ISSN 0030-400X, Optics and Spectroscopy, 2015, Vol. 119, No. 2, pp. 238–242. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © A.I. Ignat'ev, D.A. Ignat'ev, N.V. Nikonorov, A.I. Sidorov, 2015, published in Optika i Spektroskopiya, 2015, Vol. 119, No. 2, pp. 249–254.

CONDENSED-MATTER SPECTROSCOPY

The Influence of UV Laser Radiation on the Absorption and Luminescence of Photothermorefractive Glasses Containing Silver Ions

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Received March 19, 2015

Abstract—It is experimentally shown that irradiation of silver-containing glasses by nanosecond laser pulses with a wavelength of 248 nm leads to the formation of unstable point defects (having absorption bands in the UV and visible spectral ranges) in the irradiated region and causes the transition of ions and charged molecular silver clusters to the neutral state, which is accompanied by an increase in the luminescence intensity in the visible spectral range. The influence of pulsed laser irradiation is compared with the effect of exposure to cw UV light of a mercury lamp. Some models are proposed to explain the influence of the laser effect on the optical properties of glasses.

DOI: 10.1134/S0030400X15080093

INTRODUCTION

Photo-thermo-refractive (PTR) glasses [1, 2], which contain silver ions, a photosensitizer (cerium ions Ce^{3+}), and a reducer (antimony ions Sb^{5+}), are convenient matrices for synthesizing and studying the optical properties of silver ions, neutral atoms, and molecular clusters, as well as silver nanoparticles. In addition, heat treatment of PTR glasses may lead to the formation of a nanoscale crystalline phase on the surface of silver nanoparticles (e.g., silver and sodium bromides and sodium fluoride); this process is used to record bulk phase holograms [3, 4]. Changing the chemical composition of glass, as well as UV irradiation or heat treatment conditions, one can control the optical properties of synthesized microcrystals and nanoparticles. For example, silver in PTR glass exists initially in the form of Ag^+ ions and molecular ions Ag_n^{m+} [5, 6]. Under UV irradiation into the absorption band of cerium ions Ce^{3+} ($\lambda = 305–315$ nm), electrons pass from cerium ions to the glass, where they can be captured by silver and antimony ions. Thus, some of atomic and molecular silver ions can be transferred to the neutral state. Subsequent heat treatment at a temperature exceeding the glass-formation temperature leads to the formation of silver nanocrystals, which have metallic properties and exhibit plasmon resonance [1]. Thus, by changing the chemical composition of the PTR glass matrix, varying the donor and acceptor concentrations and the UV irradiation dose, and choosing appropriate heat treatment conditions, one can control the optical and spectral-luminescence properties of synthesized silver microcrystals and nanocrystals in wide limits. Silver nanoparticles and luminescence centers in PTR glass can be formed either throughout the entire glass sample volume or locally.

In addition to the above-described "classical" methods for controlling the optical properties of glasses containing silver ions, there exist methods such as irradiation by X and γ rays [7, 8], femtosecond laser pulses [9, 10], and electrons [11–13]. It has been shown in some studies (see, e.g., [14, 15]) that the properties of silver-containing glasses can be modified by UV excimer laser radiation. At the same time, the mechanisms of influence of short-wavelength UV laser radiation on PTR glasses have not been comprehensively investigated to date.

The purposes of this work were to investigate the influence of nanosecond pulses of excimer KrF laser on the absorption and luminescence of PTR glasses of different compositions, compare the effect of pulsed laser radiation with the effect of cw UV light of a mercury lamp, and analyze the processes occurring in PTR glasses under the aforementioned effects.

EXPERIMENTAL

We investigated the samples of PTR glasses of the sodium–aluminum–zinc silicate system, $Na_2O–Al_2O_3–ZnO–SiO_2–NaF–NaHal$ (Hal = Cl, Br), activated with CeO_2, Sb_2O_3, and Ag_2O. The objects of study were prepared at ITMO University (St. Peters-

