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PARAMAGNETIC CENTERS IN GAMMA IRRADIATED $(RaO)_x(SiO_2)_y$ SAMPLES WITH ADSORBED WATER

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Abstract: *The γ- irradiated 77K samples $(RaO)_x(SiO_2)_y$ with adsorbed water were studied using EPR spectroscopy, and EPR spectrum with g=2.0028 and hyperfine splitting constant A(H)=505.3 G belonging to hydrogen atoms was registered. EPR, presumably attributed to paramagnetic hole $(\equiv Si\text{-}O)^+$, electronic $(\equiv Si\text{-})^-$ centers and products of their interaction with water molecules spectra was registered. It is assumed that the main part of atomic hydrogen was oxidized to the $HO_2^{\bullet}$ radical, and some of the $H^{\bullet}$ atoms participate in surface radiative hydrogenation reactions with the formation of hydrogen-containing radicals when irradiated samples were heated from 77 K to room temperature. It is also assumed that •OH radicals are formed on the surface of γ--irradiated at 77K (RaO)x(SiO2)y samples.*

Keywords: *$(RaO)_x(SiO_2)_y$ system, γ-radiation, electron paramagnetic resonance, hydrogen atom, electron and hole centers*

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Introduction

One of the most important and highly productive processes in nuclear-hydrogen energy is the fragment radiolysis. Fragments formed as a result of nuclear transformations perform 80-85% of the conversion process. Therefore, under the conditions of nuclear transformations, the use of fragmentation energy and radiant radiation for the direct production of hydrogen is one of the topical problems [1,2]. One of the decay products of uranium isotopes is radium. Radium is an alpha active isotope, like uranium. Therefore, the heterogeneous radiolysis of water in the presence of radium is of great model value. Besides, natural isotopes of radium are widely distributed in the environment in the form of uranium fission products, for example, in various rocks, bottom sediments of oil and gas fields. Chemical transformations under the effect of radiation in terms of uranium-containing rocks contacting with water are relevant from the point of view of studying the mechanism of geochemical processes [3,4].

In this work, a silicate system, which is closer to the natural environment and has a high radiation resistance, was taken as a model; at that, various amounts of natural radium isotopes were introduced.

Experimental

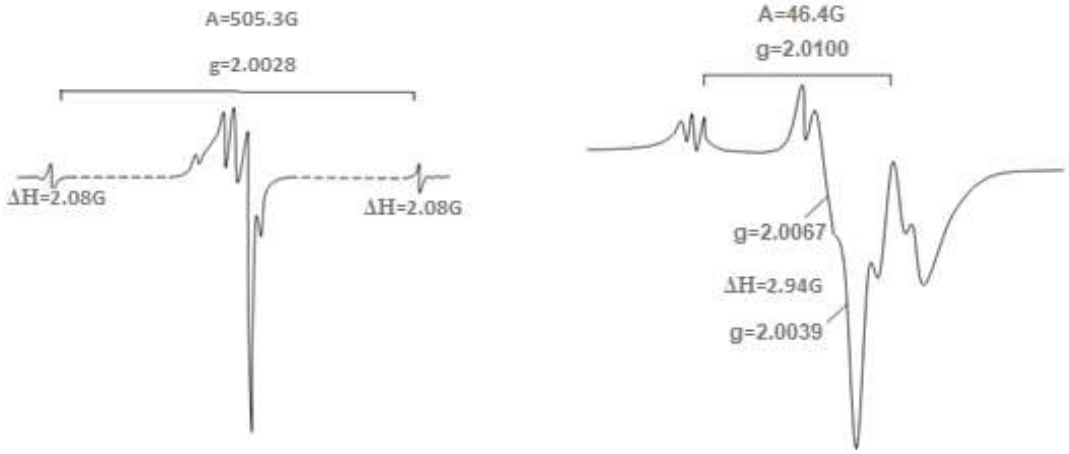
The radium-silicate samples with size ≥20 μm were prepared and filled into thin-walled "LUCH" glass ampoules, sealed and vacuumed up to 10^{-2} Pa. The samples were irradiated for 5, 10, 15 hours at a temperature of 77K using a ^{60}Co isotope source with a dose rate of D=0.38 Gy/s). Measurements were made before and after influence of radiation at liquid nitrogen and room temperature, using an EMX Plus, Bruker. For more accurate determination of the spectra, the spectrum accumulation method was used to increase the signal/noise ratio. The Cr^{3+} in ruby single crystals as reference sample was used to determine the number of paramagnetic centers. The EPR spectrum of the reference sample at room and liquid nitrogen temperatures was taken and a two-step integration process was performed, and the amount of paramagnetic centers (N_x) was calculated by the following formula :

