

# UV Pulsed Laser Irradiation Effect on Spectral Properties of Borosilicate and Phosphate Glasses with CuCl Nanocrystals

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**Abstract:** The results of the study of the pulsed UV laser radiation effect on the spectral properties of the borosilicate and the phosphate glasses doped with the copper chloride nanocrystals with the mean size of 26-70 Å are discussed. The changes of the exciton absorption spectra of the CuCl nanocrystals with various mean sizes induced by different duration of the laser exposure are studied. The effect of the phosphate glass transmission reduction in the visible region upon pulsed UV laser irradiation is obtained for the first time. The nature of the transmission reduction is discussed. The assumption is made that the transmission reduction is carried out through the formation of the color centers consisted of the Cu<sub>n</sub> (n>13) clusters which have the absorption bands in the visible region. In conclusion the presence of the irreversible photochromism in the phosphate glass is stated.

## 1 INTRODUCTION

In the semiconductor crystal field the study of properties of the copper chloride crystals is of a great interest for the development of photonics nowadays. Copper chloride is a wide-gap semiconductor with allowed direct interband electron transitions. Macrocrystals of CuCl have been well studied (Cardona, 1963) and are known to demonstrate the intense exciton absorption at the edge of the band gap and the negative spin-orbit splitting (Goldmann 1977).

Borosilicate (BS) glasses, activated by the CuCl nanocrystals with the mean size of more than 70 Å, are known to exhibit reversible photochromism (Dotsenko et al., 1998): continuous exposure by ultraviolet radiation leads to the reduction of the glass transmission in the visible region, when the activating irradiation is switched off the glass transmission returns back to its initial level. Composite materials with the reversible photochromism are widely used for the protection of the human eye and the detectors of the optoelectronic systems from UV and stray visible radiation. In case of the nucleation of the CuCl crystals having the mean size of over 100 Å the glass transmission reduction under UV irradiation occurs due to the presence of the surface plasmon

resonance absorption band of metallic Cu<sub>0</sub> nanoparticles centred at 560-580 nm (Sheng et al., 2009; Morse, 1981). With the presence of the CuCl crystals having the mean size between 70 and 100 Å the transmission of the silicate glass during UV irradiation is reduced due to the nucleation of the Cu<sub>n</sub> clusters (n> 13), the absorption bands of which occupy the region of 360-460 nm (Vázquez-Vázquez et al., 2009). It is noteworthy that the copper nanoparticles are formed only in the presence of the interface between the nanocrystalline phase (NCP) and the “vacuum pore” (Golubkov, 1986). The certain interface appears only when the large size droplets of the copper halide phase at temperatures above glass transition temperature and, consequently, the large size crystals at room temperature exist. When the size of the phase droplet is small, the difference between the volumes of liquid and crystal phases will be too small for the formation the vacuum pore of full value (Golubkov, 1982), on the boundary of which the nucleation of the copper particles or clusters can take place under the UV irradiation.

Phosphate glasses doped with CuCl nanocrystals, which have recently been discussed for the first time in works (Shirshnev et al., 2015; Babkina et al., 2015), show the effect of nonlinear optical limiting due to the two-photon absorption under the pulsed

laser irradiation of 532 nm. Hitherto there are no papers dedicated to the interaction of these glasses and the laser irradiation of UV range.

Therefore, in the present paper we carry out the comparison study on the pulsed UV laser irradiation effect on the spectral properties of the borosilicate and the phosphate glasses activated by the CuCl nanocrystals.

## 2 MATERIALS AND METHODS

The following glass systems are used as the objects of this study: borosilicate and phosphate. The composition of the BS glass is similar to the glass matrix described in (Golubkov, 1982) and comprises : 56.3 SiO<sub>2</sub> – 28.3 B<sub>2</sub>O<sub>3</sub> – 12.1 Na<sub>2</sub>O – 3.3 Al<sub>2</sub>O<sub>3</sub> – 1.2 Cu<sub>2</sub>O – 1.2 P<sub>2</sub>O<sub>5</sub> – 1.7 Cl<sup>-</sup> - 0.7 F<sup>-</sup> (wt. %). The phosphate glass of the following composition: 45 P<sub>2</sub>O<sub>5</sub> – 19 BaO – 12 Na<sub>2</sub>O – 7 Al<sub>2</sub>O<sub>3</sub> – 8 F<sup>-</sup> - 1 Cu<sub>2</sub>O - is used as a constant with a variable value of Cl<sup>-</sup> from 8 to 11.6 (wt. %). All glasses were prepared in the high temperature furnace Gmp (*Gero*) using a platinum and a carbon crucible for the BS and the phosphate glass respectively and a platinum stirrer for the glass melt homogenization. After the synthesis the phosphate glass was quenched to room temperature and the BS glass was annealed in a stepwise regime. The final glass chemical composition determination was obtained by X-ray fluorescence spectrometer ARL PERFORM'X 4200 (*Thermo Scientific*). Glass transition temperatures were determined by differential scanning calorimeter STA 449F1 Jupiter (*Netzsch*) and were found to be 757 K and 673 K for the BS and the phosphate glass respectively.

