Conference materials
UDC 535.341
DOI: https://doi.org/10.18721/JPM.161.122

Alkali ion effect on phase transition temperatures of CuCl nanocrystals in potassium-alumina-borate glass

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Abstract. The effect of the Na/K ratio on the phase transition temperatures of CuCl nanocrystals in potassium-alumina-borate glass is studied. The size effect in the location of the exciton absorption is confirmed. By increasing the content of sodium ions in glass, it is possible to increase the melting point of CuCl crystals with a mean size of 3.1 nm from 152 to 168 °C. It is assumed that in the matrix of potassium alumina-borate glass, instead of pure CuCl crystals, a CuCl-RCl (R = Na, K) solid solution crystallizes during the heat treatment.

Keywords: copper halides, melting temperature, crystallization temperature, solid solution

Funding: This research was supported by Russian Science Foundation (Agreement No. 19-72-10036).

Citation: Babkina A.N., Zyryanova K.S., Kulpina E.V., Gavrilov R.R., Alkali ion effect on phase transition temperatures of CuCl nanocrystals in potassium-alumina-borate glass, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (1.1) (2023) 131–136. DOI: https://doi.org/10.18721/JPM.161.122

Материалы конференции
УДК 535.341
DOI: https://doi.org/10.18721/JPM.161.122

Влияние вида щелочного иона на температуры фазовых переходов нанокристаллов CuCl в калиево-алюмоборатном стекле

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Аннотация. В работе показаны результаты исследования влияния соотношения Na/K на температуры фазовых переходов нанокристаллов CuCl в калиево-алюмоборатном стекле. Подтвержден размерный эффект в месте поглощения экситона. С увеличением содержания ионов натрия в стекле температура плавления нанокристаллов CuCl среднего размера 3,1 нм увеличивается с 152 до 168 °C. Предполагается, что в матрице калиево-алюмоборатного стекла вместо чистых кристаллов CuCl при термообработке кристаллизуется твердый раствор CuCl-RCl (R = Na, K).

Ключевые слова: галогениды меди, температура плавления, температура кристаллизации, твердый раствор

Финансирование: This research was supported by Russian Science Foundation (Agreement № 19-72-10036).

Ссылка при цитировании: Бабкина А.Н., Зырянова К.С., Кульпина Е.В., Гаврилов Р.Р. Влияние вида щелочного иона на температуры фазовых переходов нанокристаллов CuCl в калиево-алюмоборатном стекле // Научно-технические ведомости СПбГПУ.

Физико-математические науки. 2023. Т. 16. № 1.1. С. 131–136. DOI: https://doi.org/10.18721/ JPM.161.122

Introduction

Tsekhomsky and Golubkov [1, 2] showed that temperature measurements of X-ray scattering at small angles can show phase transformations of copper halide crystals in photochromic glass. In addition, it was found that not pure CuCl microcrystals, but a CuCl-NaCl solid solution [2] are precipitated in the borosilicate glass matrix, which was confirmed by the dependence of phase transformation temperatures and photochemical response on the content of sodium chloride in the glass composition. It was shown in the work that at a constant concentration of chloride ions and successive equimolecular replacement of sodium by potassium, the temperatures of phase transformations of copper halides decrease [3]. This once again confirms the theory of the presence of a CuCl-RCl (R = Na, K) solid solution in the glass matrix. However, unlike borosilicate glass, borate glass with copper halide nanocrystals does not exhibit photochromism [4] and, probably, the composition of the crystalline phase in it may differ.

Therefore, in this work, we studied the phase transition temperatures of CuCl nanocrystals in potassium-aluminum-borate glass depending on the alkali ions content in the composition.

Experimental methods

In this work, nanosized copper (I) halide crystals were nucleated in potassium-aluminum-borate glass matrix with different ratios of alkali ions dopants: 4K-1Na (# 1), 3K-2Na (# 2), 2K-3Na (# 3), 1K-4Na (# 4). Synthesis was carried out in a laboratory electric furnace (Gero, Germany) at a temperature of 1350 °C in a corundum crucible with stirring of the melt with a platinum stirrer for 1 hour. After synthesis, the initial glasses were thermally treated at temperatures of 410, 430, and 450 °C for nucleation of copper (I) chloride crystals in the glass matrix.

