

Multicolour laser recording of optical information in silicate glasses with europium, silver and cerium ions

D.A. Klyukin, A.Yu. Khmelev, A.S. Pshenova, A.I. Sidorov, Yu.K. Fedorov

Abstract. We have shown experimentally that the effect of cw UV radiation and pulsed UV radiation from a nanosecond laser as well as thermal treatment of glasses with europium, silver and cerium ions (photosensitizer) allow the local formation of the areas in glass, having different luminescence colour or the areas of different colouration. These effects are caused by a change in the charge state of molecular clusters and the formation of silver nanoparticles possessing plasmon resonance in glass. This allows recording of multicolour optical information by means of a focused beam from a UV laser, both near the glass surface and within its volume. We have revealed the influence of chlorine on the formation and properties of silver nanoparticles in glass in the course of thermal treatment following the laser impact.

Keywords: luminescence, molecular silver cluster, laser pulse, glass.

1. Introduction

The use of optical information recording allows surpassing traditional two-dimensional devices both in writing and reading speed as well as in storage density. Such optical techniques include, in particular, the formation of luminescent and absorbing centres by means of focused laser radiation.

Glass is considered to be a promising 3D data storage material because it has an advantage over crystals in the cost and manufacturability, and over polymers – in the resistance to mechanical and chemical impacts [1].

As we have previously shown, in the case when a glass comprising ions and charged molecular clusters (MCs) of silver is exposed to nanosecond UV laser radiation, neutral MCs of silver, possessing intense luminescence in the visible spectral region [2], are formed. We have also shown that thermal treatment at a temperature less than the temperature T_g of glass transition increases the number of neutral clusters due to the restoration of charged MCs [3]. If the thermal treat-

ment temperature exceeds T_g , silver nanoparticles (NPs) are formed in glass [4], with the luminescent and optical properties differing significantly from those of the MCs of silver [3, 5]. These effects can be used to locally change the luminescent properties of glasses with silver by means of laser irradiation, which opens up the possibility for three-dimensional recording of high-density optical information. It is therefore of interest to study the influence of alloying elements, in particular, ions of rare-earth metals, and also the laser and other external impacts to expand the functionality of glasses with silver ions in terms of optical information recording.

The aim of this study was to investigate the effect of europium ions as well as cw and pulsed UV irradiation and thermal treatment on the formation and destruction of luminescent and colouration centres in silver-containing glasses. We have also investigated the effect of chlorine ions on the formation and properties of silver nanoparticles in glasses after laser exposure and thermal treatment.

2. Experimental

In order to conduct research at the ITMO University, silicate glasses were synthesised, whose compositions are given in Table 1 below. These glasses are similar in composition to the photo-thermo-refractive glasses studied by us earlier [2]. The main feature of the glasses in question is a high (for silicate glasses) concentration of silver and europium ions, and also the presence or absence of chloride ions. The samples containing chlorine are hereinafter denoted as AgEu–Cl, the samples without chlorine – as AgEu. It should be noted that most of cerium ions are transformed in glass synthesis from the tetravalent state to the trivalent one, whilst antimony ions – from the trivalent state to the pentavalent one. The luminescence band of Ce^{3+} ions lies in the UV spectral region; therefore, these ions only perform the role of a photosensi-

Table 1. Compositions of glasses.

Glass	Concentration of glass components (mol.%)									
	SiO ₂	Na ₂ O	ZnO	Al ₂ O ₃	Cl	F	Sb ₂ O ₃	CeO ₂	Ag ₂ O	Eu ₂ O ₃
AgEu	74.8	15.0	5.4	2.3	0	1.87	0.045	0.007	0.12	0.5
AgEu–Cl	72.5	15.6	5.2	2.2	2.2	1.81	0.043	0.007	0.12	0.5

D.A. Klyukin, A.Yu. Khmelev, A.S. Pshenova, A.I. Sidorov, Yu.K. Fedorov ITMO University, Sablinskaya ul. 14, 197101 St. Petersburg, Russia; e-mail: kliukinda@gmail.com

Received 8 June 2016
Kvantovaya Elektronika 46 (10) 930–934 (2016)
Translated by M.A. Monastyrsky

tizer [4]. The Sb^{5+} ions play the role of a reducing agent in thermal treatment of glass [4]. Putting halogen into glass is stipulated by the fact that it accelerates the formation of silver NPs in thermal treatment. Furthermore, in the process of growth of silver NPs, a shell of silver halide is formed on their surface, which allows controlling the spectral position of the plasmon resonance of silver NPs [6]. The glass transition tem-

perature measured by a STA6000 differential scanning calorimeter (PerkinElmer) was 507 °C. The samples of glasses were polished plane-parallel plates with the size of 10×5×1.5 mm.

