Efficient photobleaching of 390-nm luminescence in germanosilicate preforms by the third harmonic of a Nd:YAG laser

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Permanent photobleaching of blue luminescence with a maximum at ~390 nm in Ge-doped fiber preforms by exposure to the third harmonic (354 nm) of a Nd:YAG laser has been observed. The experimental results show that photodestruction of a germanium oxygen-deficient center can occur without photoionization. © 1996 Optical Society of America

The effect of photosensitivity of doped silica glasses and optical fibers has attracted much attention. Particular interest has been concentrated on the study of Ge-doped silica glass. The photosensitivity of this glass is due to GeO\textsubscript{2}-deficient centers (GODC’s).\textsuperscript{1,2} These centers are associated with a strong absorption band with its maximum at ~5 eV (~240 nm, singlet–singlet \textit{S}_0–\textit{S}_1 transition), a weak absorption band with its maximum at ~3.7 eV (~330 nm, forbidden singlet–triplet \textit{S}_0–\textit{T}_1 transition), and blue triplet–singlet \textit{T}_1–\textit{S}_0 luminescence with its maximum at ~3.1 eV (~390 nm) (see Fig. 1). Optical excitation of the 5-eV band results in GODC photodestruction and bleaching of the band. The resulting index change is correlated with a decrease of blue luminescence.\textsuperscript{3,4}

The accepted mechanism of GODC photodestruction consists of one-photon photoionization of this defect during 5-eV \textit{S}_0–\textit{S}_1 excitation. This mechanism is confirmed by investigations of color-center formation\textsuperscript{1} and direct photoconductivity measurements.\textsuperscript{5} The excitation of forbidden transition \textit{S}_0–\textit{T}_1 also results in 3.1-eV blue luminescence.\textsuperscript{1,2} However, during this excitation efficient coloration of the glass, which corresponds to one-photon ionization, is not observed. The typical color-center formation with low efficiency and bleaching of the 240-nm band was ascribed to a multistep process with participation of the triplet state.\textsuperscript{6}

The excitation of Ge-doped silica glass with 5-eV photons has an essential influence on the glass’s properties. An increase of photoinduced second-harmonic generation (SHG) in glass exposed to the fourth harmonic of a Nd:YAG laser (\(\lambda = 266\) nm) has been reported.\textsuperscript{7} It was found that an increase in photoinduced SHG is connected with excitation of color centers with a 10 ns \(<\tau<<1 \text{ ms} \) characteristic lifetime. It was supposed that the effect of UV radiation on photoinduced SHG is connected with the color center that is responsible for blue luminescence. The permanent increase in photoinduced SHG by UV argon laser exposure (\(\lambda = 351\) nm) and by exposure to the third harmonic (TH) of a Nd:YAG laser was also observed.\textsuperscript{8} The reported investigations of the photoinduced SHG increase in UV irradiation power have supposed the one-photon process. This result is surprising, because UV radiation in the 350-nm region can excite only the singlet–triplet transition, which does not produce one-photon ionization of GODC’s and does not form the typical color centers that result from 5-eV excitation.\textsuperscript{1} Therefore investigation of the processes that take place after excitation of the triplet state is very important for a consistent model of GODC defects.

In this Letter the influence of UV excitation of the Nd:YAG laser TH (\(\lambda = 354\) nm) on blue luminescence in Ge-doped fiber preforms is reported. The experimental setup is shown in Fig. 2. The radiation of the Nd:YAG Q-switched (4-kHz repetition rate) and mode-locked (pulse duration \(~400\) ps) laser was frequency doubled in a KTP crystal, and then the fundamental-frequency and the second-harmonic radiation were mixed in the KDP crystal to produce the TH radiation. The TH radiation was then separated from the fundamental-frequency and the second-harmonic radiation by a prism, a diaphragm, and a UV color filter. Then the UV radiation was focused into 500-\(\mu\)m-thick fiber preform samples by a 2.5-cm-focus fused-silica lens. Modified chemical-vapor deposition fiber preforms with 8% and 20% GeO\textsubscript{2} were investigated. The focusing of the UV radiation into the samples resulted in intense blue luminescence, which was collected by a 10-mm- or a 30-mm-focus lens.

