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Effects of Ge concentration on one-quantum UV photo-reactions of oxygen deficient centers in germanosilicate glasses

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ABSTRACT

The effects of Ge concentration, spectroscopical and photochemical inhomogeneity on GODC photochemistry in germanosilicate fibers and preforms are established and their mechanisms are discussed.

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Introduction.

Germanium oxygen deficient centers (GODC) in germanosilicate glasses play a key role on the photosensitive effect in optical fibers [1]. Both one-quantum [2] and two-quantum [3] photo-reactions of GODC can occur, but the mechanisms and role of these reactions are far from clear. We report here the results of studies of one-quantum UV photo-processes in germanosilicate fibers and preforms. The effects of Ge concentration, UV light frequency, sample temperature, spectroscopic and photochemical inhomogeneity on one-quantum photo-reactions of GODC are revealed and discussed.

Experimental

To provide a singlet-singlet (S_0 -S_1) photo-excitation of GODC, we have used the KrF excimer laser pulses (λ=248 nm, τ_p=20 ns), UV light from Hg lamp with strong 254 nm line , and narrow-band UV light ($\Delta\lambda$=3 nm) from D_2 lamp selected between 220 nm and 260 nm. A double luminescence spectrometer has been used for spectral luminescent studies. The time-resolved photo-luminescence signals have been measured with photo-multiplier and transient digitizer.

Results

Decomposition of germanosilicate samples by UV light from KrF lasers and UV lamps results in a decrease of GODC UV absorption at 242 nm (Fig1). In all cases the non-exponential kinetics of GODC photo-decomposition take place (Fig.2). The yield of photo-reaction *Y* grows with GeO_2 concentration dramatically (Table 1). Similar results were obtained with fibers, and, also, when preforms or fibers have been irradiated with KrF laser pulses at low fluences F<20 mJ/cm^2.

To reveal the effect of spectral inhomogeneity of GODC [4] on their photochemistry, we have measured the change of shape of absorption band after photo-decomposition of GODC with different wavelength. Table 2 demonstrates a correlation between peak wavelength in subtracted UV absorption spectrum and irradiation wavelength.

Table1.

% GeO_2	2.3	3.8	6.8	10.2	16.3
Y	0.015	0.030	0.070	0.17	0.5

Table 2.

λ_{exc} (nm)	239.5	241.0	242.0	243.0	246.0	248.0
λ_{subt}^{max} (nm)	240	241.2	242.0	242.3	242.6	243.0

UV irradiation of S_1 state of GODC (Fig.1) gives two luminescence bands: singlet (S_1 - S_0) band with λ_{max} at 293 nm and $\Delta\lambda$=37 nm (FWHM bandwidth); triplet (T_1 -S_0) with λ_{max}=398 nm and $\Delta\lambda$=61 nm. At the same time, the direct excitation of T_1 state gives the only triplet band. Curves 2 and 3 in Fig. 1 demonstrate the excitation spectra of singlet and triplet luminescence respectively. Both these bands are long wavelength shifted with respect to UV absorption band (curve 1).

The photo-decay of GODC causes degradation of intensity of photo-luminescence. We have used this effect to measure the relative yield of photo-decomposition of GODC in fibers. Curve 4 at Fig.1 shows, that the shorter is the wavelength of UV irradiation, the higher is the quantum yield of GODC photo-decomposition (yield being the probability of GODC photo-decomposition per one absorbed UV photon).

The temperature plots of I_T (Fig.4) are different for the fibers with different GeO_2 concentration.

Fig.4 shows the results of our measurements of τ_T traces for GODC excited with KrF laser. All these traces are non-exponential, and τ_T increases with wavelength.

Discussion

Spectral inhomogeneity of GODC. Spectral inhomogeneity [5] of GODC absorption band is confirmed, firstly, by the fact (see Table 2), that the maximum of subtracted absorption spectrum of GODC (before and after UV irradiation) is dictated by the wavelength of UV light. The results of our triplet life-time measurements (Fig.4, curve 2), give the direct indication to the inhomogeneity of triplet luminescence band. Indeed, the non-exponential $I_T(t)$ traces are caused by the contribution of different GODC groups with slightly different triplet levels and life-times. The observed shortening of τ_T, with wavelength is caused by the $1/\lambda^2$ factor for the probability of T_1-S_0 transition [6].

Photochemical inhomogeneity. The effect of photochemical inhomogeneity of GODC is demonstrated on Fig. 1 (curve 4). The highest quantum yield of photo-reaction has been observed at short-wavelength side of the UV absorption band. This corresponds to the photo-excitation of GODC with the highest E_T. It is clear, that in the case of homogeneous absorption band, the quantum yield should be the same for all excitation energies.

Non-exponential decay of GODC. In our opinion, the spectral and photochemical inhomogeneity of GODC plays the key role for the effect of non-exponentially observedon Fig.2. The decay curve of the whole ensemble of GODC can be described as follows

$$N(D)=\Sigma N_i \exp[-\sigma_i(\nu)\, D\, \phi_i/h\nu], \qquad (1)$$

where N_i, σ_i and ϕ_i are the concentration, absorption cross-section and quantum yield of photo-reaction for *i*-th sub-group of GODC in ensemble. Both dispersion in $\sigma_i(\nu)$ and dispersion in ϕ_i contribute to non-exponential dependence (1). The specific $N(D)$ plot will be controlled by N_i, σ_i and ϕ_i distributions over different GODC groups and, also, by photo-excitation wavelength.

