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Luminescence quenching and recovering in photo-thermo-refractive silver-ion doped glasses

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ABSTRACT

A spectroscopic investigation of luminescent centers transformation in photo-thermo-refractive glass by using ultraviolet (UV) nanosecond laser pulses with radiation wavelength 355 nm was performed. Initially the glass was irradiated by UV lamp and thermal-treated that causes a neutral silver molecular clusters luminescence in a visible spectral region. After the laser irradiation a luminescence quenching was observed in the irradiated region. The thermal treatment below glass transition temperature restores the luminescence of silver molecular clusters with complex spatial distribution of luminescence intensity inside the irradiated region. UV lamp irradiation achieves the same result without any inhomogeneity. The observed effects are caused by photoionization and reduction of subnanosized silver molecular clusters with the participation of cerium and antimony ions.

1. Introduction

Photo-thermo-refractive (PTR) silicate glasses are a complex glass system which is doped by Ag, Sb and Ce ions [1]. Generally they are used as a holographic media and also as a base for the developing of new materials for photonic devices [2–4]. On the other hand they are a convenient matrix for the researches of silver molecular clusters (MC) and nanoparticles properties [5]. The luminescence characteristics of MC and nanoparticles of noble metals are, for decades, the subjects of thorough investigation. This is due to not only because of the necessity in the fundamental research of the variations of matter properties when passing from the atomic state to the nanocrystal but also for the prospects of MC application in photonics, nanoelectronics, sensorics, biology, and chemistry [6,7]. Luminescent properties of silver MC in PTR glasses were well described previously [5,8]. It was shown that UV exposure results in the increase of luminescence in a visible spectral range. The subsequent thermal treatment at the temperature less than the glass transition temperature (T_g) produces the additional increase of luminescence intensity. This makes PTR glasses promising for the use as optical data storage media. Luminescent centers in silver containing glasses can be also created by ultrafast laser pulses [9–13], gamma irradiation [9], and by the ion-exchange method [14,15]. The glasses doped with silver by the ion exchange method also possess luminescent properties in visible, which indicates that silver in glass after the ion exchange is not only in the ionic state, but also in the MC state [14,16]. In PTR glasses, both the Ag MC and the Ag nanocrystals can be formed. Luminescence characteristics of silicate glasses containing the MC and nanocrystals of Ag and Au were studied in [17]. In silver-ion-exchanged glasses luminescence quenching process was investigated in [18] with the use of high-power Ar^+ laser. They suppose that luminescence of central part of the interaction area demolishes with the formation of neutral silver MC. The following irradiation by the same laser causes a luminescence recovering in this area. Full luminescence quenching of glasses doped with Er^{3+} and Ce^{3+} ions was achieved in [19] by 18,000 pulses of excimer laser with radiation wavelength 248 nm. But the ability of the initial luminescence recovering was not described in that work.

The main goal of our investigation was the study of the possibility of the erasing of luminescence in the small region of PTR glass by nanosecond laser irradiation and the possibility of the subsequent recovering of luminescence in the same glass region for the future application of PTR glasses as optical data storage materials.

2. Experimental

PTR glasses based on the Na_2O–ZnO–Al_2O_3–Si_2O–NaF–NaCl system and doped with Ag_2O (0.12 mol%), photosensitize – CeO_2 (0.01 mol%) and reducer – Sb_2O_3 (0.04 mol%) were synthesized

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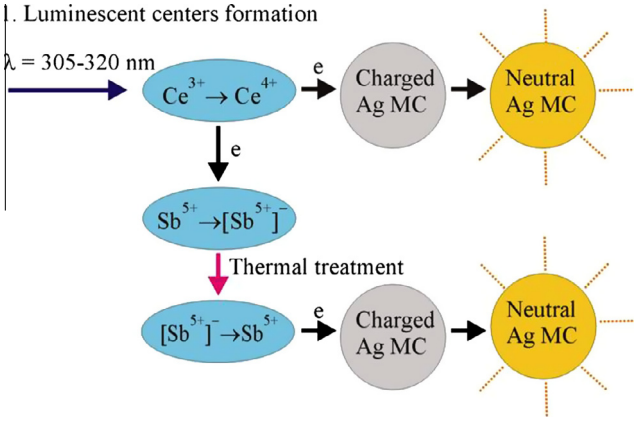
in ITMO University. The glass transition temperature T_g was measured with STA6000 (Perkin–Elmer) differential scanning calorimeter, its magnitude being found to be 494 °C. It must be noted, that during the glass synthesis the part of Ce ions change the valence state from IV to III, and the part of Sb ions change the valence state from III to V. The samples to be investigated were prepared in the form of the plane-parallel polished plates 1.0 mm thick. The as-prepared glass was transparent, colorless and had a very weak luminescence in a visible range caused by the silver ions Ag^+ and the charged silver MC Ag_n^{m+} which appear in the glass during its synthesis [5]. The samples were uniformly irradiated by UV mercury lamp with the radiation band matching the absorption band of Ce^{3+} ions (λ = 305–315 nm) during 10 min per each side. During this process some of free electrons produced by Ce^{3+} ions are trapped by Ag^+ ions, by charged silver MCs and by Sb^{5+} ions (see also Scheme 1 at Fig. 6). The last in this process form the complex $[Sb^{5+}]^-$. During the subsequent thermal treatment the electrons trapped by Sb^{5+} ions became free and can be trapped by the remained charged silver MC and Ag^+ ions [5,15,17–19]. These procedures produce the intense luminescence of the samples in a visible spectral region with luminescence excitation by UV radiation. The absolute quantum yield of luminescence after these procedures was measured at room temperature by C9920-02G (Hamamatsu Photonics) and was equal 18.8% and 16% for excitation wavelengths 360 nm and 400 nm correspondingly.

