of electrons stabilised in silicon (${\geqslant}Si^{-}$). The doublet of atomic hydrogen ($\alpha = 50.3$ mT) testifies the stabilization of $H^{\bullet}$ that is accumulated in smaller amounts than in MPC. The doublet of atomic hydrogen disappears without transforming to the signal of $HO_2^{\bullet}$ at 150 K when heating γ-irradiated glass in the oxygen atmosphere. Thus, oxidation of $H^{\bullet}$ does not happen. The signal of peroxide macroradical ${\geqslant}SiOO^{\bullet}$ was not detected. The shape of the main spectrum and the concentration of PMC remain way up to room temperature (see Fig. 4, *b*, curve *2*). Unlike heating, the effect of UV light for radiolized glass samples leads to a fast decrease in the concentration of PMC (see Fig. 4, *b* and curve *1*). Photobleaching proceeds during light irradiation ($\lambda \leq 300$ nm, trap depth is 4–5 eV).

The spectrum takes the form of a saw under the short action of light with $\lambda \geq 236$ nm (see Fig. 4, *a*, spectrum 2). During long exposures and heating of samples to 100 °C, the visible spectrum of silyl radical ${\geqslant}Si^{\bullet}$ (highlighted with an asterisk) that represents an asymmetric singlet with $\Delta H = 0.2$ mT, $g_{\parallel} = 2.0018$, $g\perp = 2.0007$ (spectrum *4*) can be seen in the fifth line of the sextet (spectrum *3*).

The use of transparent glass samples allowed removing optical absorption spectra of γ-irradiated and bleached glass and assessing extinction coefficients of PMS of radiolized glass based on EPR and UV spectroscopy. There are two visible maxima at $\lambda \approx$ of 400 and 330 nm (Fig. 5, spectrum 2) in optical adsorption spectrum of γ-irradiated glass (45 kGy, 77 K).

According to the literature data, the longwave maximum (400–600 nm) in the optical spectra of irradiated glass refers to the ${>}Al{-}O^{+}{-}Si{\leqslant}$ hole centres, and the maximum at 350 nm – to the band of ${\geqslant}Si^{-}$ electron centres [14]. The maximum at ~330 nm completely disappears under the action with $\lambda \geq 236$ nm on irradiated glass (spectrum 3); the maximum at ~400 nm (${>}Al{-}O^{+}{-}Si{\leqslant}$ band) substantially decreases but is completely removed during glass annealing of burner flame, as demonstrated by our experiments.

The extinction coefficient of PMC in glass calculated by ESR and UV spectroscopy data at $\lambda_{max} = 330$ nm (band of the entrapped electrons of ${\geqslant}Si^{-}$) with the total yield of PMC of $1.4 \cdot 10^{18}$ spin/g; the amount of bleached centres $1.24 \cdot 10^{18}$ spin/g (or $2 \cdot 10^{-3}$ mol/l) and glass sample thickness of ~1 mm (0.1 cm) is equal to $\varepsilon_{330} \approx 1.3 \cdot 10^{3}$ ($M^{-1} \cdot cm^{-1}$).

The hole centre nearby the aluminium atom ${>}Al{-}O^{+}{-}Si{\leqslant}$ was isolated in γ-irradiated sodium glass. It is characterized by high thermal stability and remains in the irradiated samples without a change in the concentration and EPR spectrum shape above room temperature. The original