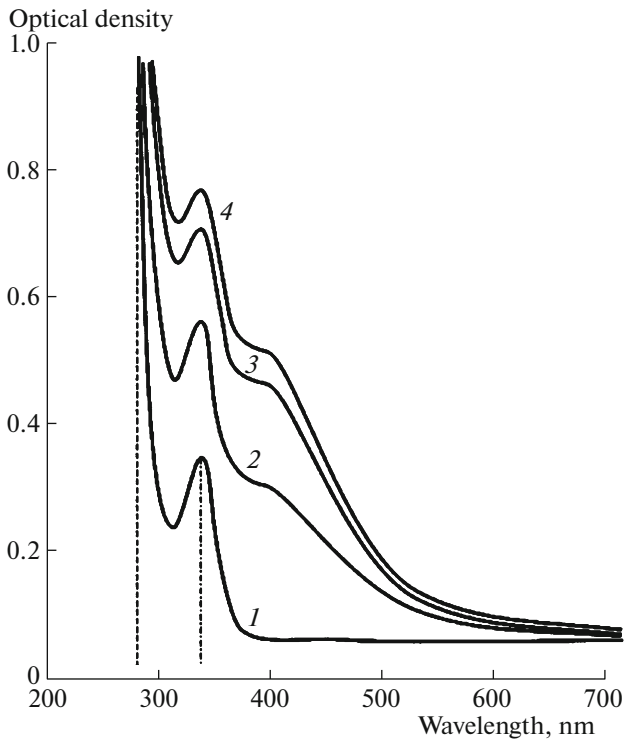

Fig. 1. Optical density spectra of sample Ag-Br (*1*) before laser irradiation and (*2–4*) after irradiation to doses of (*2*) 1.7 J/cm^2 (30 pulses), (*3*) 8.5 J/cm^2 (150 pulses), and (*4*) 17 J/cm^2 (300 pulses). The dashed and dash-dotted lines indicate the radiation wavelengths of excimer laser and high-pressure mercury lamp, respectively.

burg). In this system, cerium ions play a role of photosensitizer for λ = 305–320 nm, while antimony ions act as a reducer at elevated temperatures [1]. Glasses were synthesized in quartz or platinum crucibles at a temperature of 1450°C, and the melt was stirred by a platinum agitator during synthesis. Glass-formation temperature T_g of the samples measured with an STA 449 F1 Jupiter system for synchronous thermal analysis (Netzsch) turned out to be in the range of 475–495°C, depending on the content of fluorides in the glass.

The following types of glasses were synthesized:

(i) bromide glass with 0.006 mol % silver oxide, denoted below as Ag-Br;

(ii) chloride glass, with 0.006 mol % silver oxide (Ag-Cl-I); and

(iii) chloride glass, with 0.06 mol % silver oxide (Ag-Cl-II).

Glass samples were prepared in the form of plane-parallel plates about 1 mm thick. Irradiation was performed by 248-nm pulses of a Compex 102 excimer KrF laser (LambdaPhysik) and by cw light of a high-pressure mercury lamp (DRT-240) at room temperature. We chose UV radiation sources because the wavelength of excimer KrF laser radiation lies in the vicinity of the fundamental absorption edge of the PTR glass matrix, while the high-pressure mercury lamp has an emission band (λ = 305–320 nm) falling in the absorption band of cerium ions (Fig. 1). The laser pulse energy was 100 mJ, the pulse width was 11 ns, and the pulse repetition rate was 1 Hz. The laser beam was incident on a sample through a 3.5-mm diaphragm. The laser energy density on the sample was 56 mJ/cm^2. The laser irradiation dose, varied by changing the number of laser pulses, was in the range of 0–17 J/cm^2. The exposure to mercury lamp UV light lasted 10 min. Under these conditions, according to our estimates, the integral UV irradiation dose over the spectral range of 200–320 nm was within 1.7–2 J/cm^2. The samples with the aforementioned thickness absorb 90–99% radiation with λ = 248 nm and about 50% radiation with λ = 305 nm.

The irradiated samples were subjected to heat treatment in a Nabertherm muffle furnace. Absorption spectra were measured with a Lambda 650 spectrophotometer (Perkin-Elmer). Luminescence spectra were measured using an LS55 spectrofluorimeter (Perkin-Elmer). Spectral measurements were performed with a step of 1 nm at room temperature.

RESULTS AND DISCUSSION

The experiments showed that excimer laser irradiation of initially colorless samples makes them yellow and gives rise to a wide absorption band in the range of 270–550 nm (with a maximum near λ = 360–370 nm) in the optical density spectrum. The absorption band in the spectral range of 305–320 nm is due to the absorption of Ce^{3+} ions. Optical density spectra were measured directly after the laser irradiation. Similar dependences were obtained for samples Ag-Cl-I and Ag-Cl-II. However, the induced optical density in the spectral range of 350–380 nm for sample Ag-Cl-II exceeds that for samples Ag-Br and Ag-Cl-I by a factor of 1.8. This fact indicates a higher concentration of neutral silver microcrystals in sample Ag-Cl-II.

