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Effect of X-ray irradiation and thermal treatment on luminescent properties of barium-phosphate glasses doped with silver and copper

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ABSTRACT

It is shown experimentally that in silver- and copper-containing barium-phosphate glasses metal subnanosized luminescent molecular clusters are formed during the glass synthesis. X-ray irradiation and the subsequent thermal treatment of these glasses result in the considerable change of their luminescence spectra in visible spectral region. This effect is caused by the transformation of the charge state of molecular clusters. In the luminescence spectra of the glass doped with silver and copper simultaneously new luminescence bands appear in comparison with the spectra of glasses doped only with one metal. The reason of this can be the formation of hybrid Ag_nCu_m molecular clusters. The computer simulation of the structure and optical properties of such stable clusters by TDDFT method is presented.

1. Introduction

In non-organic glasses transition and noble metals, such as Ag, Au, and Cu can exist in the states of ions, atoms, charged or neutral subnanosized molecular clusters (MCs) and nanoparticles [1–8]. Structural and electronic properties of stable charged and neutral silver and copper MCs were numerically studied in [9–12] by DFT methods. Atoms of different metals can also form stable hybrid MCs, such as X_nY_m. Structural and electronic properties of some hybrid Ag_nCu_m MCs were studied theoretically in [13–15]. In silver-containing photo-thermo-refractive sodium-silica glass silver can also exist in the state of hybrid "silver-sodium" MCs [16].

There are many methods of metal MCs synthesis in glasses and of their charge state transformation [1,2,5,6,17–21]. In particular, UV irradiation of photo-thermo-refractive silver-containing glasses doped with photo-sensitizer (Ce^{3+}) and reducer (Sb^{3+}) transforms silver MCs from the charged state (Ag_n^+) to the neutral state (Ag_n) which results in the considerable increase of glass luminescence intensity in visible spectral region [3]. Nano- or femtosecond laser irradiation of silver-containing glasses can also change the charge state of silver MCs which causes the increase or quenching of glass luminescence depending on glass pre-history [4,5,19]. During the ion exchange in silicate glasses silver or copper ions can be reduced by electrons from defects of glass network to the neutral state and form luminescent neutral MCs in the near-surface glass layer [20,21]. X-ray, gamma, electron or synchrotron irradiation of silver- or gold-containing glasses also change the charge state of metal MCs [17,18,22].

Glasses, containing silver, gold or copper luminescent MCs are of interest for the application in photonics and sensors. They can be used as spectral convertors in white LEDs [1,7], photovoltaics [23], for the recording of optical information [3–5,24], in spark detectors and UV dosimeters [25] and in temperature sensors [26]. It is evident that the investigation of different glass matrixes doped with different metal MCs and the study of effects of external treatments on these glasses will make possible to optimize the glass luminescent properties of such glasses for specific application.

The goal of the present work was the study of the X-ray irradiation and thermal treatment (TT) influence on the luminescent properties of barium-phosphate glasses doped with silver, copper and silver and copper simultaneously. The comparison of luminescent characteristics of glasses with different dopants was performed. The attention was payed to the possibility of hybrid "silver-copper" MCs formation and to their luminescent properties.

2. Experimental and theoretical methods

Barium-phosphate (BP) glasses of the following composition $Al_2O_3(5)$–$Ba(PO_3)_2(75)$–$NaPO_3(20)$ were synthesized in the ITMO University. In brackets are the concentrations in mol%. Silver and copper were added from $AgNO_3$ (0.2 mol%) and Cu_2O (0.2 mol%) correspondingly. To ensure the reduction conditions during the glass synthesis SnO (0.7 mol%) was added. This allowed obtaining glasses after synthesis with silver and copper mostly in neutral state. The

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Table 1
Denotations of the samples.

Sample	Ag, mol. % (± 1%).	Cu, mol. %. (± 1%).
BP	0.2	0
BPAg	0.2	0
BPCu	0	0.2
BPAgCu	0.2	0.2

temperature of glasses synthesis was 950 °C. To delete mechanical stresses glass samples after the synthesis were annealed at 400 °C and then cooled down to room temperature in accord with a prescribed program, the cooling rate being 5 °C/h. Denotation of the samples is presented in Table 1.

The glass transition temperature was measured by the differential scanning calorimeter STA 449 F1 Jupiter (NETZSCH-Gerätebau GmbH) and was equal 400–410 °C depending on the silver or copper concentration. The samples were prepared as polished plates 1 mm thick.

For X-ray irradiation we used X-ray tube with copper anode. X-ray tube voltage was 30 kV, and the current was 15 mA. Exposure dose was 8 MJ. The measured absorption of X-ray radiation in the samples was 10%. Half-parts of the samples were protected from irradiation by the lead masks. The irradiation was performed at room temperature.

Our preliminary experiments have shown that for some glass compositions luminescence intensity considerably depends on the subsequent thermal treatment. So after X-ray irradiation glass samples were thermally treated at 300 °C (less than glass transition temperature) during 1 h in the muffle furnace (Nabertherm). The luminescence spectra were measured by LS-55 (Perkin-Elmer) spectrofluorimeter with the step 1 nm. The optical density spectra of the samples were recorded in the 300–800 nm region using Lambda 650 (Perkin–Elmer) spectrophotometer with the step 1 nm. The optical density and luminescence spectra were registered at room temperature.