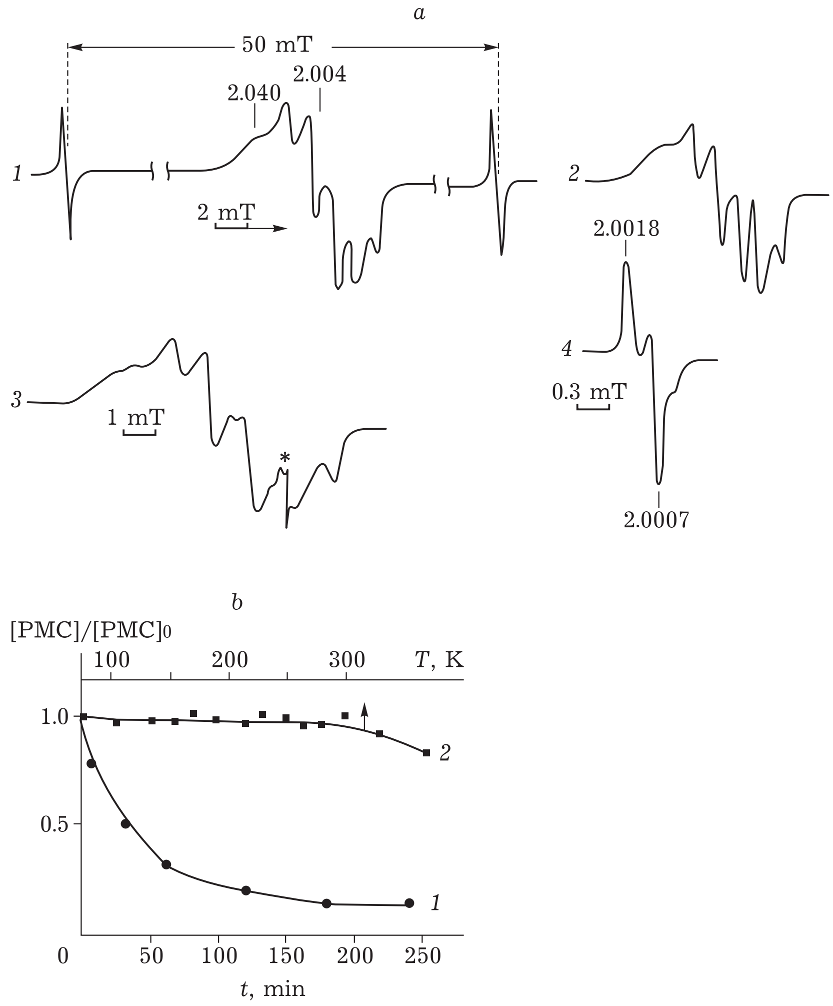


Fig. 4. *a* – Transformation of the EPR spectrum of γ-irradiated glass (*1*) during photobleaching for 5 min, $\lambda \geq 236$ nm (*2*); *3* – sample *2* is heated to 100 °C; *4* – signal of component of spectrum *3* (asterisk) on the scan of 0.2 mT/mm ($\geqslant\mathrm{Si}^-$ radical signal). Spectral registration at 77 (*1*, *2*) and 300 K (*3*, *4*); *b* – changes in PMC concentration of γ-irradiated glass during photobleaching, $\lambda \geq 236$ nm (*1*) and after irradiation (*2*). Preliminary γ-irradiation dose is 50 kGy in air at 77 K ($[\mathrm{PMC}]_0 = 1.4 \cdot 10^{18}$ spin/g).

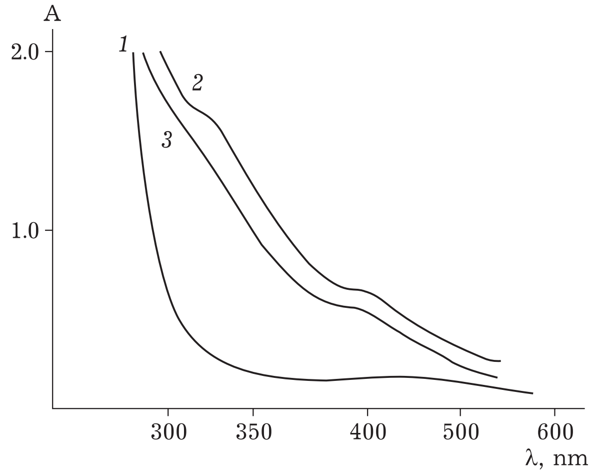


Fig. 5. Spectrum of optical absorption of sodium glass: *1* – unirradiated initial sample, *2* – after irradiation (dose is 45 kGy) in air at 77 K and photobleaching $\lambda \geq 236$ nm at 77 K (3).

shape of the $>\mathrm{Al{-}O^{+}{-}Si}\leqslant$ sextet in glass differs from the spectral forms of these centres in MPS by central line break due to the small contribution of the singlet line of entrapped electrons ($\geqslant$Si–).

Atomic hydrogen and $\geqslant\mathrm{Si}^{\bullet}$ radicals were detected among radical particles. Their EPR spectrum was isolated from the total spectrum after photobleaching and heating of the radiolized samples to 373 K (100 °C). The stability of hole centres $\geqslant\mathrm{Si{-}O^{+}{-}Al}<$ and the absence of signals for hydrogen radicals and oxidation reactions of $\mathrm{H}^{\bullet}$ and $\geqslant\mathrm{Si}^{\bullet}$ indicate a high rigidity of the crystal structure of sodium glass.

