Laser-assisted formation of luminescent domains in metal- or semiconductor-doped silicate and phosphate glasses

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Abstract. In this study, silicate and phosphate glasses doped with Ag or CdS were exposed to femtosecond laser pulses and photoluminescence properties of the laser-written domains were investigated. Laser writing in phosphate glass doped with CdS was found to induce very weak photoluminescence, while laser-written domains in silicate glass had a comparatively high photoluminescence intensity, that was assigned to the formation of the sulphur vacancies in the CdS nanocrystals precipitated under the ultrafast laser pulses. Observed photoluminescence bands in Ag-containing glasses we assigned to the formation of different silver nanospecies which provide photoluminescence bands with the maxima at 685 and 600 nm in Ag-doped silicate and phosphate glasses, respectively.

1. Introduction
Glasses doped with noble metals as well as semiconductor nanocrystals have been known for a long time but still play a significant role in the development of materials with enhanced optical properties for light-emitting diodes, optical fiber amplifiers, modulators, sensors, etc. [1, 2]. Moreover, space-selective modification of optical properties in these glasses using ultrafast laser pulses is a very attractive technique paving the way for the development of optical memory based on photoluminescence emission from the laser-written domains. Domains induced by the stationary focused ultrafast laser beam are typically represented as pipe-shaped structures elongated along the laser writing direction formed during multi-photoionization and subsequent rearrangement of the glass structure [3, 4].

Many studies were performed in the field of direct laser writing in glasses by functional additives. For example, the possibility of laser-induced Ag cluster precipitation, as well as Ag nanoparticles formation in silver-doped phosphate glass, was proposed to use for the optical data recording [5] and single-mode waveguide fabrication [6, 7]. The space-selective precipitation of CdS or CdSe quantum dots in glasses under femtosecond laser irradiation was also studied [8, 9]. Nevertheless, the development of a reliable functionalized glass suitable for efficient direct laser writing is still remaining a challenge and a search for the best combination of a glassy matrix and a dopant is thus going on.

Here, we studied and compared the photoluminescence (PL) properties of laser-induced domains in two different glass matrices (silicate and phosphate) doped with Ag or CdS.
2. Experimental

Two glass matrices were selected for doping including silicate glass in the K$_2$O-ZnO-B$_2$O$_3$-SiO$_2$ system (labelled as OS) and phosphate glass in the ZnO-P$_2$O$_5$ system (labelled as PZ). Both silicate and phosphate glasses were doped separately with Ag or CdS and hereafter are referred to, respectively, as OS-Ag, OS-CdS, PZ-Ag and PZ-CdS depending on glass matrix and dopant (Ag$_2$O – 0.03 mol.% for OS glass and 1 mol.% for PZ glass; CdS – 1 mol.% for OS and PZ glasses). High purity grade reagents (SiO$_2$, H$_3$BO$_3$, ZnO, K$_2$CO$_3$, P$_2$O$_5$, CdS, AgNO$_3$) were used for glass batch preparation. Glass samples were fabricated using the melt-quenching process according to the technique described elsewhere [10]. It is notable that we did not succeed in producing transparent OS glass with the content of silver over 0.03 mol.%.

Glass samples of 10 x 10 x 3 mm size were polished into plane-parallel plates for laser irradiation experiments. An experimental setup based on the Pharos SP femtosecond laser system with a central wavelength of 1030 ± 2 nm tuned to a pulse repetition rate of 100 kHz and a pulse duration of 180 fs was used for laser writing experiments. The laser beam was focused into the glass sample by an Olympus microscope objective (20X, N.A. = 0.45) at a depth of ~150 μm under the surface. The pulse energy was set to 200 nJ, which provided the most luminous domains in all investigated glasses. 10$^6$ laser pulses were deposited to each irradiated domain. The glass samples were positioned by means of a three-coordinate motorized air-bearing translation stage (Aerotech ABL1000) synchronized with the laser.

PL spectra and integral intensity distribution maps of the laser-written domains were recorded using an NTegra Spectra nanolaboratory (NT-MDT) with the 488 nm argon laser beam focused with Olympus microscope objective (40X, N.A. = 0.75) as excitation source and a scanning step of 0.8 μm.