The nanocrystalline phase was precipitated in the BS glass bulk by isothermal treating the samples at temperatures exceeding glass transition temperature 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 of this glass, the phase separation of the supersaturated solid solution and subsequent fluctuation nucleation of a new phase occurred (Onushchenko, 1996; Ekimov, 1996). The usage of the hydrochloride acid during the phosphate glass synthesis created the hard reducing conditions so that the nanocrystalline phase nucleation was conducted during quenching after it. In former case the average size and concentration of the nanocrystalline phase were defined by heat

treatment options, in latter one they were derived from the hydrochloride acid concentration.

The glass samples irradiation was carried out by the third harmonic of the Nd<sup>3+</sup>:YAG laser with a wavelength of 355 nm, a pulse length of 9 ns, a peak power of 13.2 MW/cm<sup>2</sup> and frequency of 10 Hz. The absorption spectra of the samples were recorded at room temperature before and after the irradiation process. The deuterium lamp AvaLight-DH-S-BAL (*Avantes*) was used as a light source and the fiber optic spectrometer AvaSpec-2048L (*Avantes*) as a detector.

## 3 RESULTS

Fig. 1 shows the absorption spectra of the initial BS glass, the BS glass with the CuCl nanocrystals, precipitated after the heat treatment at 823 K, and the BS glass with the CuCl nanocrystals after irradiation of various duration. The BS glass heat treatment at temperature of 823 K leads to the precipitation of the CuCl nanocrystals with the mean size of 70 Å. The strong exciton absorption bands occur near the edge of the crystal band gap after the heat treatment at temperatures exceeding glass transition temperature. The mean crystal size calculations are produced from the optical spectra according to the method described in (Efros, 1982). According to the work (Dotsenko et al., 1998) such treatment leads to the arising of the glass sensitivity to the UV radiation, i.e. the photochromic effect occurrence. UV laser irradiation of the BS glass promotes the occurrence of the strong absorption band centered at 340 nm (3.65 eV) and the weak absorption band at 450 nm (2.76 eV). The increase in the duration of the exposure leads to the increase in the intensity of the laser-induced absorption and the CuCl exciton absorption bands. The difference in the absorption intensity between the non-irradiated and irradiated during 10 minutes the BS glass samples at the wavelength of 340 nm is 35.5 cm<sup>-1</sup>, at 367 nm (maximum of Z<sub>1,2</sub> CuCl absorption band) is 18 cm<sup>-1</sup> and at 450 nm is 5.7 cm<sup>-1</sup>. The transmission decrease in the visible region is about 53%. In case of the precipitation of the CuCl nanocrystals having the mean size 26 Å the BS glass does not become photochromic, and the radiation-induced increase of absorption at the same wavelengths is about two times less than in the first sample.

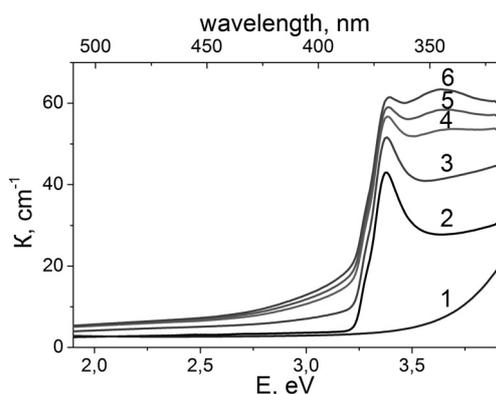


Figure 1: The absorption spectra of the BS glass before heat treatment (1), after heat treatment and before irradiation (2) and after irradiation for 100 sec (3), 300 sec (4), 400 sec (5), 600 sec (6).

