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Effects of molecular hydrogen on low-intensity UV photochemistry of germanosilicate glasses.

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Abstract

The one-quantum photo-reactions of oxygen deficient centers (GODC) in H_2 loaded germanosilicate preforms and fibers are studied using time-resolved photo-luminescence and ESR spectroscopy.

Effects of molecular hydrogen on low-intensity UV photochemistry of germanosilicate glasses.

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Introduction.

Germanosilicate glasses are known to posesses photorefractive (photosensitive) properties [1], that allows to fabricate refractive index gratings in germanosilicate optical fibers [2]. Hydrogen loading silica and germanosilicate glasses enhances its photosensitivity significantly [3-6]. Since the germanium-oxygen deficient center (GODC) is the main photosensitive defect in germanosilicate glasses, it is of particulary importance to reveal the role of molecular H_2 in the processes of GODC phototransformation. In this work, we study the influece of molecular hydrogen impregnated into the glass network on the triplet decay time τ_T, luminescence intensity (T_1 - S_0, λ_{max}=397 nm) and efficiency of GODC photodecay when excited with low-intensity UV light.

Experimental.

The triplet lunminescence kinetics was recorded as follows. The pulse radiation of nitrogen laser (λ=337 nm, $\tau_{pulse}=10^{-8}$ s, f=100 Hz) was focused on preliminary cleaned optical fiber, the maximum irradiation density was 0.23 J/cm^2. A peace of the fiber to be irradiated was fixed in a thermostate with variable temperature (from 90 to 600 K).

In measurements of temperature dependence of triplet photoluminescence intensity I_T for GODC excited into the singlet absorption band (transition S_0-S_1), we used the same apparatus, but with a deuterium lamp serving as a source of irradiation. Besides, for the high- and low-intensity UV irradiation the KrF excimer laser has been used.

All the optical fibers studied were drawn from preforms produced by the MCVD method. For ESR measurements the MCVD germanosilicate films were used.

The fibers ans films were treated in a hydrogen atmosphere at room temperature in a chamber under a gas pressure of 24 atm for 2 weeks. The hydrogen concentration was about $5x10^{19}$ cm^{-3} in the core of single mode fiber and $3x10^{19}$ cm^{-3} in the film.

The ESR measurements of irradiated samples were performed with RE-1306 radiospectrometer working in the X-range (f=9.4 GHz).

Results and Discussion.

The presence of molecular hydrogen in the network of germanosilicate glass strongly affects the temperature dependences of the decay time of the excited state T_1. Figure 1a displays the temperature dependences of τ_T for the unloaded (curves 1-3) and H_2-loaded (curves 4) optical fibers with various GeO_2 concentratios in fiber core. Measurements were carried out routinely for a week. As hydrogen escapes from the fiber core, i.e., with a decrease in the hydrogen concentration, the curves 4 $\tau_T(T)$ become similar in shape to curve 1-3 for the hydrogen-free sample.

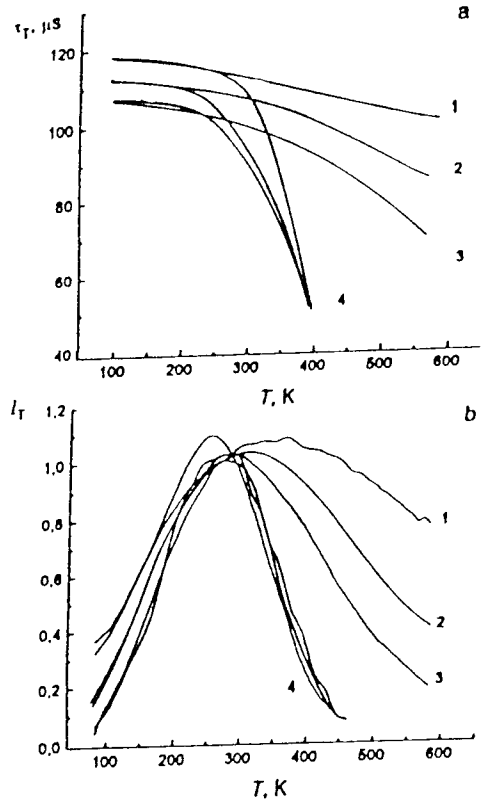

Fig.1. Temperature dependences of triplet life-time (a) and intensity of tiplet luminescence (b) in fibers with 2.3 (1),11(2) and 23 mol.% GeO_2 (3); H_2-loaded fibers (4).

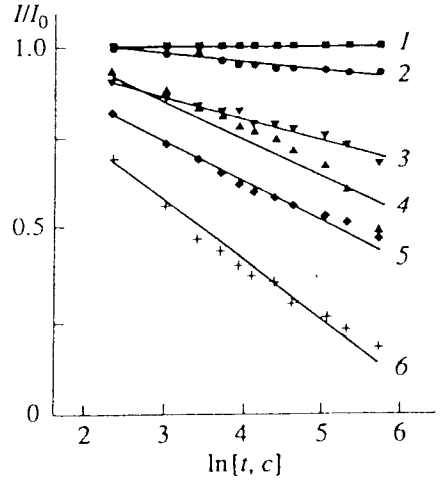

Fig.2.Dependence of the intensity of triplet photoluminescence in fiber with 23 mol.% GeO_2 on the laser irradiation dose (λ=337 nm) at fixed irradiation temperatures T, K: (1) 290, (2) 390 and (3) 480 for the initial samples; and (4) 90, (5) 290, and (6) 390 for H_2-loaded samples.