For continuous exposure to UV radiation, a mercury lamp was used, with a radiation band falling within the absorption band of cerium ions. For pulsed UV laser irradiation of samples, a multimode nanosecond solid-state Nd³⁺:YAG laser having a wavelength of the third harmonic generation $\lambda = 355$ nm was used. The pulse duration was 9 ns, and the energy density was varied from 0.01 to 0.5 J cm⁻². The laser beam was focused onto the glass surface into the spots with 1 mm and 50 μ m in diameter, or into the glass volume. The lens with a focal length of 18 mm and a micro-objective (20 \times , NA = 0.4) were used for focusing. The selection of irradiated zone diameters was dictated by the convenience of optical measurements.

Irradiated samples were thermally treated for 1–13 h in a muffle furnace (Nabertherm) at temperatures of 350–530 °C. The optical density spectra of the samples were measured using a Lambda 650 spectrophotometer (PerkinElmer) in the spectral range of 200–800 nm. To measure the luminescence spectra, we used a C9920-02G integrating sphere (Hamamatsu Photonics). The absorption and luminescence spectra were measured at room temperature.

3. Results and discussion

Initially, the AgEu and AgEu–Cl glasses were colourless and possessed a relatively weak luminescence in the red spectrum region, with major peaks at wavelengths of 590, 613 and 705 nm, which is typical for Eu³⁺ ions [Fig. 1, curve (1)] [7]. Exposure to cw UV radiation from a mercury lamp in the absorption band of Ce³⁺ ions ($\lambda = 305$ –310 nm) for 20 min and the succeeding thermal treatment at $T = 350$ °C lead to the emergence of a broad luminescence band within the spectral range of 430–800 nm [curves (2) and (3) in Fig. 1]. We have shown previously [8–10] that this luminescence band is caused by the transformation of charged MCs of silver, which are originally present in glass, into the neutral MCs. Such a transformation is a result of capturing by the charged MCs of free electrons that appear in glass in the process of photoionisa-

tion of cerium ions and thermal ionisation of [Sb⁵⁺]⁻ complexes. The analysis conducted in paper [3] has shown that the contribution of luminescence to this band is made mostly by neutral MCs of silver (Ag₂, Ag₃ and Ag₄) and also by Ag⁰ atoms. As seen from photographs 1 and 2 presented in Fig. 2, the luminescence colour of samples changes from red to light yellow. The UV radiation also leads to a slight increase in the amplitude of the luminescence bands of Eu³⁺ ions [curve (2) in Fig. 1]. The subsequent thermal treatment at $T = 350$ °C is accompanied by a significant (more than 15 times) increase in the luminescence intensity of Eu³⁺ ions [curve (3) in Fig. 1]. The reason for this is an increase in the concentration of neutral MCs of silver in the glass and a shift of their luminescence maximum into the blue spectrum region [curve (3) in Fig. 1]. This contributes to a greater overlap of the luminescence bands of neutral MCs of silver and the absorption bands of Eu³⁺ ions, which is accompanied by the energy transfer from the neutral MCs of silver to Eu³⁺ ions [9]. Similar effects were observed in AgEu–Cl glasses.

Further irradiation of the samples by intense UV laser radiation leads to partial or complete suppression of the luminescence of neutral MCs of silver in the irradiated areas of glass [curve (4) in Fig. 1 and photograph 2 in Fig. 2a]. The luminescence intensity of Eu³⁺ ions also decreases due to the reduced efficiency of energy transfer. Thus, the luminescence colour in the exposed areas changes to red or the luminescence disappears when using short-wave UV excitation radiation. The reason for this effect is that the laser radiation with $\lambda = 355$ nm falls within the absorption band of neutral MCs of silver [11, 12] and transforms them from the neutral state to the charged state. Subsequent exposure of the samples to cw UV radiation or thermal treatment leads to either partial or complete restoration of luminescence of neutral MCs in irradiated areas (photographs in Figs 2b and 2c). This is due to the appearance of free electrons in the glass as a result of the processes described above.

