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Features of copper chloride nanocrystals formation in potassium aluminoborate glass

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ABSTRACT

An unexpected sequence of forming different crystal lattices for the CuCl nanophases in potassium aluminoborate glass depending on the preceding heat treatment temperature is revealed. The hexagonal wurtzite-like nanocrystals are shown to crystallize from the liquid CuCl nanosize droplets separated at the lower heat treatment temperatures (380 °C to no more than 400 °C) than in the case for the cubic sphalerite-like CuCl nanocrystals (higher than 400 °C). This sequence is inverse with respect to the standard temperature sequence of crystallizing the bulk hexagonal and cubic phases from a melt that is known for both CuCl and its structural prototype, ZnS. A tentative explanation for the effects revealed is proposed, the explanation assuming the principal role of internal pressure in the CuCl nanodroplets in setting the location of a phase point at the phase diagram.

1. Introduction

CuCl macrocrystals are well known [1–6] and are characterized by intense excitonic absorption at the band gap edge and also, unlike other semiconducting copper halides [1,7–9], by inverse locations of Z_3 and $Z_{1,2}$ excitonic levels (the negative spin-orbit splitting). The CuCl crystals of nano scale embedded in dielectric matrix possess photochromic [2] and nonlinear-optic effects [4]. Materials activated by CuCl nanocrystals can be used as cut-off filters and limiters for optoelectronic detectors protection from pulsed laser radiation. Moreover, the exciton states in nanosized crystals are influenced by the quantum size effect, in other words, the finiteness of crystal lattice since the edges of the crystal are the edges of quantum well containing an electron and a hole. In quantum dots with the effective Bohr radius exceeding the crystal size, the blue shift of exciton energy is basically described by the sum of particular kinetic energy shifts for an electron and a hole (so-called electron-hole confinement). Due to the small Bohr radius of exciton (a_{ex} = 0.68 nm [5]) and large Rydberg constant (Ry = 213 meV [5]) in CuCl nanocrystals, the quantization of exciton translational motion (or exciton confinement) is observed.

In several sources [5,10], the effect of exciton confinement on the size and shape of CuCl microcrystals precipitated in the NaCl and KCl crystalline matrices was studied. The crystal shape was found to be flat and the effect of quantum confinement was shown to produce the blue shift of the excitonic bands with a decrease in the crystal size (optical measurements). In [2,3,8], the results of optical studies on the spherical CuCl nanocrystals precipitated in the transparent glass matrices are reported and strong correlations between the crystal size and locations of bands in the absorption and luminescence spectra of free excitons are revealed.

According to a set of basic research studies [1,6,11], many semiconductor crystals can exist in three crystal modifications such as those with the zincblende type lattice (γ-phase, space group T_d^2), wurtzite type lattice (β-phase, space group C^4_{6v} [12]), and intermediate "statistically disordered" structure (α-phase) occurring usually at the higher temperatures than two former. In accord with the phase diagram [13], CuCl macrocrystals with wurtzite type lattice occur in a limited temperature range (407–422 °C), which is why γ-CuCl is the only phase stable at the normal conditions. A few studies on AgI crystals (see, for example, [6]) are devoted to differences in the optical spectra of β- and γ-phases of semiconductors. In the zincblende AgI, the top of the valence band (Γ_{15}) is triply degenerated with no spin-orbit interaction taken into account. This degeneracy is reduced by spin-orbit splitting, thus resulting in the doubly degenerated zone (Γ_8) and singlet zone (Γ_7). Hence, two bands in the optical spectrum correspond to two direct allowed transitions at $k = 0$. Namely, a transition from the Γ_8 state results in the $Z_{1,2}$ exciton band and that from the Γ_7 state provides the Z_3 exciton band. The degeneracy of Γ_8 state turns out to be greater in samples with internal stresses.

In borosilicate glasses [13] the nucleation of CuCl nanocrystals is occurred via thermo-induced crystallization at temperatures above glass transition temperature. The growth of semiconductor particles in

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glass matrices is based on the thermodynamics of the diffusion-controlled phase decomposition of oversaturated solid solutions. This process is divided into three stages: nucleation, growth on account dissolved matter, and recondensation growth when the largest particles grow at dissolution of the smaller ones [14]. It is known [15,16] that a nanophase formed in the borosilicate glasses during heat treatment consists of the CuCl - NaCl solid solution inheriting some structural elements of CuCl hexagonal modification.

Potassium aluminoborate (PAB) glass was first used [17,18] as a medium for the precipitation of the magnetic particles of manganese ferrite. The mean size of the ferromagnetic particles ranged from 10 to 23 nm. Later [19], the CuCl nanocrystals were precipitated in the potassium aluminoborate glass host [19]. The CuCl nanophase in such glasses was formed due to the occurrence of the phase separation or segregation under the heat treatment [17,18].

Various studies have shown [2,13] that the melting temperature of CuCl nanocrystals can be significantly lowered depending on their size and total nanophase composition. For CuCl nanocrystals in potassium aluminoborate glass, the melting temperature ranges from 80 to 150 °C [9]. The crystallization processes in the liquid CuCl nanosize droplets around 10 nm in diameter were found [9] to start at temperatures as low as 40–85 °C due to the effect of supercooling.

The aim of the given research is to investigate the conditions of the CuCl nanocrystals formation in borate inorganic glass using the X-ray diffraction (XRD) and optical measurements.