Such a decrease in the decay time τ_T in optical fibers saturated with hydrogen should manifest itself in the dependences $I_T(T)$, specifically at temperature higher than room temperature. Indeed, comparison of curves 1-3 and 4 in fig.1b shows that, at all germanium concentrations, the presence of molecular hydrogen in glasses leads to a strong decrease in $I_T(T)$ with temperature. The maximum of hydrogen effect on $I_T(T)$ appears in the fiber at the minimum GeO_2 concentration, and eventually the high-temperature wings of curves 4 in Figs.1a and 1b turn out to be close to each other. This indicate that the presence of hydrogen molecules at high concentration almost completely determines the temperature behavior of the intensity of triplet photoluminescence of GODC, irrespective of the germanium concentration.

From our viewpoint, the results obtained from the hydrogen-contaning fibers are explained by the participation of H_2 in photochemical reactions of GODC in the excited T_1 state. Note that the efficiency of these reactions increases with an increase in temperature of irradiation samples. We observed an increase in the efficiency of GODC decay in the H_2-loaded samples, which is a direct confirmation of the above reactions. The experimental data for hydrogen-containing samples with 23 mol.% GeO_2 show photodecay efficiency of GODC considerably increases with an increase in the irradiation temperature. This manifests itself in a rise of the slope of the $I_T(lnt)$ dependences as the irradiation temperature increases (Fig.2).

It is seen from Fig.2 that no decay of GODC occures in the hydrogen-free samples at room temperature and only at T>300 K, the efficiency of decay markedly increases. For H_2-loaded samples, the photodecay of GODC occurs even at temperature close to that of liquid nitrogen (Fig.2, curve 4); i.e., H_2 molecule interact with electron-excited GODC even at 90 K. No such effect is observed in similar processes in pure silica glasses [3]. This is caused by the fact, at liquid nitrogen temperatures, the diffusion of H_2 molecules over the network of amorphous SiO_2 appears to be "frozen", and at

rather small concentration of silicon ODC (10^{16} cm^{-3}), their nearest environment $r<10^{-8}$ cm does not exhibit H_2 molecules at the instant of photoexcitation. An estimated concentration of GODC in germanosilicate glasses is as high as 10^{19}-10^{20} cm^{-3}. Because of excitation migration over GODC, there can appear some chance for frozen H_2 molecules to be located in the nearest environment of GODC excited in T_1 state. It is quite probable that the presence of hydrogen in the immediate vicinity of the excited center affects the efficiency of its decay.

The activation energy of the photodecay of the GODC was estimated from the experimental dependences $\tau_T(T)$ and $I_T(T)$ for the initial and H_2-loaded optical fibers. The activation energies E_a^{τ} and E_a^{I} odtained from Arrhenius dependences $ln[1/\tau_T^{H}-1/\tau_T]$ and $ln[I_T/I_T^{H}-1]$ as functions $1000/T$ are given in table:

C, mol.% GeO_2	E_a^{τ}, eV	E_a^{I}, eV	E_a^{R}, eV
2.3	0.37±0.05	0.36±0.05	0.03
11	0.22±0.05	0.36±0.05	0.05
23	0.25±0.05	0.37±0.05	0.05

The activation energy of the reaction of GODC with hydrogen E_a^{R} can roughly be estimated from the experimental dependences of photodecay of GODC by analysis of their initial portions at the temperatures of 290 and 390 K (see Fig.2 and table).

One could expect the coincidence of activation energies E_a^{τ}, E_a^{I} and E_a^{R}, becaise in principle, they describe the same physical process: the interaction of molecular hydrogen with GODC in the metastable triplet T_1 state. In our opinion, the activation energy E_a^{τ} obtained from the temperature dependences of T_1 state life time is closest to the realistic value. It is noteworthy that the activation energy E_a^{R} obtained from measurements of the photodecay yield is significantly less than E_a^{τ} and E_a^{I}. This is because the E_a^{R} quantity is representative of some overall process in which the recombination (including both photo-stimulated processes and those after pulse), leading to the recovery of GODC, plays an important part. In addition, these processes are termally activated.

It is known that at high-intensity laser irradiation of H_2-loaded silica glasses (two-quantum photochemisrty of ODC) the passivation with hydrogen of laser induced radicals takes place [3]. The same situation is realized for germanosilicate glasses at $F>$ 200 mJ/cm^2. Some of laser induced Ge(n) radicals interacts with H_2 molecules, creating a new stable optically unactive products.

The low-intensity UV irradiation (Hg-lamp; KrF laser, F=2 mJ/cm^2) of GODC leads to formation of paramagnetic Ge(n) and H(II) centers as well. In contradistinction to the case of high-intensity laser irradiation the contribution of Ge(3) centers in total concentration of Ge(n) is increased, but the value [Ge(n)]/Δ[GeOGC] is decreased. Thus, the one-quantum photoreactions of triplet excited GODC with H_2 molecules gives quite different composition of paramagnetic products.

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