$$\frac{N(x)}{N(etalon)} = \frac{S(x)\cdot Q(et)}{S(et)\cdot Q(x)};\quad [N] = \frac{N(x)}{\Delta m};\ N(x) = N(etalon)\cdot\frac{S(x)\cdot Q(et)}{S(et)\cdot Q(x)}$$

where, N(x) is the number of paramagnetic center in the samples with mass Δm, S(x), S(et) numerical values of the areas under the absorption curve of the test and reference samples, respectively, and Q(x), Q(et) - correction coefficients for the test and reference samples, respectively.

Results and discussion

The EPR spectrum of the sample $(RaO)_x(SiO_2)_y$ registered at 77 K is presented in Fig.1.



a) b)

Fig.1. EPR spectrum at T=77K of irradiated for 15 hours $(RaO)_x(SiO_2)_y$ sample contacted with water (the activity A = 6100 Bk/g; mass of sample was $4*10^{-2}$ g) (a); central part of this spectra (b).

The EPR spectrum shown in Fig.1 consists of the superposition of a clearly distinguished doublet belonging to the EPR spectrum of hydrogen atoms and a number of signals in the central part of the spectrum. The recorded EPR spectrum of hydrogen atoms is characterized by g– factor =2.0028 and hyperfine splitting constant $A(H^{\bullet}) = 505.3$ G. The width of each hyperfine component of the EPR spectrum of hydrogen atoms is $\Delta H = 2.08$ G. The central part of the EPR spectrum (Fig.1,b) consists of the superposition of, at least, two signals. The main paramagnetic particles in γ- irradiated silicon dioxide at 77K are exactly atomic hydrogen and can be hole $(\equiv Si\text{-}O)^{+}$ and electronic $(\equiv Si\text{-})^{-}$ centers. The total amount of these paramagnetic centers is approximately more than 60% of the total amount of paramagnetic centers. When the irradiated samples are heated, the main part of atomic hydrogen is oxidized to the $HO_2^{\bullet}$ radical, and a part of the $H^{\bullet}$ atoms participate in the reactions of radiation hydrogenation of the surface with the formation of hydrogen-containing radicals. In the process of radiolysis, during the homolytic dissociation of water molecules located in the pores of silicon dioxide and its surface, two paramagnetic particles - a hydrogen atom and a hydroxyl radical are formed:

$$H_2O \quad -\gamma\text{- irradiation} \rightarrow \quad H^{\bullet} + {}^{\bullet}OH$$

However, the EPR spectrum of the hydroxyl radical was not detected in any radiolyzed SiO_2 matrix. According to [6], $HO^{\bullet}$ was highly reactive and its EPR spectrum cannot always be recorded due to the degenerate orbital state. Fig. 2 shows the dependence of the concentration of paramagnetic centers as a function of irradiation time.

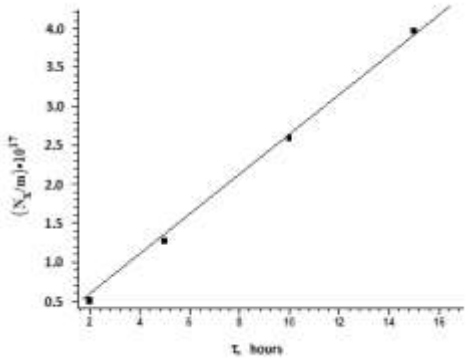


Fig. 2. Dependence of the concentration of paramagnetic centers in the $(RaO)_x(SiO_2)_y$ with adsorbed water due to the central part of the EPR spectrum shown in Fig. 1 on the irradiation time (D = 0.38 Gy/sec, T=77 K)

As can be seen from Fig. 2, the concentration of paramagnetic centers belong to the central part of the EPR spectrum which, as shown in Fig.2, increases as the irradiation time of the sample increases. It is assumed that under the effect of gamma irradiation the electron and hole centers are formed and these formed centers interact with adsorbed water according to the following scheme [7,8]:

$$(RaO)_x(SiO_2)_y \rightarrow (RaO)_x(SiO_2)_y + n + p$$
$$n + L_A \rightarrow L_n$$
$$P + L_D \rightarrow L_P$$

$$H_2O_s+p\rightarrow H_2O_s^*$$
$$H_2O_s+e\rightarrow H_2O_s^*\rightarrow H+OH$$
$$H+S\rightarrow H_s$$
$$OH+S\rightarrow OH_s$$

where L_A, L_D, Ln and L_P are free electrons and holes and their localized states (lines b and c in the EPR spectrum), H, OH, Hs and OHs are hydrogen and hydroxyl groups and their localized states.