2. Experimental section

The heat-treated samples of PAB glass containing Cu and Cl were studied, the glass composition (wt%) being 17,5K_2O - 21Al_2O_3 - 46B_2O_3 - 8,9NaCl - 2,42Cu_2O - 0,23 SnO_2 - 0,23Sb_2O_3 - 0,82Na_3AlF_6 - 2,9P_2O_5. The chemical composition of the glass obtained was determined by X-ray fluorescence spectrometer ARL PERFORM'X 4200 (Thermo Scientific) with an error of 0,01 wt%. The 100 g of batch were admixed from the high purity chemical precursors. The synthesis was conducted for 2 h in the corundum crucibles at 1280 °C in the air atmosphere by the standard melt quenching technique, the melt was mixed by the quartz stirrer. After completing the synthesis, the melt was poured into a metal mold; then, the mold with glass was placed into a muffle oven with temperature of 380 °C and, further, cooled down inertially. The glass obtained was homogenous, light green, chemically and humidity resistant. The glass samples were subjected to the heat treatment at various temperatures.

The upper limit of the heat treatment temperature (T ~440 °C) was picked up empirically: above this temperature, the macroscopic crystallization occurred. The nanocrystalline phase was precipitated in the glass bulk by isothermal treating the samples at temperatures exceeding the glass transition temperature [10] and subsequent quenching to room temperature. Because the concentrations of both copper and halogen exceeded the solubility limit for the matrix, the system obtained might be considered to be the supersaturated solid solution. During the high-temperature heat treatment and subsequent cooling of this glass, the phase separation of the supersaturated solid solution and subsequent fluctuation nucleation of a new phase occurred [13,14]. The size of NCs was controlled through the duration and temperature of heat treatment.

Samples were heat-treated in a gradient oven for 3 h at temperatures of 380, 390, 410, 420, 430, and 440 °C. After the heat treatment, the samples were transferred to a muffle oven with temperature of 370 °C and cooled down in it inertial to room temperature.

3. Results

A Netzh Jupiter STA 445 differential scanning calorimeter (DSC) was used for estimating the glass transition temperature T_g of glass samples under study (heating rate 10 °C/min). The measured T_g magnitude of initial PAB glass was found to be 381 °C (Fig. 1) with the error of 0,5 °C. DSC curve contains no crystallization peaks for CuCl due to a small volume fraction of the nanocrystalline phase obtained after the heat treatment.

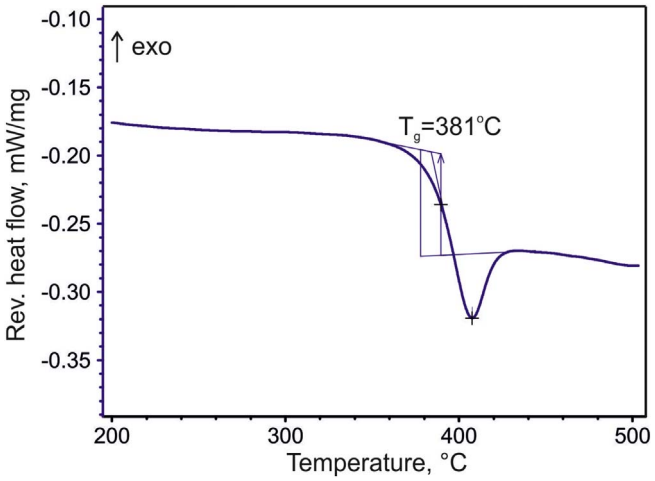

Fig. 1. Heating DSC curve for PAB glasses doped with CuCl nanocrystals.

The occurrence of CuCl NCs in the glass bulk was revealed with the optical absorption and X-ray diffraction (XRD) methods. The optical absorption spectra were recorded using Lambda 650 UV–Vis spectrophotometer (Perkin Elmer) with 0.2 nm resolution in the 0,5–4,0 eV range at room temperature. Fig. 2 shows the low-energetic shift of the absorption UV edge in the spectrum of the heat-treated glass activated by the CuCl nanocrystals (curve 2) compared to spectrum of the initial glass doped with monovalent copper ions (curve 1). In view of intense excitonic absorption to be investigated, the thicknesses of glass samples did not exceed 250 μm [20]. Optical measurements were carried out in a cryostat equipped with Specac Inc. temperature controller at boiling point temperature of liquid nitrogen, thus minimizing the electron-phonon interaction.

XRD was used to identify a crystalline compound in a mixture based on the set of its interplanar spacings and relative intensities of the corresponding lines at X-ray diffraction patterns. The identification was performed using PDWin 3.0 software package. The search of analogues was carried out within the ICDD database of PDF-2 powder X-ray diffraction patterns. Diffraction patterns were recorded with Rigaku X-ray diffractometer using CuKα radiation. A 0,02-mm-thick Ni foil was applied to suppress CuK_β radiation. In view of the relatively small volume of segregating crystalline phases (several tenths of percent), the

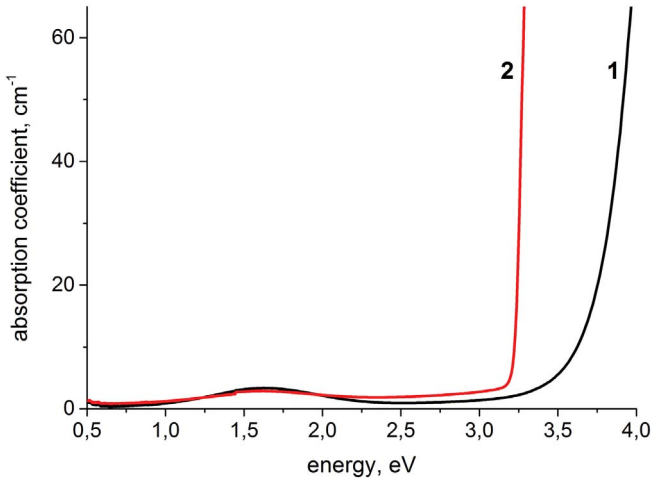

Fig. 2. Visible absorption spectra of PAB glass doped with copper ions (1) and CuCl nanocrystals (2).