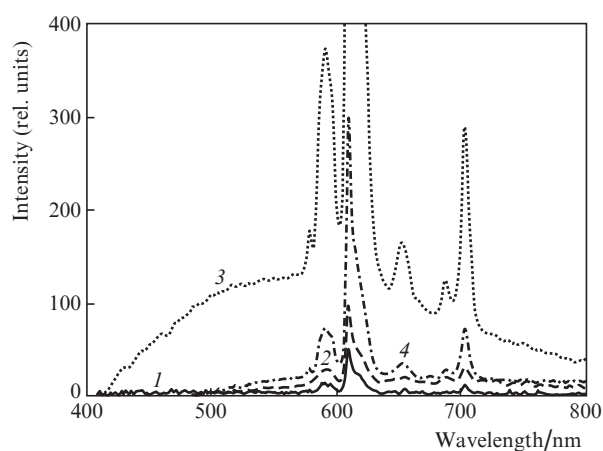


Figure 1. Luminescence spectra of AgEu glass before (1) and after (2) irradiation by a UV mercury lamp or a UV nanosecond laser, and also after thermal treatment at 350 °C for 3 h (3) and at 530 °C for 13 h (4). The intensity maximum at $\lambda = 613$ nm is 1500 rel. units, the excitation wavelength is 350 nm.

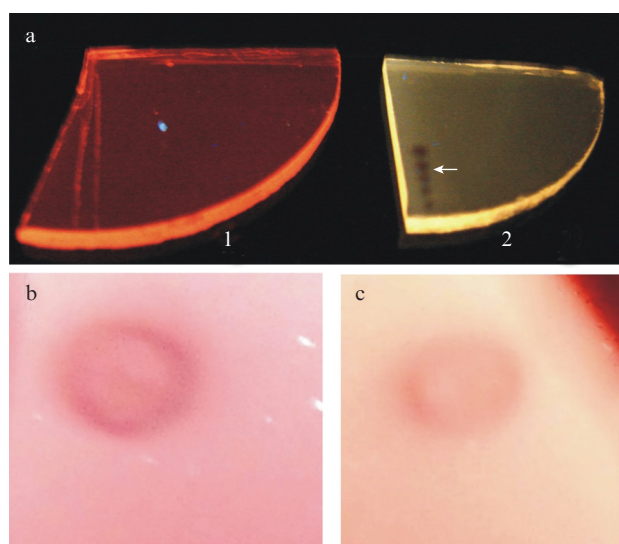


Figure 2. (Colour online) Photographs of glass luminescence before (1) and after (2) UV irradiation by a mercury lamp and UV laser irradiation (the arrow indicates the areas irradiated by a UV laser) (a), and after UV irradiation of AgEu (b) and AgEu–Cl (c) by a mercury lamp, UV laser irradiation, and thermal treatment at 530 °C for 15 min. The luminescence excitation wavelength is 365 nm.

If AgEu and AgEu–Cl glass samples had not been pre-exposed to cw UV radiation, but were irradiated by a pulsed UV laser, the luminescence colour in the irradiated areas changed from red to light yellow or white with increasing laser energy density (Fig. 3). The luminescence spectra of the irradiated areas of glass are similar to those shown in Fig. 1 [curves (2) and (3)], which points to a transformation of the charged MCs of silver into the neutral state in the irradiated area. In this case, the source of free electrons are not Ce^{3+} ions having an absorption band at $\lambda = 305\text{--}310$ nm, but the charged defects of the glass network. Figure 4 shows the luminescent tracks in the glass volume, obtained after the laser beam focusing; the beam waist diameter at the focus is approximately 10 μm . At an energy density of $E > 10$ J cm^{-2} , there occurs an optical breakdown in the focal area, causing an increase in the luminescence brightness within that region due to multiple reflections from the walls of microcracks (Fig. 4b). Another reason for an increase in brightness may be a growth of the concentration of free electrons during the glass network destruction by a laser pulse. This leads to an increase in the concentration of neutral MCs of silver. The formation of silver nanoparticles in this area in the course of thermal treatment testifies in favour of this assumption.