Structure and oscillation strength spectra were calculated for stable neutral tetramers Ag_nCu_m (n + m = 4) as an example. The calculations were performed within the time-dependent TDDFT [27] using the Amsterdam Density Functional (ADF2014.08) program [28,29]. The long-range exchange-correlation functional LC-ωPBE [52] (ω = 0.4 as recommended by Rabilloud in [30]) was employed with the triple-ζ plus double polarization (TZ2P) Slater-type basis set for all calculations. Only the first 20 dipole-allowed transitions were considered to evaluate the MCs oscillator strengths. In our calculations we did not took into account the influence of MC matrix surrounding.

3. Experimental results

Optical density spectra of BP glasses before and after X-ray irradiation are shown in Fig. 1. It can be seen from the Figure that X-ray irradiation results in the increase of optical density in a wide spectral range (350–750 nm) for all the samples. For BPAg and BPCu glasses absorption bands appear in a spectral range 380–550 nm. For BPAgCu glass there is no manifested absorption band, but the increase of absorption in the whole spectral region of registration is observed. An interesting fact is that in the pure BP glass the radiation-induced absorption is much more than in glasses, doped with silver and copper. The corresponding absorption band is located in 380–750 nm spectral region with maximum at λ = 520 nm. The nature of these absorption bands and the influence of glass composition on them will be discussed in Section 4. The described absorption bands disappear after the thermal treatment at temperatures above 200 °C.

Photos of the samples luminescence before and after X-ray irradiation and thermal treatment are shown in Fig. 2. One can see that X-ray irradiation and thermal treatment weakly effect on the luminescence intensity of BPCu and BPAgCu glasses (b and c in Fig. 2). In BPAg sample these treatments result in the appearance of intense red

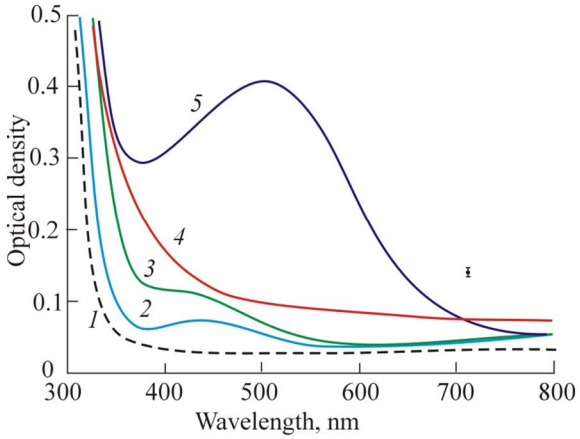

Fig. 1. Optical density spectra of BP glasses before (*1*) and after X-ray irradiation (*2–5*). *2* – BPAg, *3* – BPAgCu, *4* – BPCu, *5* – pure BP glass without Ag and Cu.

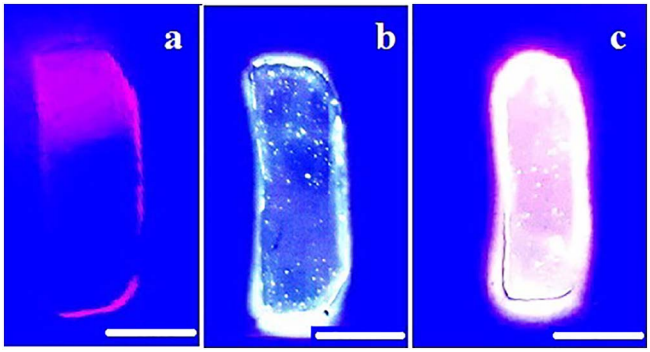

Fig. 2. Photos of samples luminescence after X-ray irradiation and thermal treatment. The upper parts of samples were irradiated. **a** – BPAg, **b** – BPCu, **c** – BPAgCu. Excitation wavelength is 365 nm. Scales are 1 cm. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

luminescence in the irradiated area (a in Fig. 2). As it will be shown below luminescence is present in this sample also before irradiation, but it is very weak in a visible spectral region. In pure BP glass very weak luminescence, caused by defects of glass network, is observed. It can be registered only with the help of spectrofluorimeter.

Luminescence spectra of BPAg, BPCu and BPAgCu for two excitation wavelengths are shown in Fig. 3, Fig. 4 and Fig. 5. Here and below the maxima of overlapping bands were defined by decomposition of luminescence spectra by Gaussians. It can be seen from Fig. 3a that luminescence spectrum of BPAg glass before X-ray irradiation, excited by 260 nm, is structured and consists of at least four overlapping bands. The maxima of luminescence bands are located at 370 nm, 410 nm, 455 and 490 nm. Luminescence band, excited by 330 nm, is not structured, but has a “tail” in a spectral range 450–600 nm. Decomposition shows that this “tail” is formed by the wide luminescence band with maximum at 490 nm. X-ray irradiation changes the luminescence spectra considerably (Fig. 3b). New overlapping luminescence bands appear with maxima at 420 nm, 460 nm, 510 nm and 560 nm for excitation wavelength 260 nm, and at 510 nm for excitation wavelength 330 nm. But luminescence intensity in visible spectral region remains weak. The subsequent thermal treatment results in the further luminescence spectra transformations (Fig. 3c). Three luminescence bands with maxima at 370 nm, 410 nm and 490 nm appear for excitation wavelength 260 nm, and two luminescence bands with maxima at 420 nm and 660 nm – for excitation wavelength 330 nm. The last band produces intense red luminescence of the sample (see Fig. 2a). The comparison of Fig. 3a,b,c shows that for excitation wavelength 260 nm thermal treatment partially returns luminescence spectrum to the initial state. For excitation wavelength 330 nm the changes in luminescence