Effects of GeO_2 concentration. The observed effect of GeO_2 concentration (Table 1) allows to conclude, that the presence of Ge in the coordination sphere of GODC is important for the irreversible GODC photo-reaction. In [7] the mechanism of electron tunneling from long-lived triplet state to the states of impurities was considered for one-quantum photo-reaction of SODC in silica glasses. According to [7], the strong effect of Ge concentration observed, is caused by increasing probability of electron tunneling from T_1 state of GODC to electronegative Ge^{4+} with GeO_2 concentration.

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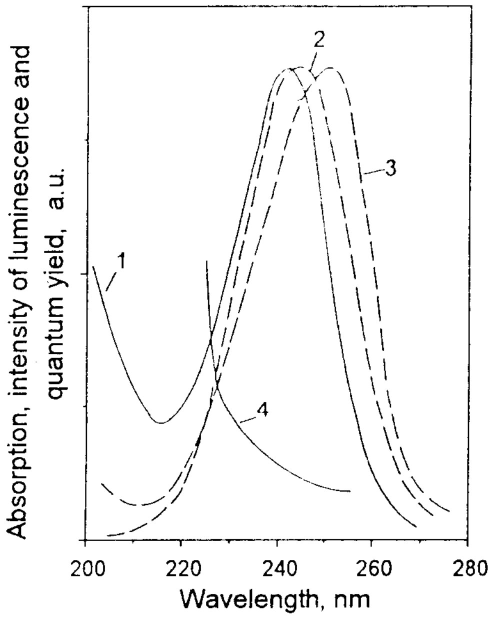

Fif.1. Absorption spectrum (curve 1), triplet luminescence excitation (curve 2) and singlet luminescence excitation (curve 3) spectra for GODC in germanosilicate glass; curve 4 - relative quantum yield of GODC UV photo-reactions.

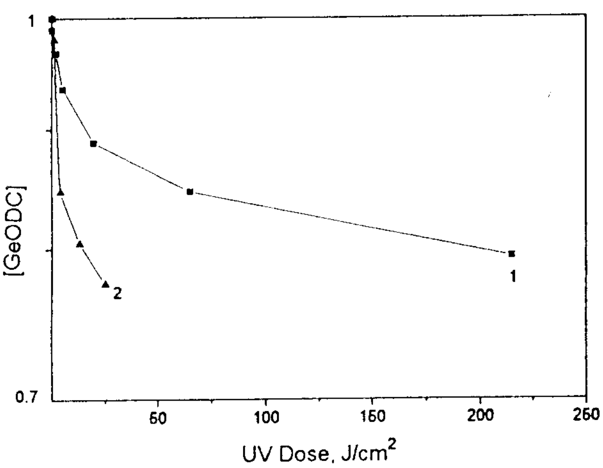

Fig.2. Concentration of GODC in germanosilicate preform (logariphmic scale) as a function UV light dose (10.2 mol.% GeO_2):
curve 1 - KrF laser irradiation, F= 15 mJ/cm²;
curve 2 - Hg lamp irradiation, I= 5 mW/cm².

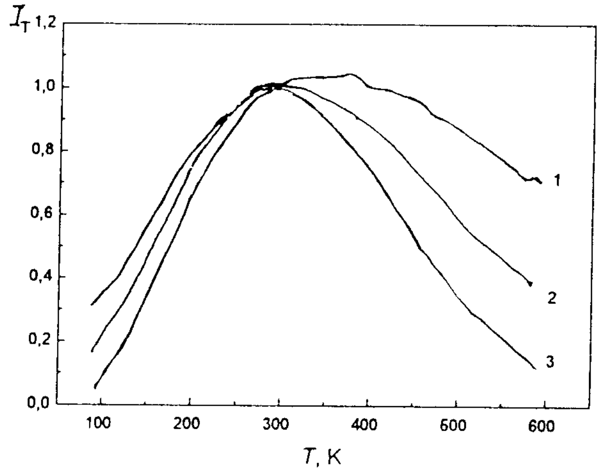

Fig.3. Integral intensity of triplet luminescence as a function of germanosilicate fiber temperature for different GeO_2 concentration in fiber (λ_{exc}=242 nm).

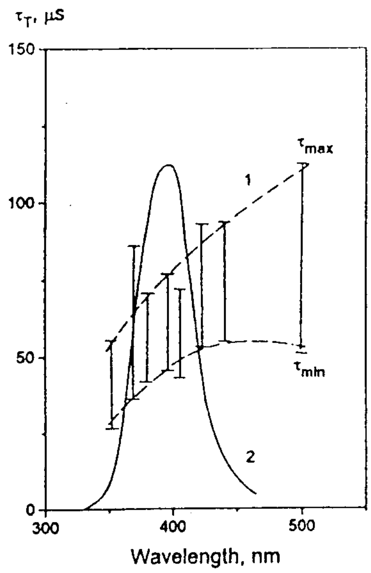

Fig.4. Triplet life times as a function of wavelength of triplet luminescence for germanosilicate fiber with 11 mol.% GeO_2 (λ_{exc}=248 nm); τ_{min} - corresponds to the begining of trace, while τ_{max} - to $1/e^2$ level; curve 2 - spectrum of triplet luminescence of GODC.