Fig. 1. Schematic diagram of the transitions and energy levels of a GODC. The excitation of the singlet–singlet \textit{S}_0–\textit{S}_1 transition by a 5-eV photon is followed by photoionization or nonradiative relaxation to triplet state \textit{T}_1 and blue ~3.1-eV luminescence. The excitation of forbidden singlet–triplet \textit{S}_0–\textit{T}_1 transition also results in blue luminescence. CB, conduction band.
Then the blue luminescence signal was separated by glass color filters or by an interference filter with a 16-nm bandwidth and a transmitting maximum at 405 nm. The luminescence signal was registered by a photomultiplier or a TV camera. The measured relaxation time of luminescence was \( \sim 100 \mu s \), which corresponded to excitation of the GODC triplet state.

The time dependencies of the luminescence signal were also studied. It was found that TH exposure results in a permanent decrease in the luminescence intensity. The typical dependencies of the signal relaxation for fiber preforms with 8% and 20% GeO\(_2\) are shown in Fig. 3. During long UV exposure (>10 min) a decrease of the signal by three times in the 20% GeO\(_2\) fiber preform was obtained. The displacement of the sample after the bleaching procedure resulted in increased luminescence intensity, and the bleached region could be easily identified by the minimum of luminescence. This displacement was used for the estimation of the bleaching area size and the UV bleaching intensities.

For elucidation of the bleaching mechanism the dependence of relative bleaching on UV intensity at the initial stage \( t = 100 \, \text{s} \) was studied. The obtained results for the 8% GeO\(_2\) fiber preform is shown in Fig. 4. The close-to-linear dependence at low UV intensities favors the one-photon bleaching mechanism, as in previous experiments on photoinduced SHG in Ge-doped optical fibers, but it can be also explained by a two-photon process with saturation of the intermediate \( T_1 \) state. The stationary value for cw radiation of saturation TH intensity \( I_s \) can be obtained with

\[
I_s = h\nu/2\sigma\tau,
\]

where \( \sigma = \alpha_{\text{TH}}/N_{\text{GODC}} \) is the absorption cross section \( \alpha_{\text{TH}} \) is the absorption and \( N_{\text{GODC}} \) is the concentration of GODC’s), \( h\nu \) is the TH photon energy, and \( \tau \) is the relaxation time of the triplet state. In accordance with the available data for a molecular chemical-vapor deposition fiber preform with a 10-mol. % GeO\(_2\) concentration, \( N_{\text{GODC}} \sim 10^{19} \, \text{cm}^{-3} \), \( \alpha_{\text{TH}} \sim 10^{-2} \, \text{cm}^{-1} \), and \( \tau \sim 10^{-4} \, \text{s} \). In this case the estimation of TH stationary saturation intensity \( I_s \) gives the value \( 3 \times 10^6 \, \text{W/cm}^2 \). Mention should be made of the fact that the intensity required for the saturation state is greater for the pulsed radiation than the stationary value \( I_s \). The peak experimental bleaching intensities were approximately an order of magnitude greater than \( I_s \). For this case the transitional process of saturation will have the time constant \( \sim \tau/10 = 10^{-5} \, \text{s} \). The duration of the \( Q \)-switched batch was \( 3 \times 10^{-7} \, \text{s} \), or 2 orders of magnitude smaller than required for the saturation of the \( T_1 \) state with the intensity used. The time delay between \( Q \)-switched batches was \( 2.5 \times 10^{-4} \, \text{s} \), which corresponded to a decrease in the triplet-state population by more than an order of magnitude. It becomes evident that for the experimental conditions that existed the saturation of the triplet state can be neglected, and the obtained linear dependence of relative bleaching on the TH bleaching intensity favors the true single-photon process.