The absorption spectra of glass samples in the temperature range from -196 to 20 °C were recorded on a Lambda 650 spectrophotometer in the range of 200–900 nm. Sample was cooled down using a Specac two-chamber cryostat (Great Britain), a West 6100+ temperature control unit, a vacuum pump (KNF Laboport, Germany), and liquid nitrogen. In the temperature range from 18 to 200 °C, the optical density spectra of glass samples were recorded on an opto-thermal setup consisting of a broad-spectrum lamp as a radiation source, an Avaspec 2048 fiber spectrometer (Avantes) as a radiation detector, a temperature cell with quartz windows, a sample holder inside it and a platinum thermocouple for monitoring the sample's temperature the during measurements. The change in the sample's temperature had the form of a continuous cycle of heating and subsequent cooling with temperature change at a rate of 2.5 °C/min.

Experimental results

The absorption spectra of glasses after the heat treatment (HT) acquired an intense absorption band in the near UV region (Fig. 1), which corresponds to the absorption of CuCl nanocrystals [5, 6]. The crystallization of CuCl nanophase in amorphous environment is described by the diffusion-induced phase separation process [7]. During their growth the nanocrystals can be represented as a semiconductor ball with a size corresponding 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 [8] and then confirmed by optical spectroscopy data of CuCl nanocrystals in borosilicate glass [9]. Since this method was tested specifically on CuCl crystals, we also use during calculations.

Since CuCl crystals for most cases were bigger than the Bohr exciton size [5], the case of weak confinement was used. The calculation was carried out using E_g(CuCl) = 3.2949 eV,– bandgap of the bulk crystal at 77 K, E_b = 0.190 eV – exciton binding energy, M (CuCl)=1.9·m_0 [10, 11] – effective exciton mass (m_0-electron rest mass) via equation used in [12].

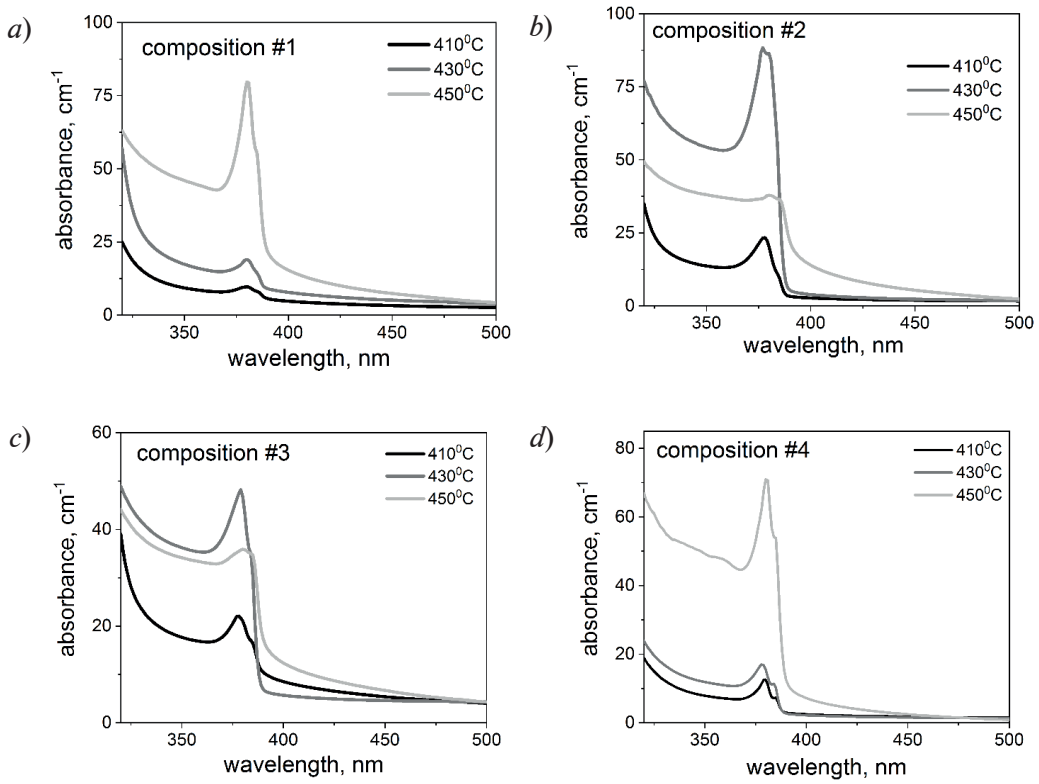

Fig. 1. Absorption spectra of compositions #1(*a*), #2 (*b*), #3 (*c*), #4 (*d*) after different HT temperatures (registration temperature= –196 °C)

According to calculations, the mean size of CuCl nanocrystals in all compositions was 2.3 ± 0.5 nm after 410 °C HT, 2.7 ± 0.5 nm after 430 °C HT, 3.1 ± 0.5 nm after 450°C HT.

