X-ray-induced fluorescent centers formation in zinc-phosphate glasses doped with Ag and Cu ions

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Abstract. Fluorescent properties of silver and copper doped zinc-phosphate glasses were studied. By X-ray irradiation of silver and copper co-doped glasses we could create and identify new emission centers which do not exist in single-doped samples. Doping of the glass with both silver and copper ions leads to the increase of quantum yield by 2.7 times. The study was complemented by quantum chemical calculations using the time-dependent density functional theory. It was shown that fluorescence may be attributed to the formation of mixed Ag-Cu molecular clusters.

1. Introduction
Over the last decades, fluorescent molecular clusters (MCs) consisted of a few metal atoms have attracted tremendous interest since their unique electronic structure and the optical properties [1]. Doping MCs with different transition metals may strongly affect their physical and chemical properties. Inorganic oxide glasses provide a solid matrix that stabilizes clusters and makes them promising polyfunctional materials for use in various fields including photonics, solar power engineering and optical data storage [2].

Here, we report a result of combined experimental and theoretical investigation of the luminescent properties of silver- and copper-containing zinc-phosphate glasses. In particular, we have studied the effect of the formation of new emission centers by subsequent X-ray irradiation and thermal treatment.

2. Experimental section
Several types of zinc-phosphate glasses composed of Na2O-ZnO-P2O5 (ZPG) with additives of AgNO3 and CuO as activators were synthesized in the ITMO University by melt-quenching approach. The glasses are further denoted by ZPG-X, where X refers to a dopant of the following elements: Ag and/or Cu. The prepared glass samples were irradiated with the radiation of a CuKα (λ=1.54Å) sealed X-ray tube working at 50 kV and 50 mA. After the irradiation, the samples were heat-treated for 1 hour at 200 °C.

Figure 1a shows photographs of the samples and their luminescence after X-ray irradiation and thermal treatment. The excitation spectrum of ZPG-Ag-Cu differs significantly from the samples with one type of activator (Figure 1b). Its maximum is red-shifted by 15 nm and 45 nm in comparison with single doped ZPG-Ag and ZPG-Cu respectively. The silver and copper co-doped glasses (ZPG-Ag-Cu) with concentrations of AgNO3 0.1 mol.% and CuO 0.1 mol.% have a very intense emission with the excitation peak at 365 nm and in the nearly whole visible spectral range (Figure 2). The difference in excitation spectra can be caused by the appearance of new emission centers in ZPG-Ag-Cu. This is
confirmed also by the increase of luminescence intensity in this glass with the comparison with other two glass types: the measured absolute quantum yields are equal 9.6% for ZPG-Ag, 0.5% for ZPG-Cu, and 27% for ZPG-Ag-Cu.

3. Computation

In order to gain insight into the structure of possible species, the effect of Cu doping of neutral homonuclear Ag₄ MCs have been investigated with the linear response formalism of time-dependent density functional theory (TDDFT). The silver tetramer (Ag₄) doping was chosen as an example. The calculations were performed using the Amsterdam Density Functional program package at the CAM-B3LYP/TZ2P level. The long-range corrected exchange correlation functional CAM-B3LYP with parameters recommended by Rabilloud [4] was used. It has been shown to perform well for the calculation of ground and excited state properties of silver MCs [5].

Calculated optical absorption spectra for the lowest energy 4-atom Ag-Cu MCs in the photon energy range $h\omega = 1.5$–$5.0$ eV are given in Figure 3. Before reporting on the results, it should be noted that our calculations on monoatomic MCs show remarkably good agreement with previously reported theoretical data as well as with experimental results [6]. To best of our knowledge, there were no experimental studies on the optical absorption of such small mixed Ag-Cu MCs. The overall structure of the spectra is the same. All calculated spectra are characterized by one dominant band between 2.5 and 4.0 eV, except for the copper tetramer (Cu₄) which possesses three pronounced lines. It can be

Figure 1. (a) Photographs (top) and luminescence (bottom) of the samples after X-ray irradiation and thermal treatment at 200 °C. Excitation wavelength – 365 nm; (b) Normalized excitation spectra of ZPG-Ag (1), ZPG-Cu (2), and ZPG-Ag-Cu (3)

Figure 2. Fluorescence excitation-emission map of ZPG-Ag-Cu
seen that for silver-containing MCs the main absorption peak continuously red-shifted from 2.9 eV to 2.7 eV with increasing number of copper atoms. The copper tetramer (Cu$_4$) exhibits a dominant peak located at 3.75 eV. This behaviour is also observed in the experiments (see Figure 1b). In addition, the oscillator strength of the main transitions of the lowest energy MCs gradually become weak with increasing Cu atoms. Weak oscillator strength of copper tetramer (Cu$_4$) can explain the weak luminescence of copper-containing zinc-phosphate glass.

Figure 3. Calculated normalized vertical excitation spectra for Ag$_n$Cu$_{4-n}$ ($n < 4$) MCs

4. Conclusions
In summary, we have examined the luminescent properties of silver- and copper-containing zinc-phosphate glasses after subsequent X-ray irradiation and thermal treatment. The obtained results of a joint experimental and first-principles investigations demonstrate that the addition of Ag and Cu ions could lead to the formation of emission centers most likely attributed to bimetallic Ag-Cu MCs. The unique tunable optical properties of MCs in a broad spectral range make the studied glasses a promising candidates for photonic and sensing applications including wavelength converters and radio-photoluminescent dosimeters.

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References
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