A long-term (10-day) exposure of the samples at room temperature led to a decrease in the induced absorption in the spectral range of 270–550 nm (Fig. 2). Note that the absorption is reduced most drastically in the range of 340–500 nm. Heat treatment of laser-irradiated PTR glasses at 300–400°C increases the reduction rate of induced absorption significantly. A similar effect was observed for glass samples Ag-Cl-I and Ag-Cl-II.

UV laser irradiation of PTR glasses with a wavelength falling in the fundamental absorption edge of the glass matrix is accompanied by break of chemical bonds in the glass network and formation of structural defects. There are several known types of point defects of silicate glass network, which lead to the formation of absorption bands in the spectral range of 210–250 nm. They include *E'* centers, having the

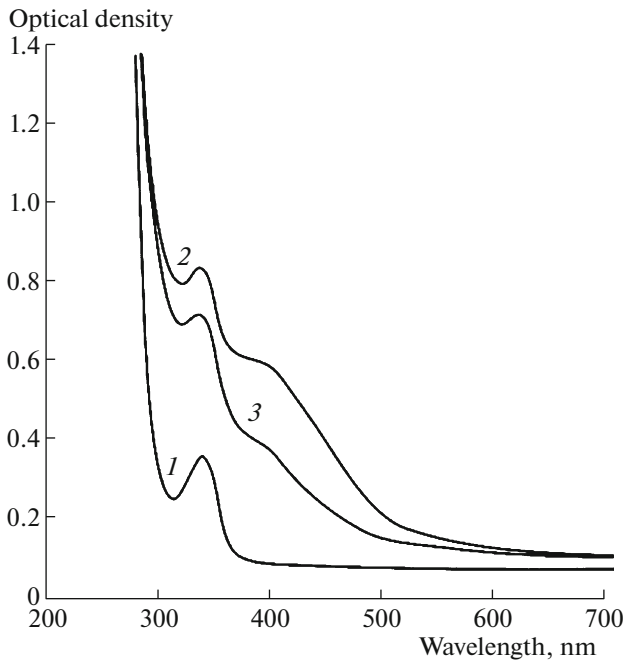

Fig. 2. Optical density spectra of sample Ag-Br (*1*) before laser irradiation, (*2*) after irradiation to a dose of 17 J/cm^2 (300 pulses), and (*3*) after a 10-days exposure at room temperature.

structure ≡Si· (from here on, the symbol "≡" indicates chemical bonds of silicon atom with three oxygen atoms, and the symbol "·" indicates a dangling chemical bond), *L* centers with the ≡Si–O$^-$–Na$^+$ or ≡Si–O$^-$–Ag$^+$ structure, *B*2 centers in the form of oxygen vacancy (≡Si–Si≡), POR (peroxide radical) centers with the ≡Si–O–O· structure, etc. [16–18]. Point defects of some types in silicate glasses lead to the formation of absorption bands in the visible spectral range. They include, e.g., the hole center formed by nonbridging oxygen (non-bridging oxygen hole center, ≡Si–O·) [16–18]. The occurrence of these defects under UV laser irradiation may lead to enhanced absorption in the spectral range of 400–600 nm. In addition, it is known [5, 6] that charged silver microcrystals Ag_n^{m+} (n = 2–4) are formed in PTR glasses during their synthesis and subsequent annealing. These microcrystals have absorption bands in the UV spectral region and low-intensity luminescence in the visible spectral range under UV excitation [5, 6]. UV laser irradiation of PTR glass leads to photoionization of the glass components. Under these conditions, charged silver microcrystals may capture some of the newly formed free electrons and thus pass to the neutral state. This process also leads to enhanced absorption in the spectral range of 230–500 nm. For example, Ag_2 microcrystals have seven absorption bands in the range of 237–441 nm [19], Ag_3 microcrystals have nine absorption bands in the range of 321–492 nm [19], and Ag_4 microcrystals have nine absorption bands in the range of 235–405 nm [20]. The formation of neutral silver microcrystals in PTR glasses after laser irradiation is confirmed by the luminescence measurement data (see below). Neutral silver microcrystals are stable structures, which retain their properties in glass both during long-term storage and upon heating to 250–400°C (see below). At the same time, many types of point defects in the glass network are unstable and may disappear, both during storage and upon heating [7]. The reduced absorption in PTR glass after its long-term storage (Fig. 2) indicates that both the point defects and neutral silver microcrystals contribute to the glass absorption after laser irradiation.