Thus, depending on the prehistory of glass with europium and silver ions, the exposure to UV nanosecond laser pulses may either suppress the already existing luminescence of the

MCs of silver, or, conversely, result in the formation of luminescent areas containing the emitting neutral MCs of silver. These effects can be used for two-colour recording of optical information by varying the luminescence colour. At the same time, a question arises: why in the first case the luminescence turns out suppressed, while in the second case it emerges? The reasons for this difference are as follows. In the first case, the source of free electrons is cerium ions which pass from the trivalent into tetravalent state in the photoionisation process. Under pulsed laser irradiation, there occurs photoionisation of neutral MCs of silver and glass network defects as well as formation of new defects having absorption bands at the laser radiation wavelength (see below). Free electrons emerging in this process may again be captured by the MCs of silver, glass network defects, and also by cerium ions, thus transforming the latter into the trivalent state. Therefore, after the laser pulse impact, the number of neutral MCs of silver decreases, which is accompanied by a decrease in the luminescence intensity within the irradiated area. In the second case, the MCs of silver are initially in the charged state, while cerium ions are in the trivalent state. The absorption bands of these objects are located outside the wavelength of radiation exposure, and so the glass network defects are the only source of free electrons in the glass. During a few nanoseconds of the laser pulse action, free electrons are unable to reach the charged MCs of silver, and therefore they remain in the charged non-absorbing state until the pulse is terminated. The transition of the MC of silver to the neutral state occurs after the laser pulse termination, when the MC photoionisation is no longer possible.

The exposure to UV laser pulses gives rise to induced absorption in the near-UV region [2]. The absorption band at $\lambda = 305\text{--}310$ nm corresponds to that of Ce^{3+} ions. It is known that induced absorption is due to the formation of the glass network defects such as non-bridging oxygen centres, L centres, E' centres, as well as the formation of neutral MCs of Ag_n silver ($n = 2\text{--}4$) and the transition of silver ions into the neutral state [13].

Subsequent long-term thermal treatment at a temperature above T_g results in the formation of silver nanoparticles in glasses. This is confirmed by the presence of an intense absorption band at a wavelength of 430 nm (Fig. 5), corresponding to the surface plasmon resonance of silver NPs [4]. According to the results obtained by means of transmission electron microscopy, the NPs of silver in the test glasses possess a near-spherical shape and the average diameter of 4–5 nm [14]. The appearance of a plasmon absorption band leads to intense colouring of glasses in the irradiated area (see insets in Figs 5 and 6); herewith, with increasing laser energy density, the irradiated area colour changes to yellow, red, brown or black, depending on the concentration and size of NPs. Obviously, such a local change in colour may also be used for multicolour recording of optical information. Figure 6 shows the localisation areas of silver NPs after irradiation by means of a UV laser beam focused in the glass volume and on its surface. It can be seen that the coloured areas containing silver NPs are localised along the laser beam waist. The region length increases with increasing energy density of radiation. The minimum diameter of these areas constitutes 10–20 μm , and their length is 30–50 μm . These areas are formed most effectively at an energy density exceeding the energy required for the optical breakdown of glass. The reason for this is the fact that the optical breakdown is followed by the generation of many free electrons that transform the ions and charged

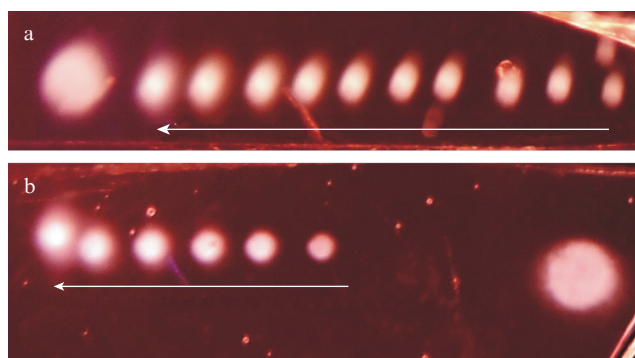


Figure 3. (Colour online) Photographs of luminescence of AgEu (a) and AgEu–Cl (b) glasses after UV laser irradiation. Arrows are directed towards an increase in the laser pulse energy density. The luminescence excitation wavelength is 365 nm.