Radiolysis of quartz

Quartz glass or melted quartz represents a disordered structure, an unstable form that is preserved as long as necessary under normal con-

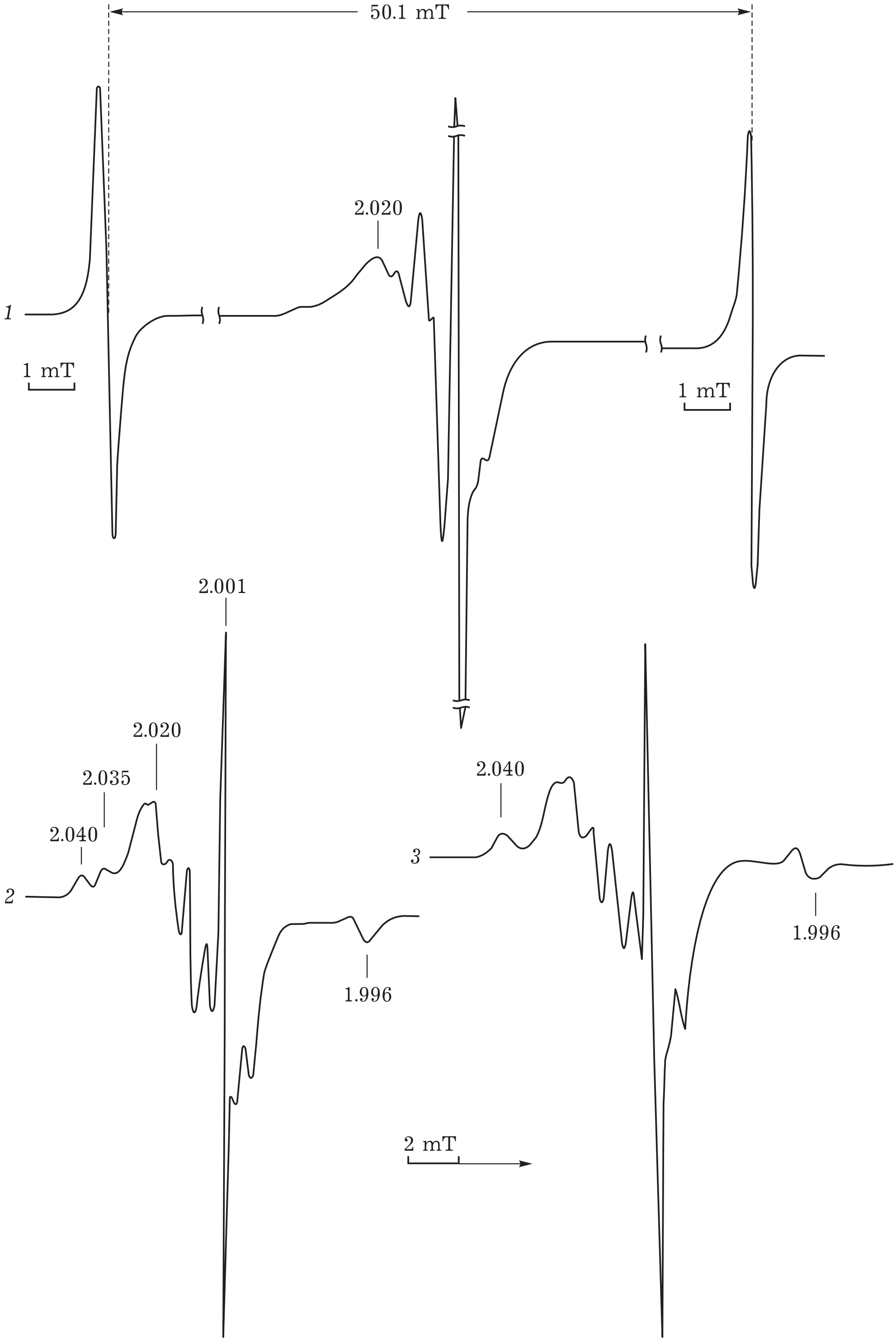


Fig. 6. EPR spectrum of fused quartz γ-irradiated (*1*) at 77 K and heated to 190 (*2*) and 330 K (*3*). Air radiation dose is 45 kGy. Spectral registration at 77 K.

