Copper-containing Potassium-Alumina-Borate Glass
Structure and Nonlinear Optical Properties Correlation

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Abstract: The paper describes the technology of obtaining potassium-alumina-borate glass with nanocrystalls of copper chloride. Glass has transmission more than 75 % in visible range and nonlinear threshold less than 10^{-5} Joules (at the wavelength of 532 nm). Such low threshold can be explained by special structure of copper-containing nanophase in potassium-alumina-borate glass. In PAB glass low-melting temperatures of nanophase induce nonlinear effects in optics. In phosphate glass copper ions and clusters are responsible for optical nonlinearity.

1 INTRODUCTION

For the problems of photonics the special position among transparent in visible range materials is taken by crystal of copper chloride CuCl. CuCl is a wide gap semiconductor, in which direct transitions of electrons from the valence band to the conduction band is allowed (Lucas, Cowley, McNally, 2008). It has an extremely high exciton binding energy (190 meV), which allows to observe the exciton spectra at room temperature and also at higher temperatures (Efros, Onushchenko, Yekimov, 1985). The excitonic absorption intensity in near-UV (384 nm) is extremely high - more than 10^4 cm^{-1} (Rivera, Murray, Hoss, 1967; Cordona, 1963; Cowley, 2011).

Copper chloride has a high nonlinear optical properties - due of two-photon absorption and of radiation-induced changing of refractive index (Yano, Goto, Itoh, 1996; Yasuaki, Makoto, Hideyuki, 1988; Kondo et al, 2000; Ichimiya et al, 2009).

It's known that temperature of melting of a CuCl is 426ºC (Rivera, Murray, Hoss, 1967). CuCl has one big disadvantage - it's hygroscopic (Lucas, 2008), that's why it's not easy to use it in practical applications.

The solution of such problem is a formation of nanocrystalls of copper chloride inside dielectric matrix. The composite media based on dielectric matrices with dispersed semiconductor nanoparticles (glass pottery) have been extensively studied for several decades. Copper chloride nanocrystalls was grown in silicate glass host by metastable phase separation (Dotsenko, Glebov, Tsekhomsky, 1998). Usually such glasses are photochromic (Dotsenko, Glebov, Tsekhomsky, 1998). Temperatures of melting point of copper chloride nanocrystalls in this glass are reached 380ºC and of crystallization 200ºC (Onuschenko, Petrovskii, 1998; Valov, Leiman, 2009).

Potassium-alumina-borate glass host - is a perspective host with high liquation ability (Imaoka, Yamazaki, 1957; Kornilova, Petrovskii, Stepanov, 1980; Edelman et al, 2001). Copper chloride nanocrystalls have been grown in potassium-alumina-borate glass host (Nikonorov, Tsekhomsky, Shirshnev, 2012) (PAB pottery). It was found, that such glass pottery is non-photochromic (Nikonorov, Tsekhomsky, Shirshnev, 2012). Also it was found, that such glass pottery has optical nonlinear properties (Kim et al, 2011). In (Golubkov et al, 2012) it was shown by small angle X-ray scatering method (SAXS) that PAB pottery has a complicated composition of nanophase which affects on melting processes of nanocrystalls in glass. In (Babkina et al, 2014) it was shown, that copper clusters are formed

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in PAB glass besides CuCl nanocrystalls which affects in luminescence properties of glass pottery.

2 MATERIALS AND METHODS

In this paper three glass of different compositions were synthesized. Glass with the content (mol %) $17{,}5K_2O - 21Al_2O_3 - 46B_2O_3 - 8{,}9NaCl - 2{,}42Cu_2O - 0{,}23SnO_2 - 0{,}23Sb_2O_3$-$0{,}82Na_3AlF_6$-$2{,}9P_2O_5$ with a glass transition temperature of about 380°C was prepared as the basis for preparation of halidecontaining glass crystalline materials. The glass was synthesized in amounts of 100 g in a corundum crucible with the use of a quartz stirrer at a temperature of 1350°C for 2 h. To release mechanical stresses, the annealing was conducted in a stepwise regime, starting from 380°C (a fine annealing according to the program for this glass). In the following we denote it as glass 1.