Due to relatively small size of nanocrystals, it is difficult to use X-ray methods to determine the mean size and phase transformation temperatures. Therefore, to study phase transitions, an opto-thermal method was chosen, which consisted in recording the absorption spectra of CuCl nanocrystals during heating and subsequent cooling of glass samples. Since exciton absorption is directly inherent only in CuCl nanocrystals, a decrease in its intensity can be associated with thermal recombination of excitons; however, its complete disappearance indicates the absence of crystals in the glass matrix. Similarly, the appearance of exciton absorption indicates the appearance of crystals in the glass matrix. This method was successfully tested on copper halide crystals [13, 14], where it was shown that the phase transformation temperatures obtained by X-ray and optical methods coincided.

During heating of glass samples with CuCl nanocrystals, the maximum of the absorption band shifted to the short-wavelength region, and the absorption intensity decreased until it disappeared completely. The temperature, at which the exciton absorption completely disappeared, was determined as the melting temperature of nanocrystals. Upon subsequent cooling of the sample from temperatures below T_g, an overcooling region was observed, in which the intensity of exciton absorption remained equal minimal. The temperature at which the increase in the intensity of exciton absorption began was determined as the temperature of crystallization onset (Fig. 2). When the composition of the glass matrix is constant, the revealed temperatures of phase transitions depend only on the mean size of crystals ensemble [14].

Discussion

Fig. 2 shows that, within the same composition, with an increase in the HT temperature the heating-cooling curves shift to higher temperatures. This is a manifestation of the size effect. It is interesting to note that for crystals with the smallest size, the intensity of exciton absorption did not reach the initial values during cooling to room temperature. Thus, at room temperature some of the crystals were still in the state of a supercooled liquid.