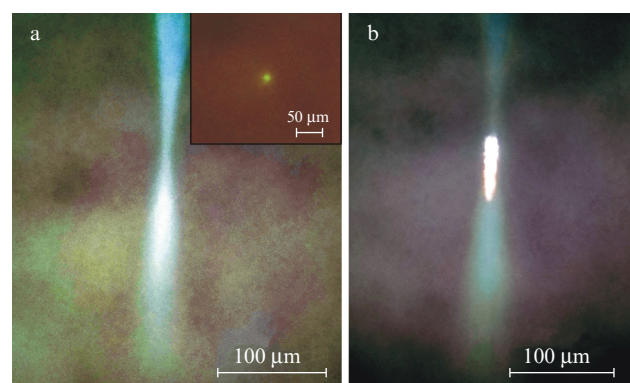


Figure 4. (Colour online) Photographs of luminescence tracks of the laser beams focused in the glass volume (the inset shows the top view) at $E =$ (a) 0.5 and (b) 2 J cm^{-2} . The luminescence excitation wavelength is 365 nm.

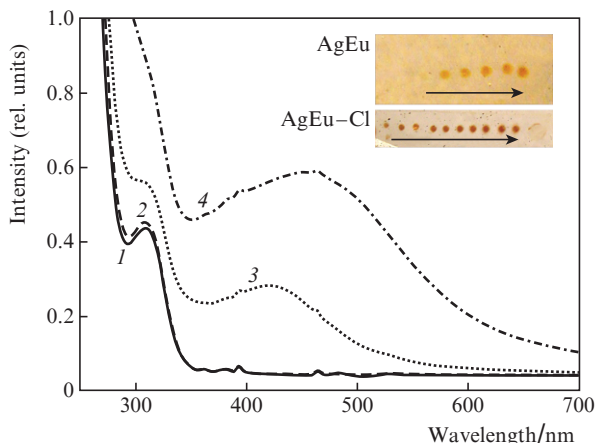


Figure 5. (Colour online) Optical density spectra of glasses after the exposure to UV laser radiation (600 pulses), and thermal treatment for 1 h at 530°C. Original glass without Cl (1) and with Cl (2), the glass after UV nanosecond laser irradiation without Cl (3) and with Cl (4). The inset shows the photographs of the AgEu and AgEu-Cl glasses after UV laser irradiation and thermal treatment. The arrows are directed towards an increase in the laser pulse energy density.

MCs of silver into the neutral state. In addition, a large number of glass network defects emerging in the breakdown region facilitate thermal diffusion of silver atoms, which accelerates the NP growth. Erasing of the recorded information in this case is possible when the glass is heated to $T = 800\text{--}900^\circ\text{C}$. Thus, thermal dissolution of silver NPs occurs in the glass.

The intensity of luminescence in the area of the silver NP formation is substantially reduced in this case (Fig. 7), and its maximum is shifted into the red [Fig. 1, curve (4)]. To explain the change in the luminescence intensity in glasses with silver NPs at a temperature above T_g , two suppositions can be put forward. The first is that, under the described conditions, ultra-small silver NPs having a size of 1–2 nm are formed [15], which in certain cases possess a weak luminescence [16]. The second supposition reduces itself to the fact that, as a result of the formation of silver NPs having the plasmon resonance with a maximum at $\lambda = 430\text{ nm}$, there occurs luminescence