In the second glass composition was (mol %): $20{,}12K_2O - 24{,}14Al_2O_3 - 52{,}89B_2O_3 - 1{,}39Cu_2O - 0{,}26\ SnO_2 - 0{,}26Sb_2O_3$-$0{,}94Na_3AlF_6$ and 1 g of $C_{12}H_{22}O_{11}$. Conditions of synthesis were the same. We denote it as glass 2.

Table 1: Properties of samples.

name of sample	Glass host	Nanophase type	details of annealing
1	PAB	CuCl	410°C 10 hours
2	PAB	copper-containing nanoclusters	Not
3	Phosphate	CuCl	Not
4	PAB	No	Not

The third one is (mol %) $20BaPO_3$ - $5Na_3AlF_6$ - 70NaPO3 - 4CuCl - HCl. We denote it as glass 3. It should be noted, that in this composition CuCl is in "clear" form.

The glass transition temperatures were determined on a differential scanning calorimeter STA 6000 (Perkin Elmer) and were 380°C for all samples.

The glass 1 sample were subjected to repeated heat treatment at 410°C for 10 h.

The absorption spectra of glass were measured by spectrophotometer Perkin Elmer Lambda 600. Luminescence was measured by LS-11 Perkin Elmer Spectrafluorimeter.

It should be noted, that measuring of absorption spectra during heating - is a very effective method for processes studying of melting and crystallization in a copper chloride containing glass pottery (Rivera, 1967). Scheme of experimental setup is in figure 1. In this work avantes spectrometer Avaspec-1028 UV-VIS and balanced halogen-deiterium lamp was used. The measurement setup scheme is vertically designed.

The scheme of experimental setup of nonlinear optics characteristics studying is shown in figure 2. The laser beam is divided on two beams. The first is the reference beam, another one is directed to the sample and after to the photodetector. An energy of laser beam is varied by a system of filters from 10^{-9} J till $3x10^{-2}$ J. This range is achieved by using two casette filters with a total transmittance range from 10^{-9} till 100%. The laser wavelength was 532,1 nm, pulse length was $5x10^{-9}$ seconds. All measurements was made in focused beam.

Spectra and nonlinear properties were measured on samples with thickness 2 mm, thermal measurements were made on samples with thickness 0,1 mm.

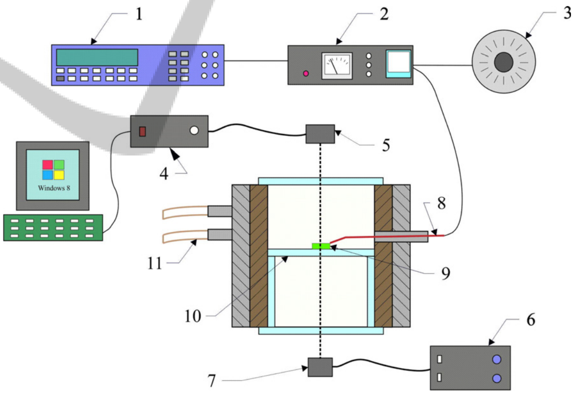

Figure 1: An experimental setup for absorption measurements: 1 – digital thermometer, 2,3 – heat controller, 4,5 - fiber spectrometer, 6,7 - deuterium lamp, 8 – thermal sensor, 9 – sample, 10 – quartz glass plate, 11 – cooling of thermocell.