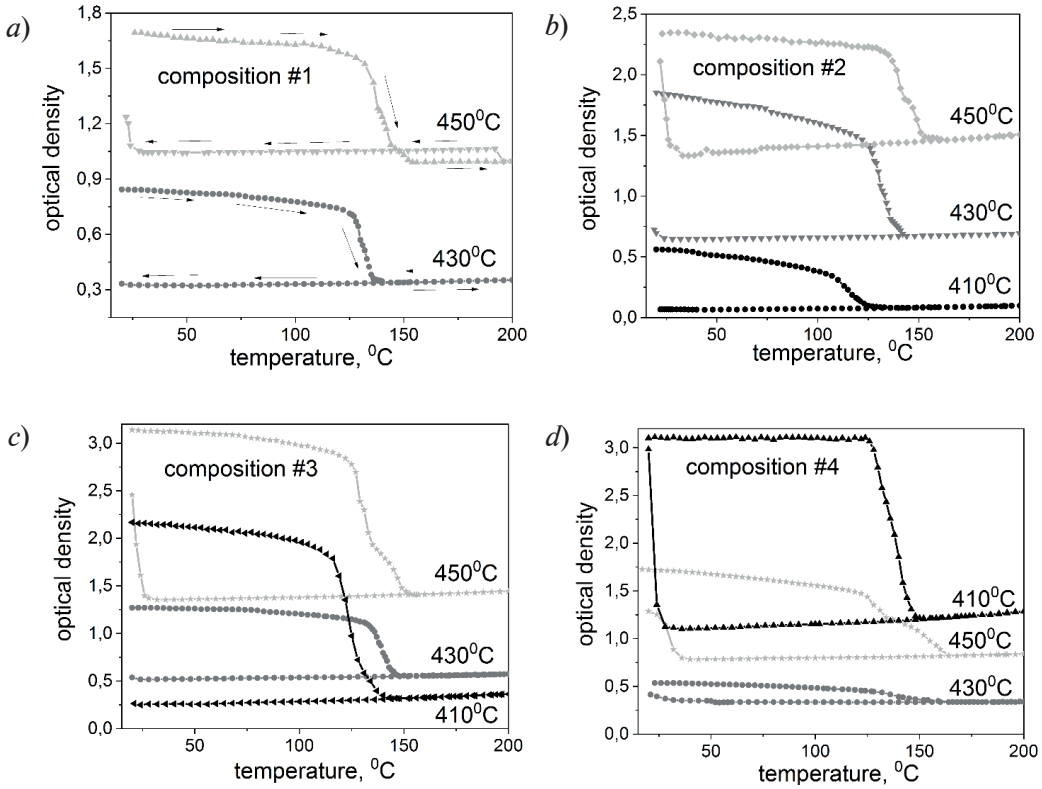

Fig. 2. Temperature dependence of optical density in the exciton absorption maximum of CuCl during heating and cooling of samples #1 (*a*), #2 (*b*), #3 (*c*), #4 (*d*) after heat treatment at 410, 430, 450 °C

The phase transition temperatures determined are shown in Fig. 3. With an increase in the sodium content in the additives, the melting and crystallization temperatures of nanocrystals increase, which was shown in [3]. The presence of potassium and sodium halides did not reveal itself either in the spectral data or in the diffraction patterns. Since the process of crystal formation in the glass matrix is of a diffusion nature, there is a high probability that a transition layer exists around the crystalline phase, the chemical composition of which differs both from the composition of the crystals and the glass matrix. Sodium and potassium chlorides were introduced into the composition in the form of ready-made reagents and were used as a source of chloride ions. Therefore, it can be assumed that the transition layer, in addition to chlorine and copper ions, is also saturated with alkali metal ions. The melting temperature of the eutectic composition CuCl-NaCl is 326 °C [15], CuCl-KCl is 146 °C [16]. Considering the influence of the size effect and the simultaneous presence of two alkali ions in the glass composition, it can be assumed that the recorded melting temperatures will have intermediate values between these two,

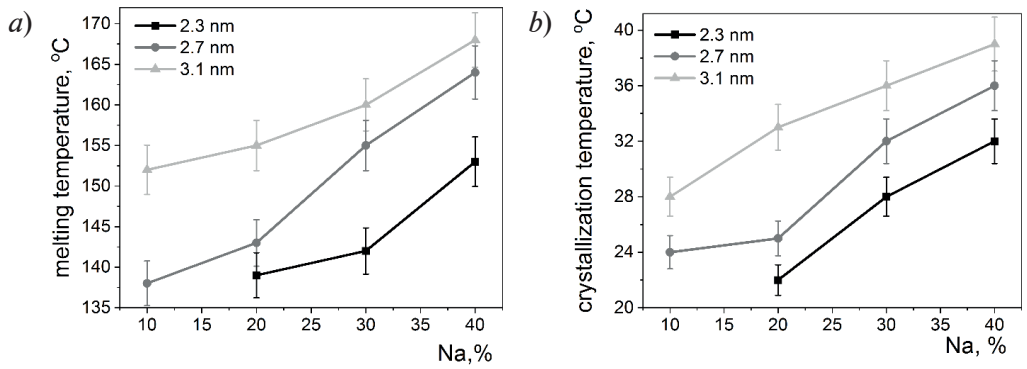

Fig. 3. Dependence of the melting (*a*) and crystallization (*b*) temperature of CuCl nanocrystals on Na/K ratio for crystals with different sizes

which we see in the experimental results. Based on these considerations, it can be concluded that in the borate glass matrix, just as in borosilicate glass, not pure copper chloride crystals are nucleated during the heat treatment, but a solid solution of copper chloride and alkali metal chloride.

Conclusion

The paper showed the influence of the size effect on the exciton absorption spectra of CuCl nanocrystals. The mean size of an ensemble of crystals precipitated during heat treatment in glass matrix was calculated depending on the heat treatment temperature. The influence of the size effect on the phase transition temperatures of CuCl was shown. When the Na/K ratio in the glass composition varied, the temperatures of phase transitions of CuCl nanocrystals of the same size changed. It has been found that the melting and crystallization temperatures of the crystalline phase increased with the content of sodium ions. Arguments were presented showing the possibility of crystallization during heat treatment in the potassium-alumina-borate glass not of pure CuCl nanocrystals but of CuCl-RCl (R = Na, K) solid solution.

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Received 26.10.2022. Approved after reviewing 09.11.2022. Accepted 09.11.2022.