The effects of irradiation by excimer laser and UV mercury lamp on the optical density spectra of sample Ag-Br are compared in Fig. 3. It can be seen that the irradiation by mercury lamp also increases absorption in the spectral range of 260–500 nm but to a smaller extent than in the case of excimer laser irradiation. At the same time, the irradiation by a mercury lamp significantly increases the absorption in the spectral range of 250–290 nm. Similar tendencies are observed for samples Ag-Cl-I and Ag-Cl-II. However, the increase in the absorption in the range of 270–290 nm is less pronounced in this case. The difference in the absorption spectra may be due to the "softer" effect of irradiation by mercury lamp on the glass. The UV light of the mercury lamp slightly affects the formation of structural defects in the glass network and leads mainly to photoionization of cerium ions, accompanied by generation of free electrons in the glass. This circumstance may increase the concentration of silver neutral atoms and microcrystals, which have absorption bands in the spectral range of 240–326 nm [19, 20].

Exposure of silver-containing PTR glasses to mercury lamp UV light is known to enhance significantly their luminescence in the visible spectral range [5, 6]. Experiments showed that 248-nm laser radiation leads to a similar effect. Figure 4 shows normalized luminescence spectra of the samples after their irradiation by a laser and mercury lamp.

It can be seen that all spectra contain at least two overlapping luminescence bands and that the luminescence bands of sample Ag-Br are blue-shifted in comparison with samples Ag-Cl-I and Ag-Cl-II. Comparison with the data in the literature [8, 19–21] suggests that the luminescence in the spectral range of 400–500 nm (excitation wavelength 365 nm) is due to silver atoms, as well as neutral Ag_2 and Ag_4 microcrystals and point defects of *L*-center type. The luminescence in the range of 550–650 nm is due to the presence of neutral Ag_3 microcrystals in glasses and, possibly, charged Ag_2^+ microcrystals and hole centers formed by nonbridging oxygen. The intensity of the long-wavelength luminescence band in the spectrum

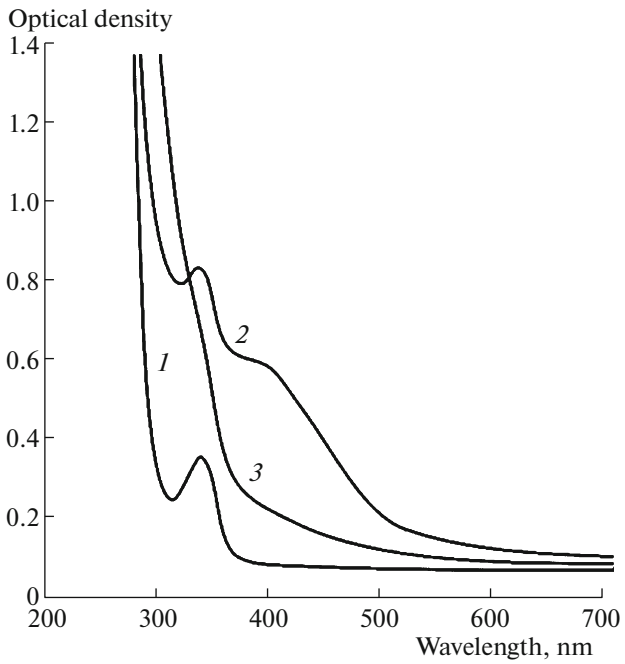

Fig. 3. Optical density spectra of sample Ag-Br (*1*) before laser irradiation, (*2*) after laser irradiation to a dose of 17 J/cm^2 (300 pulses), and (*3*) after irradiation by mercury lamp.

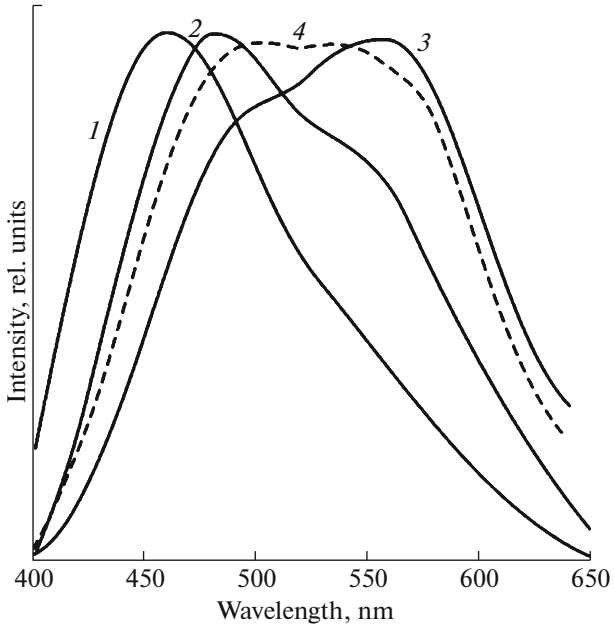

Fig. 4. Normalized luminescence spectra of samples (*1*) Ag-Br, (*2*) Ag-Cl-I, and (*3*) Ag-Cl-II after laser irradiation to a dose of 17 J/cm^2 (300 pulses) and (*4*) sample Ag-Cl-II after irradiation by a mercury lamp (the luminescence excitation wavelength is 365 nm).