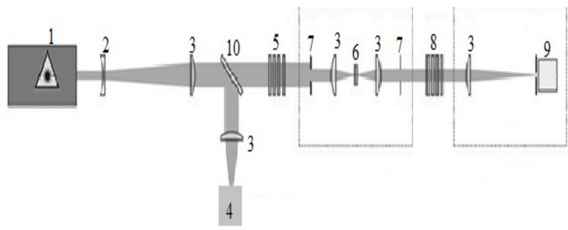

Figure 2: An experimental setup of nonlinear optical characteristics studying: 1 - laser, 2,3 - lenses, 4, 9 - photodetectors, 5,8 - blok of filters, 6 - sample, 7 - diaphragms, 10 - half-transmittable mirror.

3 RESULTS

3.1 Spectra of Optical Absorption

Spectra of absorption of glasses 1-3 are presented on the figure 3. Figure 3 shows absorption band are at 365-384 nm in glass 1 and 3. This band was identified as CuCl excitonic absorption (Dotsenko, 1998). There is no absorption at this wavelength range for the glass 2, even after heat treatment.

3.2 Spectra of Photoluminescence

Spectra of luminescence was measured for glasses 1-3 (figure 4). The excitation wavelength is 365 nm. From the figure 4 one can see that the luminescence of glasses 2-3 is identical. For the glass 1 the luminescence is not observed.

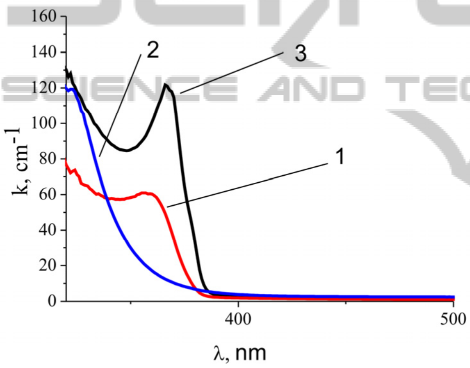

Figure 3: Spectra of optical absorption of glasses 1-3 (digits in figure the same as number of glasses).

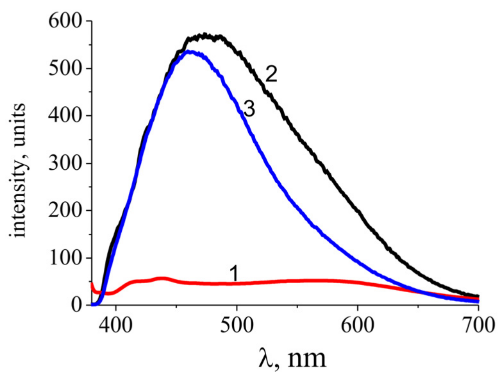

Figure 4: Spectra of photoluminescence for glass 1-3 (digits are the same as numbers of glasses).

3.3 Thermal Excitonic Spectroscopy

The dependence of excitonic absorption on temperature (glasses 1,3) is given in the figure 5 (the thickness of samples 0,1 mm). As it can be seen, the temperature of excitone destruction for glasses 1 and 3 is really different (the difference is more than 200ºC).

3.4 Nonlinear Properties Results

The dependence of optical transmission on energy of pulse for glasses 1-3 is shown in figure 6. It can be seen, that for the blank glass 1 there is no nonlinear effects. Nonlinear absorption characteristics of glasses 2 and 3 are the same, and the strongest effect is obtained on glass 1 (copper chloride containing PAB glass).

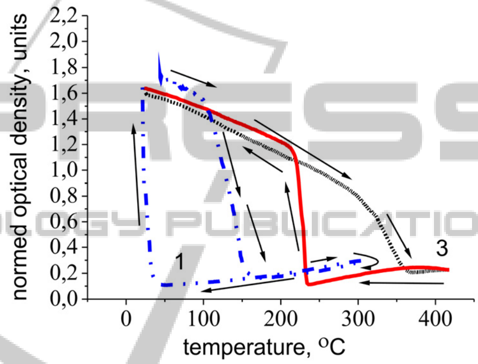

Figure 5: Excitonic absorption intensity of glass 1,3 at different temperatures.