Conclusion

The paramagnetic centers in γ- irradiated at 77K samples $(RaO)_x(SiO_2)_y$ were identified and the dependences of the concentration of these centers as a function of the irradiation time was studied. It was suggested that the main part of atomic hydrogen is oxidized to the $HO_2^{\bullet}$ radical, and a part of the $H^{\bullet}$ atoms participate in the reactions of radiation hydrogenation of the surface with the formation of hydrogen-containing radicals during the heating from 77K to room temperature of the irradiated samples. The formation of OH radicals is also suggested on the surface of γ- irradiated at 77K $(RaO)_x(SiO_2)_y$ samples.

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SU İLƏ ADSORBSİYA OLUNMUŞ, QAMMA ŞÜALANMANIN TƏSİRİNƏ MƏRUZ QALAN $(RaO)_x(SiO_2)_y$ SİSTEMİNDƏ PARAMAQNİT MƏRKƏZLƏRİN TƏDQİQİ

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Xülasə: 77K temperaturda γ-şüalmaya məruz qalmış $(RaO)_x(SiO_2)_y+H_2O$ sistemində EPR spektroskopiya metodundan istifadə edərək tədqiqatlar aparılmış və g = 2.0028 və ifrat incə quruluşlu A(H) = 505.3 G olan hidrogen atomlarına məxsus olan EPR spektri müəyyənləşdirilmişdir. Eynu zamanda spektrin mərkəzi hissəsi tədqiq edilərək paramaqnit deşik (≡Si-O)+ və elektron (≡Si-)- mərkəzlərinə aid edilən və onların su molekulları spektrləri ilə qarşılıqlı təsir məhsulları qeydə alınmışdır. Müəyyən edilmişdir ki, atomar hidrogeninin əsas hissəsi HO_2• radikalına oksidləşir və H• atomlarının bir hissəsi isə şüalanmış nümunələrin 77 K-dən otaq temperaturuna qədər qızdırıldıqda səthi radiasiyalı hidrogenləşmə reaksiyalarında iştirak edərək hidrogen tərkibli radikallar əmələ gətirir.

Həmçinin müəyyən edilmişdir ki, 77 K temperaturda $(RaO)_x(SiO_2)_y$ nümunələrində γ-şüalanmanın təsirindən nümunələrin səthində •OH radikalları əmələ gəlir.

Açar sözlər: $(RaO)_x(SiO_2)_y$ sistemi, γ-şüalanma, Elektron Paramaqnit Rezonans (EPR) metodu, elektron və deşik mərkəzləri.

ПАРАМАГНИТНЫЕ ЦЕНТРЫ В ГАММА-ОБЛУЧЕННЫХ ОБРАЗЦАХ (RaO)x(SiO2)y С АДСОРБИРОВАННОЙ ВОДОЙ

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Аннотация: С использованием метода ЭПР исследованы γ-облученные при 77 К образцы (RaO)x(SiO_2)y с адсорбированной водой и идентифицирован спектр ЭПР с g=2.0028 и константой сверхтонкого расщепления A(H)=505.3 Гс, принадлежащий атомам водорода. Зарегистрированы спектры ЭПР, приписанные, предположительно, парамагнитным дырочным $(≡Si-O)^+$, электронным (≡Si-)-центрам и продуктам их взаимодействия с молекулами воды. Высказано предположение, что основная часть атомарного водорода окисляется до радикала $HO_2^{\bullet}$, а часть $H^{\bullet}$ атомов участвует в реакциях радиационного гидрирования поверхности с образованием водородсодержащих радикалов при нагреве облученных образцов от 77 К до комнатной. температуры. Предполагается также образование радикалов •OH на поверхности γ-облученных при 77 К образцов $(RaO)_x(SiO_2)_y$.

Ключевые слова: *оксидная система (RaO)x(SiO_2)y, γ-излучение, электронный парамагнитный резонанс, атом аодорода, дырочные и электронные центры*