UV pulsed irradiation effect on the exciton luminescence of CuCl nanocrystals in borate glass

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Abstract. Heat treatment conditions effect on the characteristics of the $Z_3$ - exciton resonant luminescence of CuCl nanocrystals in potassium-aluminabrate glass is studied. The observed patterns of luminescence buildup are explained by the participation of thermal effects in recombination processes. The size effect in the resonance emission of $Z_3$-excitons at 80 K is confirmed. The inverse dependence of the defectiveness of CuCl crystals in glass on the luminescence buildup rate of $Z_3$-excitons is established.

1. Introduction

During the heat treatment of halogen-copper photochromic glasses in the temperature range close to the glass transition, a microcrystalline CuCl phase of various sizes was nucleated [1,2]. The degree of crystals defectiveness in that case depended on the temperature and cooling conditions of heat treatment. Tempering from a temperature above the melting point of CuCl crystals in glass gave the highest photochemical sensitivity and reproducibility of characteristics. Annealing the glass at a temperature below the melting point of CuCl caused a change in the optical characteristics of the glass and a decrease in its photochemical sensitivity [3].

In this work, the luminescent technique was used to study the features of electron-hole processes excited by light in the CuCl phase and the role of defects in it. The influence of glass heat treatment conditions on the characteristics of $Z_3$-exciton resonance luminescence in CuCl and thermal defects on the resonance emission efficiency was studied. The aim of the study was to measure the spectra of resonance luminescence and the curve of luminescence buildup with varying excitation intensity and thermal background.

2. Experimental methods

The object of the study was the potassium-aluminabrate system of the following composition 0.78F-1.4Cl-1.8Cu$_2$O-2.8Na$_2$O-4.3SiO$_2$-5P$_2$O$_5$-18K$_2$O-29Al$_2$O$_3$-35.4B$_2$O$_3$ (wt.%). Glass was synthesized in an oxygen-containing atmosphere using a high-temperature furnace GmpH (Gero, Germany), a platinum crucible, and a stirrer to homogenize the melt. Quenching after the synthesis was up to room temperature. During the tempering process after heat treatment at temperatures higher or equal to the glass transition temperature, a nanocrystalline phase containing copper (I) chloride was nucleated in the glass matrix. Samples in the form of a plane-parallel plate were grinded and polished with a Beta machine (Buehler, Germany) to a thickness of 2 mm.
The spectral-thermal method is one of the suitable methods for studying glasses with copper chloride nanocrystals. Since the exciton luminescence of copper chloride can be detected only at low temperatures, it became necessary to use a low-temperature setup. It consisted of a Specac two-chamber cryostat (Great Britain), a West 6100+ temperature control unit, a vacuum pump (KNF Laboport, Germany), and liquid nitrogen. The sample was placed in a cryostat; a rarified atmosphere with a pressure of about 12 mbar was created in the internal cavity using a pump. The sample was cooled by consecutive pouring of liquid nitrogen into the external cavity of the cryostat; the temperature control unit was responsible for heating.

The glass luminescence was excited by the 3rd harmonic unit radiation of the YAG: Nd<sup>3+</sup> laser (LOTIS TII, Belarus) with a wavelength of λ=355 nm. Glass was irradiated in a pulsed mode with a frequency of 10 Hz, a pulse duration of 9 ns, and at various mean power: 57 mW, 105 mW, 153 mW, 198 mW, and 240 mW. The beam diameter was 4 mm. An AvaSpec-2048L fiber spectrometer (Avantes, Netherlands) recorded luminescence spectra every two seconds from the beginning of laser exposure.

### 3. Experimental results

It should be noted that the crystallization of CuCl nanophase in glasses is preceded by the diffusion-controlled phase separation resulted in forming the nanodroplets of CuCl liquid in the vitreous matrix. This process is divided into three stages: the nucleation, the growth on account of dissolved matter, and the recondensation growth when the largest particles grow at dissolution of the smaller ones [4].

The absorption spectra of glasses doped with copper and chlorine ions after the heat treatment acquired an intense absorption band in the near UV region. According to many works, including [1–4], this absorption band related to exciton absorption of CuCl crystals. Due to the small size, it was difficult to determine the mean size of the crystals precipitated in the glass matrix using the X-ray diffraction method. Proceeding from this, we used the method of calculating the mean size, proposed and justified in [5], based on the results of optical absorption spectroscopy. The method was based on the representation of a nanocrystal as a semiconductor ball, and its size corresponded to the width of a potential quantum well that contained an exciton. Since copper halide crystals were not quantum dots, the case of weak confinement was used. The calculation was carried out according to the formula:

\[
\hbar \omega_{23} = E_g - E_b + 0.67 \frac{\hbar^2 \pi^2}{M \alpha^2}
\]

where \(E_g=3.395\) eV – bandgap of the bulk crystal, \(E_b=0.190\) eV – \(Z_3\)-exciton binding energy, \(M=0.33m_0\) – effective exciton mass (\(m_0\)-electron mass), \(\hbar=1.05457\times10^{-34}\) J/s - Planck-Dirac constant, \(\alpha\)-the crystal size. The calculation results are presented in table 1.

| Heat treatment temperature (°C) | Location of CuCl absorption band (eV) | CuCl nanocrystals mean size (Å) |
|----------------------------------|---------------------------------------|---------------------------------|
| 400                              | 3.253                                 | 50                              |
| 405                              | 3.255                                 | 48.5                            |
| 410                              | 3.257                                 | 47                              |
| 420                              | 3.248                                 | 55                              |
| 430                              | 3.247                                 | 56                              |

The experimental results on the luminescence of copper chloride crystals obtained during various isothermal treatment regimens are shown in Figure 1. Using an experimental setup, the luminescence spectra of the glasses under study were obtained at a liquid nitrogen boiling point in the 300–1100 nm range.
Figure 1. (a) Luminescence spectrum of potassium-aluminaborate glass after the heat treatment at 420°C, irradiated by 355 nm laser of 240 mW power, (b) glass luminescence spectra in near UV region after the heat treatment at various temperatures.