ditions. The yield of PMC (G_{PMC}) at low temperature (77 K) radiolysis of fused quartz in air was 3.7 particles per 100 eV of absorbed energy. An EPR spectrum corresponding to literature data [15] that is a superposition of the sextet of hole centres $\geqslant$Si–O$^+$–Al< and the singlet of stabilised electrons of $\geqslant$Si$^-$ was registered in the region $g \approx 2$ (Fig. 6, spectrum *1*). The sextet is poorly resolved at liquid nitrogen temperature; lines are narrower than in other silicas, which testifies the weak interaction between PMC and the surrounding lattice. The splitting value of the components of the sextet $\alpha = 0.8{-}1.0$ mT corresponds to spin density delocalization onto the aluminium nucleus by 1.5–2.0 %. The line of electrons stabilised in silicon ($\Delta H \approx 0.2$ mT, $g = 2.001$) is intense and easily saturated. The first component of the sextet at $g = 2.020$ is significantly shifted, compared to the first sextet line in MPC ($g = 2.040$). The doublet of atomic hydrogen ($\alpha = 50.1$ mT) is very intense; hydrogen's contribution to the total amount of PMC was ~30 %. The spectral resolution increases with rising temperature (spectrum *2*). The signal of atomic hydrogen disappears at 150–190 K, while the doublet of formyl radicals $H{-}C^{\bullet}{=}O$ (spectrum *2*, lines at $g = 2.040$ and 1.996, splitting $\alpha = 12.4$ mT) appears. The peak with $g = 2.035$ typical for the signal $HO_2^{\bullet}$ appears simultaneously with the doublet. The intensity of the $H{-}C^{\bullet}{=}O$ doublet increases with temperature rising, and the peak with $g = 2.035$ disappears at ~320 K (spectrum *3*). Since signals of hydroperoxide radicals ($HO_2^{\bullet}$) the EPR spectrum of which is characterized by the low-field component with the $g = 2.035$ in g-irradiated МПG$_{2000}$, disappear at ~320 K, these results allow concluding that during heating of γ-irradiated quartz, a part of atomic hydrogen is consumed on hydrogenation of CO (natural impurities in quartz), and the second part of H is oxidized to $HO_2^{\bullet}$ that are destroyed at ~320 K. The spectrum of $HO_2^{\bullet}$ for MPG is completely removed at room temperature (see Fig. 1, spectrum *6*), and in quartz, it is found in a superposition with the sextet of hole centres $\geqslant Si{-}O^{+}{-}Al<$ and the doublet of $H{-}C^{\bullet}{=}O$ radicals. Their amount in quartz was ~27 %, which is close to the quantity of released atomic hydrogen (~30 %). The amount of $H{-}C^{\bullet}{=}O$ radicals at 330 K does not exceed 3.0 % relatively to the initial concentration of PMC. An increase in the concentration of $H{-}C^{\bullet}{=}O$ during heating of irradiated quartz results from long thermal hydrogenation reactions of CO coming out of quartz matrix.

Ion radical centres of irradiated quartz are subjected to photobleaching under the action of light with $\lambda \approx 236$ nm. The total concentration of PMC and line intensity of stabilised electrons during several hours of photolysis at 77 K are decreased in several times and the anisotropic component appears $g_{II} = 2.0018$ (as in irradiated glass) appears in the narrow line of the $\geqslant Si^{-}$ electron centre indicating the presence of a signal of $\geqslant Si^{\bullet}$ radicals. The $\geqslant Si^{\bullet}$ spectrum in a pure form is also registered in case of ground quartz.

Atomic hydrogen, hole ($\geqslant Si{-}O^{+}{-}Al<$) and electron ($\geqslant Si^{-}$) centres are the main active species in quartz γ-irradiated at 77 K. Their total amount reaches ~ 70 %. EPR spectral lines of PMC are narrow, splitting of sextet components of $\geqslant Si{-}O^{+}{-}Al\leqslant$ ion radicals are lower than in MPs, and corresponds to unpaired electron delocalization onto the aluminium nuclei on 1.5–2.0 % due to the more rigid quartz lattice. The bulk of atomic hydrogen oxidizes to $HO_2^{\bullet}$ a part of $H^{\bullet}$ takes part in surface radiation hydrogenation reactions with the formation of hydrogen groups and $H{-}C^{\bullet}{=}O$ radicals during heating the irradiated samples. $\geqslant Si^{\bullet}$ radicals are assigned by EPR spectra, the signal of $\geqslant SiOO^{\bullet}$ radicals is not detected.