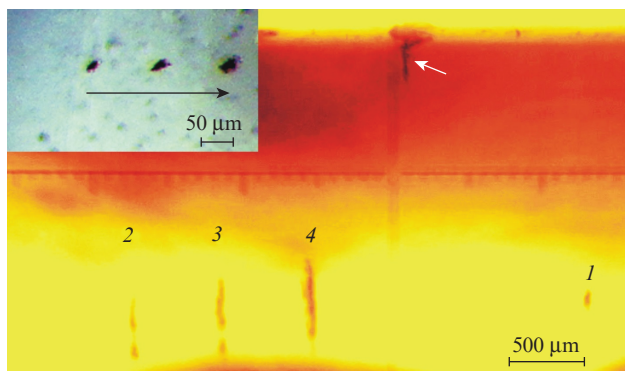


Figure 6. (Colour online) Photographs of AgEu (a) and AgEu-Cl (b) glasses after exposure to UV laser radiation (600 pulses) focused in the glass volume, and also after thermal treatment for 1 h at 530°C and $E = (1) 0.5, (2) 2, (3) 6$ and $(4) 12\text{ J cm}^{-2}$. The arrow indicates the irradiated zone when focusing the beam on the glass surface. The inset shows the top view. The arrow is directed towards an increase in the laser pulse energy density.

absorption of remaining neutral MCs of silver in the absorption area of silver NPs. This explains the shift of the luminescence maximum into the red region and a decrease in the luminescence intensity due to a decrease in the number of neutral atoms and MCs of silver in the glass volume, which become a ‘building material’ for new silver NPs. Apparently, those are the MCs of Ag_3 which still remain in the glass volume. It should be noted that the literature data on the luminescence of ultra-small NPs differ greatly, and a unified model describing the optical properties of such objects has not been yet developed.

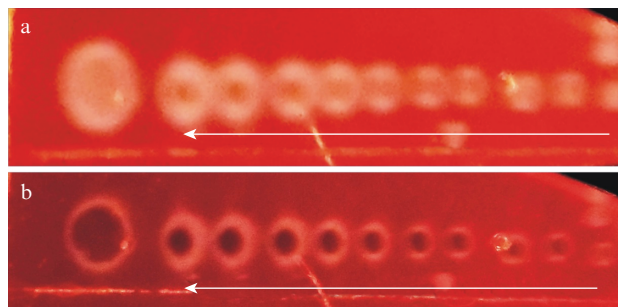


Figure 7. (Colour online) Photographs of luminescence of AgEu (a) and AgEu-Cl (b) glasses after exposure to UV laser irradiation and thermal treatment for 1 h at 530°C. The arrows are directed towards an increase in the laser pulse energy density; the luminescence excitation wavelength is 365 nm.

It is seen from Fig. 7 that a change in the luminescence colour and a decrease in its intensity with increasing laser energy density only occur in the irradiated area centre. The reason for this is a bell-shaped intensity distribution in the laser beam cross section. Since the radiation intensity along the laser beam perimeter is lower, this area produces less amount of neutral atoms and MCs of silver, and therefore, the growth of silver NP is less efficient.

The role of chlorine ions is manifested mainly during the long-term thermal treatment in the process of the formation and growth of silver NPs. As shown in [17], a thin shell of silver chloride is formed on the surface of silicate glasses during the silver NP growth. The emergence of such a shell causes acceleration in the growth of silver NPs, which leads to a more intense colouration of the laser-irradiated glass sections (see insets in Figs 5 and 6). Furthermore, such a shell, having a refractive index greater than that of glass, shifts the plasmon absorption band into the long-wavelength region of the spectrum (see also [4]). This allows changing the colouration degree and colour tones of the irradiated zone in the glass by means of adjusting the shell thickness at the expense of varying the chlorine concentration and thermal treatment duration.

Figure 6 demonstrates that the linear dimensions of the recorded regions in the waist, both fluorescent and absorbing, do not exceed 10–20 µm. However, these dimensions can be reduced by using a UV-lens with a larger aperture ($NA = 1\text{--}1.4$). This offers an opportunity, by using short-wave single-mode laser radiation with a wavelength of 355 nm, to focus radiation into the region with a waist size less than 1 µm, and, as a consequence, the information recording density may be as high as 1 Tbit cm^{-3} at the cell volume of $1\text{ }\mu\text{m}^3$. Main characteristics and mechanisms of multicolour optical informa-

Table 2. Characteristics and mechanisms for multicolour recording of optical information in the glasses with europium and silver ions.