For the irradiation of samples the linearly polarized laser pulses were used with the maximum energy of 2.7 J/cm^2, pulse duration 5 ns and repetition rate 1 and 10 Hz from the TII LS-2131M (Lotis) multimode YAG:Nd laser emitting at 355 nm (third harmonic). Number of laser pulses during irradiation was varied from 1 up to 600. The laser beam was focused by the lens with 4 cm focal length. The focus of laser beam was located at the distance of 1 cm from the backward surface of the sample with the beam diameter 1.0 mm on the forward surface of the sample. The diameter of irradiation zone was chosen for the convenience of optical measurements, but it must be noted that the UV laser beam can be focused into the spot with the size less than 1 μm. For the thermal treatment of the samples at 400 °C the muffle furnace (Nabertherm) with program control was used. For the UV irradiation of the samples after the laser action the same mercury lamp was used, as described above. The optical density spectra of the glass samples were measured in the 200–800 nm spectral region using Lambda 650 (Perkin–Elmer) spectrophotometer at room temperature. For the measuring the luminescence spectra the luminescence microscope MSFU-K (LOMO) was used with the excitation at λ = 400–440 nm.



Scheme 1.

3. Results and discussions

After the irradiation of the samples by the UV mercury lamp the initially colorless samples change the color to light-yellow (Fig. 1a) and the intense luminescence appear in them with the excitation by radiation with λ = 250–420 nm (Fig. 1b). As it was shown in [5,8] the main contribution to this luminescence make silver atoms Ag^0 and neutral silver MC Ag_2, Ag_3 and Ag_4. The Ce^{3+} and Sb^{3+} ions also have luminescence bands, but they are located in UV spectral region and in this work are not discussed. The irradiation of such samples by UV laser pulses led to some increase of the coloration in the irradiated regions (Fig. 1a) and to the luminescence quenching in them (Fig. 1b). The quenching effect increases with the increase of the number of laser pulses and the energy in a pulse. It should be noticed that there is a threshold that defines an appearance of luminescence quenching effect. The circles at Fig. 1b shows the irradiated regions without luminescence quenching. For the laser irradiation by 5 pulses this threshold is defined as 80 mJ/cm^2 per pulse.

The absorption spectra of the irradiated areas after 1, 5, and 10 laser pulses action are shown at Fig. 2. It can be seen that the optical density increases with the number of laser pulses. The experiments have shown that the optical density increases also with the increase of laser pulse energy. The optical density increases in the spectral range 300–550 nm, except the absorption band at 350 nm, which seems disappeared after 1 pulse already. This band can be attributed to Ag_3 MCs [20]. Also the increasing of optical density of the band at 440 nm can be caused by the appearance

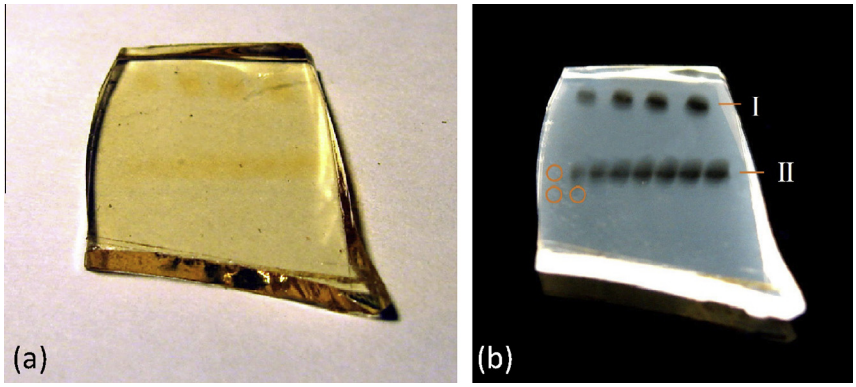


Fig. 1. Photo's of the sample after irradiation by UV nanosecond laser pulses (a) and of its luminescence under the excitation by radiation with λ = 365 nm (b). I string of spots – left to right: 1, 5, 10, 20 laser pulses with energy density 2.7 J/cm^2, II string of spots – left to right: 5 laser pulses per spot with 0.05–2.7 J/cm^2 per pulse. Empty circles show the regions where a power density of radiation was not high enough to quench the luminescence.