3. Results and discussion

Fig. 1 presents typical PL integral intensity distribution maps of the domain laser-written in OS-CdS glass sample in the top view configuration. In general, observed PL appears due to the formation of Ag or CdS nanoclusters. A ring shape of the PL zone originates from the Gaussian distribution of the incident energy in the laser writing beam: the highest energy is in the middle, and it decreases to the edges. Therefore, one can see the highest PL intensity in the edges of the ring where the conditions of metal or semiconductors luminescent nanospecies are the most favorable [5, 8]. In order to compare PL spectra from the four domains in different glasses, we extracted PL spectra from the places with the highest PL intensity.

![Figure 1 – Integral intensity map of PL in the range 520-800 nm registered for the top view of the domains laser-written in OS-CdS (a), PZ-CdS (b), OS-Ag (c) and PZ-Ag (d) glass samples](image)

Fig. 2(a) presents PL spectra recorded from the irradiated domains in the PZ-CdS and OS-CdS glass samples. PL of the domain in CdS-doped PZ glass is almost imperceptible, which is expressed in high noise of its normalized PL spectrum and is evident from the corresponding PL intensity map (Fig. 1). However, a wide PL band peaking at ~600 nm can be extracted. This can be explained by very low concentration of the luminescent CdS nanocrystals in the domain laser-written in PZ glass. Domains obtained in OS-CdS glass are characterized by intense PL with a maximum at 675 nm. It is known that a PL band at 675 nm emerging under the 488 nm excitation is attributable to the recombination of an electron trapped in a sulfur vacancy with a hole in the valence band of small CdS nanocrystals (about 2-3 nm in size) [11, 12]. Comparing the results obtained for different glass
matrices we can assume that the possible low concentration of CdS nanocrystals and therefore almost complete absence of the PL in domains laser-written in CdS-doped PZ glass may be associated with the structure of glass. For PZ glass where ZnO content higher than 50 mol.% the latter play an intermediate role of glass network former and modifier [13] because the behavior of Cd is similar to Zn. Thus, if cadmium and zinc are well embedded in structural units of the glass network then the equilibrium of laser modification process is shifted away from the formation of the sufficient quantity of CdS or ZnS.

![Figure 2](image)

**Figure 2** – PL emission spectra recorded from the laser-irradiated domains in PZ and OS glasses doped with CdS (a) or Ag (b)

In Ag-doped glasses, laser-written domains in both OS-Ag and PZ-Ag samples manifested relatively strong PL. The evident difference in the centers of the emission bands can be seen PL emission spectra for OS and PZ glass doped with Ag (Fig. 2(b)). A PL band peak of the domain in OS-Ag glass sample is located at 685 nm. In Ag-doped PZ glasses, the laser-written domains show a maximum of PL band at ~600 nm.

PL emission of silver clusters strongly depends on the excitation wavelength [14]. According to the available data [15], PL band peaking at 570 nm under the excitation of 480 nm in the oxyfluoride glass can be assigned to the electronic transitions in the Ag$_m^{m^+}$ clusters with $m=4$. In our case, excitation wavelength was 488 nm that is close to the mentioned work, thus we can assume that in PZ-Ag glass samples clusters of 4-5 atoms can be precipitated. The red-shift of the PL band registered in the domain in Ag-doped OS glass may indicate an increase of the $m$ value, that is, bigger silver aggregates are formed [16]. A further study of PL properties using different excitation wavelengths as well as the optical absorption study is required and in progress in order to precisely determine all kinds of the silver nanospecies precipitated during the laser irradiation.

4. **Conclusions**

We studied PL properties of silicate and phosphate glasses separately doped with Ag or CdS induced by the femtosecond laser irradiation. In all cases, laser irradiation leads to the formation of domains exhibiting PL. In CdS-doped phosphate glass, PL was found to be almost imperceptible that may be due to the hampered formation of the sufficient quantity of CdS nanocrystals in Zn-rich glass. On the other hand, the laser-written domains in silicate glass with CdS are characterized with intense PL with a maximum at 675 nm presumably attributed to the formation of the sulfur vacancies in the CdS nanocrystals precipitated upon the laser heating. In Ag-containing PZ glass, we found PL assigned to the formation of Ag$_m^{m^+}$ clusters. Maxima of PL spectra differ in silicate and phosphate systems. In silicate glasses, PL bands have a peak at 685 nm, while in Ag-doped phosphate glasses, a maximum of PL bands is located at 600 nm. The observed red shift of PL in silicate glass as compared to phosphate glass may indicate a size increase of the precipitated silver nanospecies. The obtained results are
essential for the future development of optical memory and the laser-assisted fabrication of functional waveguides in metal- or semiconductor-doped glasses.

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