Recording method	Recording mechanism	Reading	Irradiated zone colour (the colour outside of the irradiation zone)	Erasure
Irradiation with a UV mercury lamp followed by UV laser irradiation	Transition of the MCs of silver from the neutral to the charged state	By change of luminescence colour	Red or black, Fig. 2 (yellow or white, Fig. 2)	Irradiation with a UV mercury lamp
Irradiation with a UV laser	Transition of the MCs of silver from the charged to the neutral state	By change of luminescence colour	Yellow or white, Figs 3, 4 (red or black, Fig. 3)	No
Irradiation with a UV laser and thermal treatment above the glass-transition temperature	Formation of absorbing silver NPs	By change of luminescence colour	Black, Fig. 7 (red, Fig. 7)	Thermal treatment at $T = 800\text{--}900\text{ }^{\circ}\text{C}$
		By change of colouration in the exposed area	Yellow, red, brown, black, Figs 5–7 (no colour, inset in Fig. 6)	Thermal treatment at $T = 800\text{--}900\text{ }^{\circ}\text{C}$

tion recording in the glasses with europium and silver ions are given in Table 2.

Thus, we have experimentally shown that, by using cw and pulsed UV laser irradiation and thermal treatment in the silicate glasses containing ions of silver, europium and cerium, the multicolour luminescent centres and colouration centres are formed, which can be used for recording of multicolour optical information. These effects are associated with a change in the charge state of molecular silver clusters and the formation of silver nanoparticles possessing a plasmon resonance. It is shown that the introduction into the glass composition of chloride ions allows us to increase the colour saturation of the coloration centres and change the irradiated zone colour.

Acknowledgements. This work was supported by the Ministry of Education of the Russian Federation in the design part of the state task in the field of scientific activity (Task No. 11.1227.2014/K).

References

- Zhang J., Gecevicus M., Beresna M., Kazansky P.G. *Phys. Rev. Lett.*, **112** (3), 1 (2014).
- Ignatiev A.I., Klyukin D.A., Leontieva V.S., Nikonorov N.V., Shakhverdov T.A., Sidorov A.I. *Opt. Mater. Express*, **5** (7), 1635 (2015).
- Dubrovin V.D., Ignatiev A.I., Nikonorov N.V., Sidorov A.I., Shakhverdov T.A., Agafonova D.S. *Opt. Mater. (Amst.)*, **36** (4), 753 (2014).
- Nikonorov N.V., Sidorov A.I., Tsekhomskii V.A. *Silver Nanoparticles* (InTech, 2010) pp 177–200.
- Treguer M., Rocco F., Lelong G., Le Nestour A., Cardinal T., Maali A., Lounis B. *Solid State Sci.*, **7** (7), 812 (2005).
- Nikonorov N.V., Sidorov A.I., Tsekhomskii V.A., Lazareva K.E. *Opt. Spectrosc.*, **107** (5), 705 (2009).
- Eichelbaum M., Rademann K. *Adv. Funct. Mater.*, **19** (13), 2045 (2009).
- Miyamoto Y., Takei Y., Nanto H., et al. *Radiat. Meas.*, **46** (12), 1480 (2011).
- Eichelbaum M., Rademann K., Müller R., Radtke M., Riesemeier H., Görner W. *Angew. Chem. Int. Ed.*, **44**, 7905 (2005).
- Simo A., Polte J., Pfänder N., Vainio U., Emmerling F., Rademann K. *J. Am. Chem. Soc.*, **134** (45), 18824 (2012).
- Klyukin D.A., Sidorov A.I., Ignatiev A.I., Nikonorov N.V. *Opt. Mater.*, **38**, 233 (2014).
- Nahal A., Khalesifard H.R.M. *Opt. Mater.*, **29** (8), 987 (2007).
- Eichelbaum M., Rademann K., Hoell A., Tatchev D.M., Weigel W., Stößer R., Pacchioni G. *Nanotechnol.*, **19**, 135701 (2008).
- Klyukin D., Dubrovin V., Pshenova A., Putilin S., Shakhverdov T., Tsyppkin A., Nikonorov N., Sidorov A. *Opt. Eng.*, **55** (6), 067101 (2016).
- Kim B.H., Hackett M.J., Park J., Hyeon T. *Chem. Mater.*, **26** (1), 59 (2014).
- Zheng K., Yuan X., Goswami N., Zhang Q., Xie J. *RSC Adv.*, **4** (105), 60581 (2014).
- Seward T.P. *J. Appl. Phys.*, **46** (2), 689 (1975).