Fig. 2 shows the absorption spectra of phosphate glass doped with CuCl nanocrystals with the mean size of 70 Å before and after irradiation by pulsed UV laser. The irradiation for 10 minutes leads to the absorption increment at 340 nm (3.65 eV) and 450 nm (2.76 eV) of 23.87 and 4.25 cm<sup>-1</sup>, respectively. The transmission decrease in the visible region after irradiation is turned out to be 45%. If the CuCl nanocrystals having the mean size of 34 Å have been precipitated in the phosphate glass the radiation-induced increase of absorption in the visible and UV regions is almost the same as in case of the bigger nanocrystals.

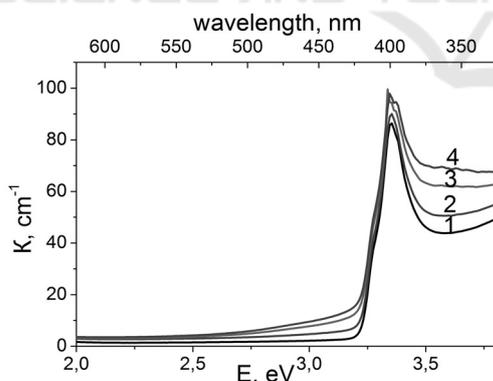


Figure 2: The absorption spectra of the phosphate glass before irradiation (1) and after irradiation for 100 sec (2), 300 sec (3), 600 sec (4).

The additional absorption spectra of the color centers formed by 20-minutes UV-laser irradiation of the BS and the phosphate glasses are shown in Fig.3. General view of the additional absorption band of different glasses is almost identical.

Figure 4 demonstrates the time dependence of the optical density at 500 nm of the glass samples

under study during I-irradiation, II-relaxation (with switched off excitation) and III-re-irradiation. The samples were chosen so that the level of their initial optical density is the same. The formed color centers show the temporal stability in the phosphate glass, while in the BS glass the laser-induced absorption relaxes for 5 days.

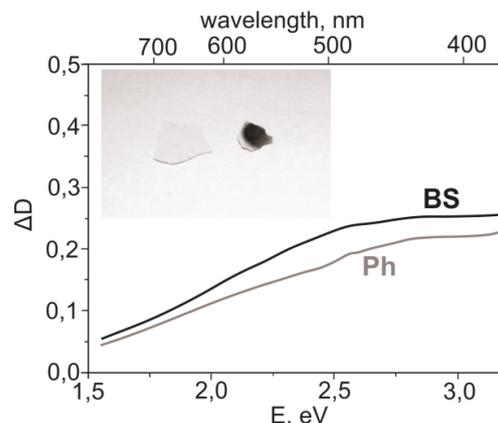


Figure 3: The additional absorption spectra of the color centers formed in glasses with CuCl NC after pulsed laser irradiation. The inset: photos of the non-irradiated (left) and the irradiated (right) phosphate glass.

## 4 DISCUSSION

Despite the difference in the glass matrices compositions, the location of the radiation-induced absorption bands is the same. As to the reasons responsible for this situation, some tentative assumptions can only be proposed for discussing.

According to the works (El-Batal, 2008; ElBatal et al., 2013; Barkatt et al., 1981; Bishay, 1970; Möncke et al., 2014; Narayanan, 2015b; Narayanan, 2015a) the phosphate glass structure comprises [PO<sub>4</sub>] tetrahedra. In the case of the pure amorphous phosphorus (V) oxide the [PO<sub>4</sub>] groups are connected to the neighbour units by three out of the four oxygen atoms, and the latter one is connected to the phosphorus by the double bond (the terminal oxygen). Although the phosphate glass structure changes take place during the introduction of the alkaline oxides, the phosphorus remains the four coordinated state in the entire range of compositions from the pure P<sub>2</sub>O<sub>5</sub> to the orthophosphate MPO<sub>4</sub> saturated by alkaline oxides. When the alkaline oxides are added to the amorphous P<sub>2</sub>O<sub>5</sub> the phosphate structural units change from Q<sub>3</sub> to Q<sub>2</sub>, then to Q<sub>1</sub>, and, finally, to Q<sub>0</sub>, together with a molar ratio of the alkali metal oxide to the phosphorus oxide M<sub>2</sub>O/P<sub>2</sub>O<sub>5</sub>=R, where R varies from 0 to 3