Figure 1 shows the luminescence spectrum consisted of two parts. The first band located in the near UV region close to the excitation. This luminescence band appeared only at cryogenic temperatures. The second part of the spectrum comprised a wide luminescence band, which occupied the 500-800 nm region. Based on Ref. [3,6], the luminescence band in the UV region referred to the exciton luminescence of monovalent copper chloride crystals, and the visible luminescence band corresponded to the luminescence of monovalent copper ions.

In Figure 1b the maximum of the exciton luminescence band shifted to the longer wavelength region (or lower energy region) with an increase in the heat treatment temperature. It is known [7] that with an increase in the mean size of crystals nucleated in the glass matrix, the exciton luminescence bands shifted to the long-wavelength region along with the exciton absorption bands. This confirmed the fact that in the present work an increase in the mean crystal size also occurred with an increase in the heat treatment temperature.

A sample irradiated with 57 mW pulsed laser initially had two exciton luminescence peaks at wavelengths of 385 nm and 390 nm (Figure 2a). But as the exposure duration increased, a peak located at 390 nm increased by 5 times, on the contrary peak at 385 nm remained the same. The samples with the same heat treatment regime irradiated with a power of 105, 153, 198, 240 mW manifested similar changes.
Figure 2. Luminescence spectra of borate glass with CuCl nanocrystals (heat treatment temperature 410°C) excited by 355 nm with different mean power: (a) 57, (b) 105, (c) 153, (d) 198 mW. Spectra were recorded at two second intervals during 200 seconds.

The following dependences of exciton luminescence intensity at 390 nm on the irradiation time were constructed in Figure 3a. The second luminescence peak was chosen since, as shown by experimental data, it was dominant. In all studied glass samples after reaching a stable maximum, the luminescence intensity did not change during further irradiation, regardless of the laser power.

Figure 3. (a) Luminescence buildup of CuCl nanocrystals; (b) luminescence attenuation of free Cu\(^{+}\) ions in borate glass, heat treated at T=410°C, after different power of UV laser irradiation.

Additionally, luminescence spectra of Cu\(^{+}\) ions were obtained. Figure 3b shows the luminescence intensity at 650 nm dependence at irradiation duration of a sample with initial heat treatment at 410°C. The attenuation rate of the intensity level grew with increasing power. For the samples irradiated with 57 mW and 105 mW power, the luminescence level decreased to constant values in 25 seconds. In the remaining samples, luminescence decreased during 100 seconds of irradiation.

Figure 4 shows the dependences of the nanocrystals’ luminescence intensity and monovalent copper ions in glass samples having different thermal history on the duration of exposure by UV pulsed radiation. With the increase of the heat treatment temperature, the dependence on the figure approached closer to the linear function.
4. Discussion
The gradual buildup in the exciton luminescence was apparently due to the filling of traps, associated with thermal defects and participated in the non-radiative recombination channel of electrons and holes, by free charges created by laser radiation. During the irradiation process, more and more such traps were filled. With the radiation density increase, they were filled faster and the emission intensity of the $Z_3^+$-exciton in CuCl crystals increased faster. Analyzing the data obtained, the number of defects in glasses with low heat treatment temperatures was greater than in glasses after high-temperature heat treatment. This was because the cooling process after isothermal heating occurred inertially: the cooling time from high temperatures was longer than from low temperatures. Since the defect centers were vacancies of the copper ion in the CuCl and interstitial copper ions - Frenkel cationic defects, - their relaxation decreased the number of free ions along with their luminescence intensity. At the same time, copper ions, which were part of the defects near the nanocrystalline phase, due to the high-power density of the laser radiation became part of this crystalline phase, increasing the number of luminescent centers in the near UV region. The absorption spectra of glasses [8], recorded before and after the laser irradiation, showed an increase in the mean size of copper chloride nanocrystals in the glass. This suggested that the process of nanocrystalline phase growth on the account of the dissolved matter was induced by laser.

5. Conclusion
From the above results, we can conclude that the heat treatment temperature of the glass under study affected the buildup duration of copper chloride nanocrystals’ luminescence and the attenuation duration of Cu$^+$ ions luminescence. With an increase in the heat treatment temperature, the Cu$^+$ luminescence intensity decreased, and the luminescence intensity of CuCl nanocrystals increased. $Z_3^+$-exciton luminescence of CuCl nanocrystals build up by several times with an increase in the UV irradiation duration. Under continuous exposure by UV pulsed laser of the borate glass with CuCl nanocrystals, degradation of luminescence after buildup did not occur. The observed patterns of luminescence buildup can be explained by the participation of thermal Frenkel effects in recombination processes. The inverse dependence of the defectiveness of CuCl crystals in glass on the luminescence buildup rate of $Z_3^+$-excitons was established.

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