To obtain further experimental confirmation of the conclusion about one-photon photodestruction of GODC’s by triplet excitation we have qualitatively compared the obtained results with UV bleaching by cw radiation. In this experiment a cw argon laser, which was operating in the multiline (333–364-nm) regime, was used as a UV source, analogous to a pulsed UV bleaching setup. For 25 mW of UV power \( (\sim 3.5 \, \text{kJW/cm}^2) \) relative bleaching of \( \sim 35\% \) in the 8% GeO\(_2\) fiber preform for 100 s of irradiation time was obtained. The test experiment performed with continuous UV radiation therefore has shown that the bleaching of blue luminescence by bleaching excitation is dependent mainly on the total UV fluence.

![Fig. 2. Experimental setup for investigations of blue luminescence bleaching by a Nd:YAG laser TH. QS, Q-switched; ML, mode locked; UVF, UV-transmitting filter; BLF, blue-light-transmitting filter.](image)

![Fig. 3. Time dependencies of the blue luminescence signal for a molecular chemical-vapor deposition fiber preforms with GeO\(_2\) concentrations of 8% and 20%. The bleaching time is 100 s. The peak TH average power is 20 mW.](image)

![Fig. 4. Dependence of blue luminescence relative bleaching on the TH average power for the 8% GeO\(_2\) fiber preform. The bleaching time is 100 s. The peak TH intensity for 20 mW is 30 MW/cm\(^2\).](image)
Because the excitation of the triplet state is not followed by photoionization,\(^1\) a conclusion about GODC photodestruction without photoionization can be made. This photodestruction can be the result of structural rearrangement\(^9\)–\(^11\) that is activated by the excited triplet state.\(^9\) In accordance with estimations based on experimental data, during the singlet–singlet excitation of GODC more than 95\% of the excited centers reach the triplet state because of nonradiative transition.\(^12\) These data give us reason to state that the experimentally demonstrated photodestruction process of GODC’s from the excited triplet state that is presented above is at least one of the possible channels of GODC photodestruction, which are responsible for photosensitivity of Ge-doped silica glass. Then more convenient sources in the near-UV region can be used for processing of photosensitive optical fibers.

The experiments with direct excitation of the triplet state are interesting in view of a consistent model of GODC photodetection. It has been suggested that the 5-eV absorption band is composed of two components, namely, a photosensitive component with a peak at 5.06 eV and a full width at half-maximum of 0.38 eV and a stable component with a peak at 5.16 eV and a full width at half-maximum of 0.48 eV, which is responsible for blue luminescence.\(^13\) The reported experiments with 5-eV radiation cannot be used for selective excitation of the considered bands. At the same time, because of the bleaching of blue luminescence by ~3.5-eV UV radiation, which has to excite only the stable component, further development of this model is required.

To overcome the contradictions of blue luminescence bleaching dynamics\(^3\)–\(^4\),\(^14\) an interesting model with energy transfer between photosensitive absorbing and stable emitting species has been proposed.\(^15\) In view of our observations modification of this model is also required: the presence of 3.7-eV absorption for the absorbing species and the resonant energy transfer from this excited state of the absorber to corresponding states of emitting species should be considered. The presence of such a set of similar levels for two different defects seems improbable. Our opinion is that the model, in which different alternative and reversible methods of modification for one type of defect are considered,\(^10\) is more consistent with our observations and explains other experimental results.\(^3\)–\(^4\),\(^14\)

In conclusion, efficient photobleaching of blue triplet luminescence by the Nd:YAG laser third harmonic (TH) in Ge-doped fiber preforms is reported for the first time to our knowledge. The obtained results are explained on the basis of photochemical destruction of GODC without photoionization under singlet–triplet excitation.

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