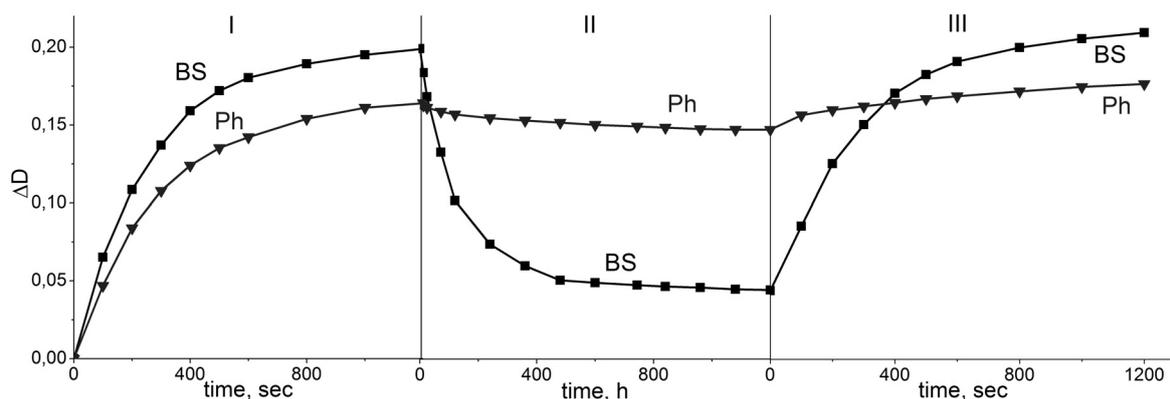


Figure 4: Optical density time kinetics of the glasses during I-irradiation, II-subsequent relaxation and III-second irradiation.

(Narayanan and Shashikala, 2015a). A similar transformation of the structure with the alkali addition occurs in the silicate glass. With the addition of  $M_2O$  a number of the terminal oxygen remains, while the number of non-bridging oxygen changes. At first, the addition of  $M_2O$  or  $MO$  (e.g.,  $Na_2O$  or  $CaO$ ) leads to the transformation of the three-dimensional amorphous  $P_2O_5$  into the linear phosphate chain. These structures lead to the destruction of the P-O-P bonds and the formation of the terminal oxygen atoms. Due to a decrease in the average length of the phosphate chain, the increasing concentration of  $Cu_2O$  enhances the covalent character of the P-O-O bonds thus leading to the glass depolymerization. The depolymerization of the ring and chain structures with the addition of the monovalent metal oxides occurs also in the silicate glasses.

In several sources (Ruller, 1991; Tsai et al., 1990) have been shown that the exposure by the ionizing radiation or by optical radiation with high energy leads to the compression of the amorphous silica due to the breaking of the Si-O-Si bonds and the formation of the  $\equiv Si$  type defects ( $E'$  centers). The strained Si-O bonds in the rings consisting of 6 or more  $SiO_4$  tetrahedra capture the radiolytic charge, which breaks them and allows the ring structure to relax and become more compact, for example, to be transformed into the ring with a small number of the tetrahedra and a more dense packing. X-ray irradiation of the multicomponent silicate glass (Tsai et al., 1989; Tsai et al., 1987) promotes the formation of the oxygen hole centers, which have the absorption in the region of 440-460 nm (Bishay, 1970). In this study the laser radiation with energy lower than the optical band gap of the material is used, therefore, the change of the glass structure, namely the Si-O bonds reflow, is not

plausible. On the other hand, if a transmittance reduction of the BS glass, depends only on the concentration of the radiation-induced  $E'$  centers, the connection of this effect with the mean crystal size remains unclear.

According to (El-Batal, 2008; ElBatal et al., 2013) the high-energy irradiation of the phosphate glasses results in the formation of several types of the glass network defects, namely: the oxygen vacancy in the  $\nu [PO_4]$  tetrahedra with two trapped electrons; the trapped electron centre; the trapped hole centre near non-bridging oxygen; the trapped hole centre near the monovalent metal ion covalently bonded with oxygen, - which have the absorption bands centred at 200, 225, 420 and 540 nm, respectively.

Due to a similar behavior of the monovalent copper ions in the structure of different glasses, the similar nature of the defects initiated by pulsed UV irradiation can be assumed. As it has been mentioned above, in all the glasses under study a possibility of the formation of the defects such as trapped electrons and holes (Bishay, 1970), and free electrons and holes does exist. The defects in a similar environment, for example, near the copper ions and the non-bridging oxygen, would have the absorption bands in the same range. The free electrons created due to the inflow of the additional energy from the laser beam cause the reduction of the divalent copper ions to the monovalent state and the monovalent copper ions to the copper atoms. Assuming the high localization of the copper atoms the opportunity of the  $Cu_n$  molecular clusters formation arises. The molecular copper clusters with  $n < 10$  demonstrate luminescence under the excitation by UV emission (Vázquez-Vázquez et al., 2009). In this study the irradiation of samples by 340 nm does not initiate any emission. However, the

