Investigation of spectral properties of potassium-aluminum-borate glass with CuCl - CuBr nanocrystals

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Abstract. Heat treatment conditions effect on the characteristics of exciton absorption and luminescence of CuCl and CuBr nanocrystals in potassium-aluminaborate glass is studied. The size effect of the band edge absorption and luminescence energy is confirmed. The simultaneous presence of copper halide nanocrystals and free monovalent copper ions in the glass matrix is shown. Possible conditions for the formation of mixed CuCl-CuBr crystals are considered.

1. Introduction

Investigations in the field of the influence by a mixed halogen ions on the spectral properties of semiconductor crystals opened a second wind in the wake of numerous works on crystals of the perovskite structure [1–3]. By using mixed forms instead of pure chloride, bromide, and iodide crystals, the properties (band edge absorption and luminescence energy) of the entire material can be varied over a wide range. [1].

However, the main problem of oxygen-free crystals based on halides is their instability when interacting with the air atmosphere [4]. Many methods have been invented to stabilize them: placing them in a polymer matrix, growing inside other oxygen-free and more stable crystals [5]. We, in turn, will focus on the method of stabilizing halide crystals by placing them in a glassy matrix.

Copper halide crystals have been extensively studied in borosilicate [6], borate [7], and phosphate [8] matrices. However, studies of the effect of mixed halogens were carried out from the point of view of phase transitions of the copper halogen phase. We will devote this work to the study of the influence of the effect of mixed halogens on the spectral properties of borate glass with nanocrystals.

2. Experimental methods

Potassium-aluminum-borate glass was the object of this research, in which the matrix composition was: 22K₂O-35Al₂O₃-43B₂O₃ (wt.%). Nanocrystals of CuCl, CuBr and CuCl - CuBr were obtained by introducing additives to the glass batch: 3 Cu₂O and 3.3 NaCl (composition #1), 2.98 KBr (composition #2), 2.48 NaCl - 2.24 KBr (composition #3) wt., respectively. The synthesis was carried out under laboratory conditions in an electric furnace (Gero, Germany) of the "bottom" load at a temperature of 1350°C in a corundum crucible with stirring the melt with a platinum stirrer for 1 hour. After synthesis,
isothermal treatment of glass samples was carried out at temperatures above the glass transition temperature \((T_g = 390 \ ^\circ \text{C})\) to nucleate the nanocrystals with copper (I) halides in the glass matrix.

The absorption spectra of glass samples were recorded on a two-beam spectrophotometer Lambda 650 in the range of 200 - 900 nm at the liquid nitrogen boiling point (77K). The luminescence and luminescence excitation spectra were recorded using a single-beam spectrophotofluorimeter LS-55 (Perkin Elmer) in the range 200 - 400 nm with the possibility of changing the excitation wavelength also at the liquid nitrogen boiling point.

Due to the strong electron-phonon interaction [9], the intensity of exciton absorption and luminescence of copper halides at room temperature was so low that it was rather difficult to study it. So, 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 a liquid nitrogen. The sample was placed in the internal cavity of the cryostat, where a rarified atmosphere with a pressure of about 20 mbar was created using a pump. The sample was cooled by the liquid nitrogen into the external cavity of the cryostat; the temperature control unit was used for subsequent heating to room temperature.

3. Experimental results

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 (Figure 1a,b). Halide crystals have a zinc blende structure. The valence band in these crystals is split due to the spin-orbit interaction into a fourfold degenerate \(\Gamma_8\) band (transitions \(Z_{1,2}\)) and a doubly degenerate band \(\Gamma_7\) (transition \(Z_8\)). Due to the difference in the degeneracy of the levels, the probability of transitions from the \(\Gamma_8\) level is greater than from \(\Gamma_7\). In CuCl crystals, the \(\Gamma_7\) level is energetically higher than the \(\Gamma_8\) level, therefore the \(Z_{1,2}\) bands are located at higher energies and have a significantly greater intensity. In CuBr crystals, the arrangement of the \(\Gamma_8\) and \(\Gamma_7\) levels is inverted.

According to numerous works dedicated to copper halides in glassy and crystalline matrices, including [10–13], the band edge absorption of CuCl nanocrystals located in 370-385 nm range and 400-415 nm was the range for CuBr nanocrystals’ exciton absorption peaks (Figure 1a shows the energy regions of the band edge absorption for the corresponding crystals). The crystallization of copper halide nanophase in amorphous environment was determined by the diffusion-induced phase separation process [14,15]. During their growth the nanocrystals can be represented as a semiconductor ball, and its size corresponded to the width of a potential quantum well inside of which the motion of the confined exciton can be calculated. The basis of this method was first proposed in [16] and then confirmed on the basis of optical spectroscopy data of copper chloride nanocrystals in a matrix of borosilicate glass [17].