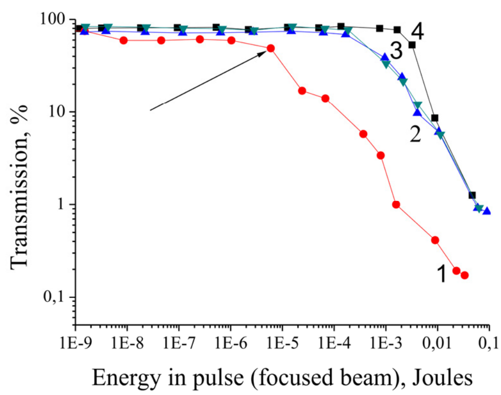

Figure 6: Nonlinear optical limiting on different samples (thickness of glass 2 mm): 1 – glass 1, 2 – glass 2, 3 – glass 3, 4 – blank (without CuCl) glass 1. Arrow shows the starting point of optical limiting process.

4 DISCUSSION

Let's discuss figure 5. As mentioned above, first glass had the lowest threshold of nonlinear limitting, first glass without nanocrystalls had the highest one.

As we can see from absorption spectra of glass 3 (figure 3) nanocrystalls of copper chloride were formed in glass. The relative concentration of CuCl in glass 1 and 3 can be estimated by absorption spectra intensity. So, for the glass 3 it's two times more than for the glass1. So, we can say that the concentration of CuCl in sample 3 it's two times more than for the sample 1, but the strongest nonlinear optical limitting effect is in glass 1. Why? Let's discuss the figure 5. The temperature of full disappearing of excitone in glass 1 is less than 150ºC, for glass 3 it's 420ºC. It was shown in (Golubkov et al, 2012), that there are two characteristic temperatures of nanophase melting in PAB glass. One of that melting points is near 150ºC another one is at 270ºC. So, if we compare processes of nanophase melting in PAB glass with similar phenomena in silicate glasses with CuCl nanophase (Dotsenko, Glebov, Tsekhomsky, 1998), we can say, that temperature of excitone absorption disappearing at 150ºC is the point of CuCl nanocrystalls melting in glass 1. Point of CuCl melting in glass 3 is 361ºC. It is known (Dotsenko, Glebov, Tsekhomsky, 1998; Golubkov et al, 2012) that CuCl containing nanophase can include another crystal components which can affects on value of melting point of nanophase. For CuCl-KCl eutectics such temperatures can be 150ºC. So, in glass 3 CuCl nanophase can be "clear" and in glass 1 – nanophase can contain mixed eutectic crystals of CuCl and K_2CuCl_3.

The phase transition in such heterogeneous material as a PAB glass with CuCl nanocrystalls can induce the optical limiting effect because of difference of refraction index of liquid CuCl-KCl solution and glass host. Also, the melting of nanophase can induce the growth of scattering and growth of optical absorption in visible range (including 532 nm).

In figure 5 the curves for glass 3 and 2 are identical. That could be mean, that the mechanisms of nonlinear limiting are the same in this glasses. As it shown in figure 4, the luminescence bands in glass 2 and 3 are the same. We suggested that glass 2 and 3 has Cu^+ ions and (maybe) Cu^0_n clusters after comparing luminescence spectra with spectral luminescence data at (Babkina et al, 2014). In the article (Qiaohong et al, 2009) authors has shown that metal clusters in glass can induce nonlinear optical effects.

5 CONCLUSIONS

The new material with low-limit optical threshold was synthesized – a PAB glass with copper chloride nanocrystalls. Numerical value of threshold was $5x10^{-6}$ Joules. This threshold is due of special structure of nanophase of such glass, which contains CuCl and K_2CuCl_3 nanocrystalls. Such complicated structure of nanophase gives low points of melting of nanophase. That's why during laser irradiation of PAB-glass phase is melting and that's induces the appearance of additional color centers in glass.
It was shown that copper clusters also induce nonlinear effects.

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