Stokes shift between the excitation and the emission of the  $\text{Cu}_n$  ( $n=3-5$ ) molecular clusters is about  $4000-5000 \text{ cm}^{-1}$ , so that the initiated luminescence bands would be located in the region of the exciton absorption of the CuCl nanocrystals. The excitation by longer wavelengths has not yielded the expected emission either. This is why, the nature of the color centers can be attributed to two possible situations: first, the glass network defects, originated from the powerful laser irradiation, and, second, the  $\text{Cu}_n$  ( $n>13$ ) clusters, which demonstrate no fluorescence, but can be characterized by the absorption bands in the visible region. The phosphate glass network defects mentioned above also do not reveal the fluorescent properties.

Let us consider a model of the nanocrystalline phase proposed in the works (Golubkov, 1998; Golubkov, 1982). During the thermal treatment of the glass doped with the copper and chlorine ions at temperatures above glass transition temperature due to the presence of spatially fluctuations in the chemical composition of the glass the regions with an increased content of the future nanocrystalline phase components are formed. The presence of the inhibitor defects in the glass allows the concentration increase of such areas. In regard of the multi-component glass the composition of these areas is not uniform: besides the copper and chlorine molecular compounds it may include some components of the glass matrix. During the cooling process the thermal contraction of the copper halide droplet phase and the glass matrix does occur in accordance with their linear thermal expansion coefficients. In the BS glass the linear thermal expansion coefficient of the glass matrix is three times smaller than the one of the CuCl (Golubkov et al., 2012; Dotsenko et al., 1998). Therefore, the contraction of the nanocrystalline phase goes faster than the contraction of the matrix, thus in the interlayer between the nanocrystalline phase and the glass matrix the "vacuum pore" is formed, whose presence has been shown in the works (Golubkov, 1986). The mechanism of the radiation-induced darkening of the BS glass is the following. UV irradiation leads to ionization on the surface of the CuCl nanocrystalline phase, to the occurrence of the so-called "halide gas" consisting of  $\text{Cl}_2^0$  in the "vacuum pore" and to the formation of the metallic copper film on the nanocrystalline phase surface with the absorption in the visible region.

The formation of the areas with high concentration of the components of the future nanocrystalline phase in phosphate glasses occurs during the glass synthesis. It is known (Ehrt, 1992)

that the introduction of a large amount of fluorine (as in our case) to the phosphate glass leads to the incorporation of the fluorine into the glass structure and, therefore, to the depolymerization of the phosphate chains and the formation of the defect end structures, next to which the components of the future nanocrystalline phase can be accumulated. The fluorine content in all phosphate glasses under study was the same, so, the probability of the formation of these defects was equal. The thermal expansion coefficients of the phosphate matrix and the CuCl are approximately equal, therefore, during quenching after the synthesis the matrix and the nanocrystalline phase are compressed in the same way. The nanocrystalline phase droplets detachment from the glass does not seem plausible, so, it is impossible to talk about the "vacuum pore" formation. Surface tension between the copper halide droplet phase and the matrix always compresses drop so that a part of its composition falls into the matrix. As a result the matrix is enriched with nanocrystalline phase components around the droplets (Golubkov, 1998). The copper ions trapped in this transition layer would be highly localized. This is a favorable condition for the creation of the  $\text{Cu}_n$  ( $n>13$ ) molecular clusters.

The difference in sensitivity to UV radiation between the BS and the phosphate glasses can be assigned to, firstly, the presence of a clear interface between the matrix and the nanocrystalline phase in the BS glasses providing greater localization of the copper ions in the transition layer unlike the phosphate glasses, where the interface does not appear; secondly, as the nanocrystalline phase in the phosphate glasses nucleates during quenching after the glass synthesis a large amount of the copper ions is distributed in the matrix in the free form, during the laser irradiation they can be reduced to the atomic form, but they concentration is too small to form the particles or the molecular clusters.

## 5 CONCLUSIONS

As a conclusion, it can be stated that the irreversible photochromism occurs in the phosphate glass activated by CuCl nanocrystals. The differences in sensitivity to UV irradiation between the borosilicate and the phosphate glasses are mostly associated with the methods of the nanocrystalline phase formation in different glass matrices and with the difference in thermal expansion coefficients of the glasses under study. Materials possessing the irreversible photochromic effect, unlike reversible one, can be

used for the amplitude image recording and for storing information in the form of the Bragg gratings.

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