Paramagnetic centres in silica gels, sodium glass, and fused quartz highlighted using EPR, and also photobleaching and heating of γ-irradiated samples are presented in Table 1.

Two paramagnetic species, such as $H^{\bullet}$ atom and hydroxyl radical are formed during radiolysis in homolytic dissociation of water molecules present in silica pores:

$$H2O + \gamma \rightarrow H^{\bullet} + HO^{\bullet} \qquad (9)$$

However, the EPR spectrum of the hydroxyl radical is not detected in any SiO_2 radiolyzed matrix. According to [19], the ($HO^{\bullet}$) radical is characterised by high reactivity and loses below 200 K; its spectrum is not always possible to register due to the degenerate orbital state.

TABLE 1

Paramagnetic centres in radioactive macroporous glass with pore size of 2000 and 1500 Å (MPG$_{2000}$, MPG$_{1500}$), sodium glass and fused quartz

Silica	Paramagnetic centres		Yield		Temperature, K
	ion radicals	radicals	G_{PMC}	[*H*], %	
MPG$_{2000}$	$>Al{-}O{+}{-}Si\leqslant$ $\geqslant Si{-}$, $\geqslant SiO^{+}$	$\geqslant Si^{\bullet}$, $\geqslant Si^{\bullet}O_2$, $H^{\bullet}$ $HO_2^{\bullet}$, $H{-}C^{\bullet}{=}O$	4.5	15	
MPG$_{1500}$	$-Si^{+}H(OH)$, $\geqslant Si^{-}$ $>Al{-}O{+}{-}Si\leqslant$	$\geqslant Si^{\bullet}$, $\geqslant SiO_2$, $H^{\bullet}$ $\geqslant Si^{\bullet}{-}H$, $H{-}C^{\bullet}{=}O$	2	5	77–310
Glass	$>Al{-}O{+}{-}Si\leqslant$	$\geqslant Si^{\bullet}$, $H^{\bullet}$	4.5	0.2	77–373
Quartz	$>Al{-}O{+}{-}Si\leqslant$ $\geqslant Si^{-}$	$\geqslant Si^{\bullet}$, $H^{\bullet}$, $HO_2^{\bullet}$ $H{-}C^{\bullet}{=}O$	3.7	30	77–320

CONCLUSION

Various paramagnetic centres carried out via anion, cation, and free radical mechanisms are stabilised in various silica modifications during low-temperature (77 K) radiolysis, depending on origins, the presence of impurities, thermal vacuum treatment conditions, and sample activation, as demonstrated by comparative analysis of paramagnetic centres. The yield of hole ($\geqslant$SiO$^+$, $>$AlO$^+$, $-$Si$^+$H(OH)) and electron ($\geqslant$Si$^-$) centres in glass reaches 90–95 %, quartz ~70 %; the yields of ($\geqslant$Si$^\bullet$, $>$ Si$^\bullet$–H, and H–C$^\bullet$=O) radicals in all silica are 3–10 %. The differences in active centres may be expressed in physicochemical processes of sorption, catalysis, grafting, and modification. The signals of peroxide, $HO_2^\bullet$ and $\geqslant SiO_2^\bullet$ radicals have been recorded during heating of irradiation samples in O_2 atmosphere. Macroradicals $\geqslant$SiOO$^\bullet$ have been detected for the first time in superfine macroporous glass by an asymmetric singlet, the parameters of which fully correspond to those of organic peroxide radicals.

According to quantum chemical calculations, the doublet with splitting $\alpha^H \approx 12.5$ mT, $g = 2.001$ is the signal of formyl radicals (H–C$^\bullet$=O) generated via the self-hydrogenation reaction of CO natural impurities in silicas; the doublet with $\alpha^H \approx 1.0$ mT refers to $-$Si$^+$H(OH) hole centres of surface Si atoms containing an OH group and H atom.

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