The case of strong size quantization is determined the motion of an exciton in a crystal with a size less than the Bohr exciton radius \((a_0)\). The case of weak confinement was for crystals with a size exceeding the Bohr exciton. For CuCl \(a_0=0.68\) nm, for CuBr \(a_0=1.7\) nm. Since copper halide crystals for most cases were bigger [10–13], the case of weak confinement was used. The calculation was carried out according to the formula [16]:

\[
\hbar \omega_{ex} = E_g - E_b + 0.67 \frac{\hbar^2 \pi^2}{2M a^2} \tag{1}
\]

where \(\omega_{ex}\) - exciton absorption band location, \(E_g(CuCl)=3.2949\) eV, \(E_g(CuBr)=2.987\) eV – bandgap of the bulk crystal at 77 K [11], \(E_b=0.190\) eV – exciton binding energy, \(M\) (CuCl)=1.9*m_0 [18], \(M(CuBr)=1.68*m_0\) [11] – effective exciton mass (m_0-electron rest mass), \(a\)-the crystal radius. Numerical factor 0.67 was introduced by authors of [16] because of the crystals size distribution (and subsequently successfully used by different scientific groups [18,19]). Its exact value was obtained based on the theory by Lyshfitzh and Sliosov of diffusion phase decomposition of a supersaturated solid solution [20] for the recondensation stage.

According to calculations by (1), the average radii of CuCl nanocrystals in composition #1 increased from 2.3 to 3 (±0.5) nm with an increase in the heat treatment (HT) temperature from 410 to 450°C.
Composition #2 provided crystals' nucleation of radii from 2.8 to 4.2 (±0.5) nm while heat treatment temperature increased in the same range.

The Figure 1c depicts the luminescence spectrum of composition #2 (HT temperature 390°C) under irradiation with different excitation wavelengths. The luminescence spectrum consisted of two bands, where the first band located in the near UV region increased with the excitation wavelength and corresponded to CuBr crystals. The second wide band located at 400-600 nm corresponded to the luminescence of monovalent copper ions [6,7] and decreased with the increase of the excitation wavelength. The main reason for the change in the luminescence intensity is that the maximum of the excitation band of monovalent copper ions fell at 250 nm. The maximum of the luminescence excitation band of CuBr nanocrystals fell on the bandgap edge of 3.18 eV (390 nm). The luminescence energy of nanocrystals shifted to smaller values along with band edge absorption with increasing heat treatment temperature (Figure 1d). The dependences shown in Figure 1 c,d were typical for all compositions.

**Figure 1.** (a) Absorption spectra of compositions #1 and #2 after different HT temperatures (the zones CuCl and CuBr separate the corresponding regions of absorption bands location); (b) absorption spectra of composition #3 after different HT temperatures; (c) luminescence spectra of composition #2 (HT temperature 390°C) at different excitation wavelengths; (d) luminescence spectra of composition #1 after different HT temperatures (excitation by 390 nm).

**4. Discussion**

The ionic radii of chlorine and bromine coincided, which did not contradict the assumption that when two halogen ions were introduced into the glass composition, they could interchange each other in the crystal structure of copper halides. Determination of the chemical composition of copper halides by X-ray diffraction was a rather difficult task. Copper bromide and chloride had the same structure (sphalerite), almost the same unit cell size and interplanar distances. Due to the small size of crystals nucleated in the glass matrix, the diffraction maxima of such objects were broadened. This led to the
fact that in the diffraction patterns, copper halides were practically indistinguishable from each other. Moreover, there was no possibility to determine whether bromine ions were partially replaced by chlorine ions (or vice versa) in the crystal structure. In other words, from the XRD data it was impossible to say whether we were dealing with mixed crystals or not. Thus, the optical spectroscopy studies were used for this task.

The band edge absorption of composition #3 possessed intermediate values between compositions #1 and #2. According to the formula (1), the mean crystal radii were calculated under two different conditions: (a) if we were dealing with copper chloride crystals, (b) with copper bromide crystals. In the former case, radii from 3.7 to 6.3 nm were obtained. In the latter case, radii from 2.3 to 2.6 nm were obtained with an increase in the HT temperature from 410 to 450°C. Based on the data obtained, it is difficult to say whether the copper halide crystals were mixed or separate in the borate glass matrix. The second situation is more plausible, especially due to the calculated mean sizes of nanocrystals. Also, based on this calculation, it is obvious that none of the crystals is prevalent in composition #3. Thus, this case requires further research.

5. Conclusion
From the above results, it can be concluded that when additives containing ions of monovalent copper and halogens were introduced into the glass composition, as well as subsequent isothermal treatment at a temperature above the glass transition, nanosized crystals of copper halides were precipitated in the glass host. Nanocrystals of copper halides were characterized by intense band edge absorption (in the near UV region) and narrow-band luminescence close to it, which can be observed only at low temperatures. With an increase in the heat treatment temperature, the mean crystal size increased, which manifested itself in a long-wavelength shift of the absorption and luminescence bands. With the simultaneous introduction of two halogen ions into the glass composition, they formed crystals of copper chloride and bromide at the same time. Wherein band edge absorption occupied an intermediate value between purely chloride and purely bromide crystals. However, it was difficult to identify whether these crystals were independent in the glass matrix or mixed, in which halogen ions interchanged each other in the part of the unit cells.

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