of sample Ag-Cl-II exceeds that of the short-wavelength band, in contrast to sample Ag-Cl-I (Fig. 4, curves *3*, *2*). This can be related to the higher silver concentration in Ag-Cl-II, which facilitates formation of Ag_3 microcrystals. The only difference in the luminescence spectra of Ag-Cl-II irradiated by mercury lamp (Fig. 4, curve *4*) and the spectrum of a similar sample irradiated by laser is the amplitude ratio of luminescence bands. This fact indicates that these samples contain identical luminescence centers but with different concentrations.

Figure 5 shows the optical density spectra of sample Ag-Cl-II after laser irradiation to a dose of 17 J/cm^2 (300 pulses) and 1-h heat treatment at different temperatures. It can be seen that the heat treatment reduces the optical density in the range of 270–450 nm. This circumstance indicates a lower concentration of the point defects induced in the glass. At the same time, enhanced optical density is retained in this spectral range. This is related to the presence of neutral silver microcrystals in the irradiated region. Heat treatment at 450°C leads to the occurrence of a new absorption band (peaking at $\lambda = 420$ nm) in the optical density spectrum; this band is characteristic of the plasmon resonance in spherical silver nanoparticles [1, 22, 23]. It is noteworthy that the formation of silver nanoparticles begins at a temperature lower than T_g by 45°C. Here, the neutral silver microcrystals located in the irradiated region play the role of crystallization and growth centers for silver nanoparticles. At the same time, it is known that UV irradiation and heat treatment of PTR glasses lead to the formation of silver nanoparticles only at temperatures equal to T_g or

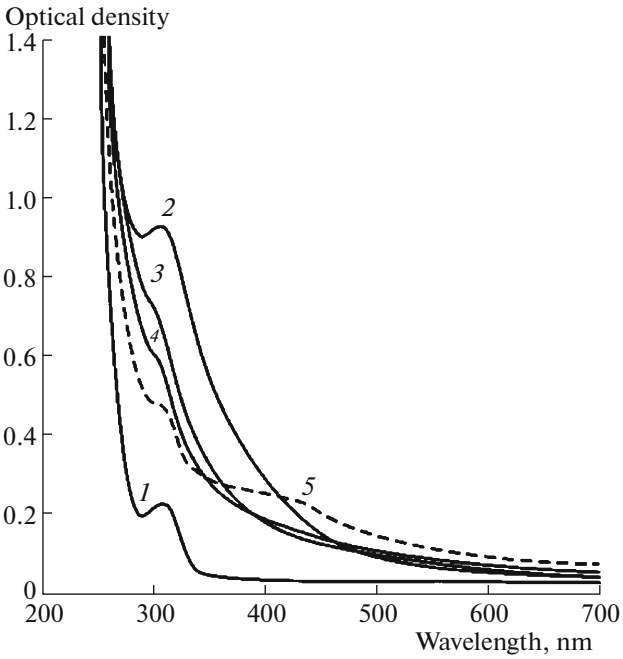

Fig. 5. Optical density spectra of sample Ag-Cl-II (*1*) before laser irradiation; (*2*) after irradiation to a dose of 17 J/cm^2 (300 pulses); and (*3*–*5*) after 1-h heat treatment at temperatures of (*3*) 250, (*4*) 350, and (*5*) 450°C.

exceeding this value. A possible cause of this effect is that laser radiation increases the concentration of defects in the irradiated region, thus facilitating both the thermal diffusion of silver ions and atoms and direct formation and growth of silver nanoparticles.

CONCLUSIONS

It was experimentally shown that irradiation of silver-containing PTR glasses by nanosecond 248-nm laser pulses leads to the formation of unstable point defects in the irradiated region, which have absorption bands in the UV and visible spectral ranges, and to the transition of silver ions and charged microcrystals to the neutral state, which is accompanied by an increase in the luminescence intensity in the visible spectral range. Irradiation of PTR glasses by cw UV light of mercury lamp only slightly affects the defect concentration and facilitates mainly reduction of silver ions and charged microcrystals.

ACKNOWLEDGMENTS

This study was supported by the Russian Scientific Foundation, state contract no. 14-23-00136.

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Translated by Yu. Sin'kov