Materials Physics and Mechanics 42 (2019) 198-203 Received: April 23, 2019

THE INFLUENCE OF GAMMA RAYS RADIATION ON OPTICALLY INDUCED LUMINESCENCE OF COPPER-CONTAINING POTASSIUM-LITHIUM-BORATE GLASS

P.S. Shirshnev[1]*, V.A. Spiridonov[1], D.I. Panov[1], E.V. Shirshneva-Vaschenko[1], A.R.Gafarova[2], R.M. Eremina[2], A.E. Romanov[1], V.E. Bougrov[1]

[1]ITMO University, Kronverkskiy prospect 49, Saint-Petersburg, 197101, Russia

[2]Zavoisky Physical-Technical Institute, FRC Kazan Scientific Center of RAS, Sibirskiy tract 10/7, Kazan, 420029, Russia

*e-mail: pavel.shirshnev@gmail.com

Abstract. The paper presents the results of potassium-lithium-borate glass containing copper ions investigations. The glass was irradiated by 1.25 MeV gamma rays. The dose of radiation was 360 Gy. The exciting of the irradiated glass at 360 nm led to the long-wavelength photoluminescence band shift from 635 nm to 671 nm in comparison with non-irradiated glass. A new luminescence band at 685 nm also appeared for excitation wavelength 405 nm in the irradiated glass. It has been assumed that the luminescence band in glass at 671 nm – 685 nm corresponds to the luminescence of copper ions in the modified environment of the first coordination sphere. Copper-containing luminescent structures in borate glass with the luminescence maximum at 671-685 nm have been obtained for the first time. For the detailed study of these luminescent centers properties, thorough study of the structural variations in the gamma rays irradiated glass is required.

Keywords: gamma ray radiation, cluster, copper, borate glass, photoluminescence

1. Introduction

The borate glasses with ions and clusters of luminescent ions occupy some intermediate place between phosphate and silicate glasses. On the one hand, these glasses are thermally stable at the temperatures more than 200 degrees Celsius compared to phosphate glasses. On the other, the solubility limit of borate glasses is higher than of silicate ones. Therefore, copper-containing borate glass attracts attention in relation to its technical application. Moreover, due to the peculiarities of boron ions in composition of the borate glass, the strong modifying of the coordination environment, including luminescent ions, that are introduced to the glass composition, is possible [1,2].

These days, the luminescent structures with monovalent copper, in particular, copper-containing glasses, are relevant as down-converters and ultraviolet detectors [3]. In addition, copper-containing glass is also a promising phosphor material [4]. Copper attracts researchers as a cheap luminescent activator.

In recent times works it was shown that in borate glass with copper a quantum yield of at least 50% is achievable for the excitation wavelength 320 nm. It was also suggested the scheme of the spark sensor based on this glass [3]. Electron paramagnetic resonance (EPR) method demonstrated the existence of additional copper-containing structures in glass – may be dimers in addition to the copper ions [5]. It was previously found [6], that lithium-borate

http://dx.doi.org/10.18720/MPM.4222019_6

copper-containing glass has luminescence in the 400–600 nm region for excitation wavelength 320 nm. The luminescence maximum shifts depending on the lithium concentration — with increasing lithium concentration, the shift occurs to the short-wavelengths.

It was also revealed that after heat treatment and nanocrystals segregation in glass, the luminescence maximum shifts to the long wavelength region [7]. Copper itself is extremely sensitive to the environment, and that makes it an interesting scientific object in borate glasses. It is also known that copper can segregate into clusters in glass and, depending on the cluster size, the wavelength of the luminescence can vary [8,9].

In recent studies of ionizing effects on the luminescent properties of borate glasses and crystals studies have been carried out. These studies are mainly focused on thermoluminescence investigations [10, 11]. In [12] the gamma rays irradiation of borate glass with bismuth ions changes its luminescence due to the breaking of covalent bonds in trigonal and tetrahedral boron groups. In 2017, the effect of X-rays on the luminescence of phosphate glass activated by silver and copper was studied [13]. It was demonstrated that an additional luminescence band appears in glasses, including in the copper-containing glass.

The purpose of this work is to study the gamma ray radiation effect on the luminescent properties of copper-containing borate glass. Since it is known that the structure modifying in borate glass under the action of gamma rays is possible, as well as copper can segregate into clusters and luminesce.

2. Objects and methods

Glasses with $15K_2O$-$10Li_2O$-$25Al_2O_3$-$50B_2O_3$ (molar percent) composition with additions of 0.5 Cu_2O and 4% graphite powder (weight percent) were synthesized for this study. The synthesis was carried out at the temperature of 1450°C for 2 hours, then the glass was poured out on a metal plate heated up to 400°C and then was cooled in a muffle from 400°C to room temperature for 10 hours. From the synthesized glass the sample was prepared. The size of the sample was 10x8x8 mm.

The sample was irradiated by gamma rays. The average energy of quanta was 1.25 MeV. The irradiation was carried out with the isotope element 60Co. The radiation dose was 360 Gy.

The luminescence spectra for excitation wavelength 405 nm were measured with an Avantes Avaspec 2048 spectrometer. The excitation with wavelength of 360 nm was carried out by UV light emitting diode (LED) with an intensity of 30 mW, the excitation with wavelength of 405 nm was carried out by a 100 mW laser diode.

3. Results

The main photoluminescence parameters of the samples are given in the Table 1.

Figure 1 (left) presents that the glass sample before gamma ray irradiation for excitation wavelength 360 nm has three luminescence bands (a): the first band is at 450 nm with a half-width of 88 nm (b), the second band is at 530 nm with a half-width of 130 nm (c), and the third band is at 635 nm with a half-width of 80 nm. After gamma ray irradiation (Fig. 1 (right) (a)), the intensity peak of the short-wave band shifts to 460 nm (b). The band at 530 nm is 7 nm shifted with an increase in half-width by 8 nm (c). The band at 630 nm shifts to 685 nm with a change in half-width to 92 nm (d). Visually, the intensity and color of the luminescence, when the glass is irradiated with a mercury lamp with excitation wavelength of 360 nm, does not change.

Table 1. The main parameters of the luminescence of the samples, λ_{exc} – excitation wavelength, FWHM – full width at half maximum

Parameter	L_{max}, λ_{ex} = 360	FWHM λ_{ex} = 360	L_{max2} λ_{ex} = 360	FWHM2 λ_{ex} = 360	L_{max3} λ_{ex} = 360	FWHM3 λ_{ex} = 360	L_{max} λ_{ex} = 405	FWHM λ_{ex} = 405
Wavelength before irradiation, nm	530	130	450	88	635	80	584	116
Wavelength after irradiation, nm	537	138	460	80	671	92	685	79

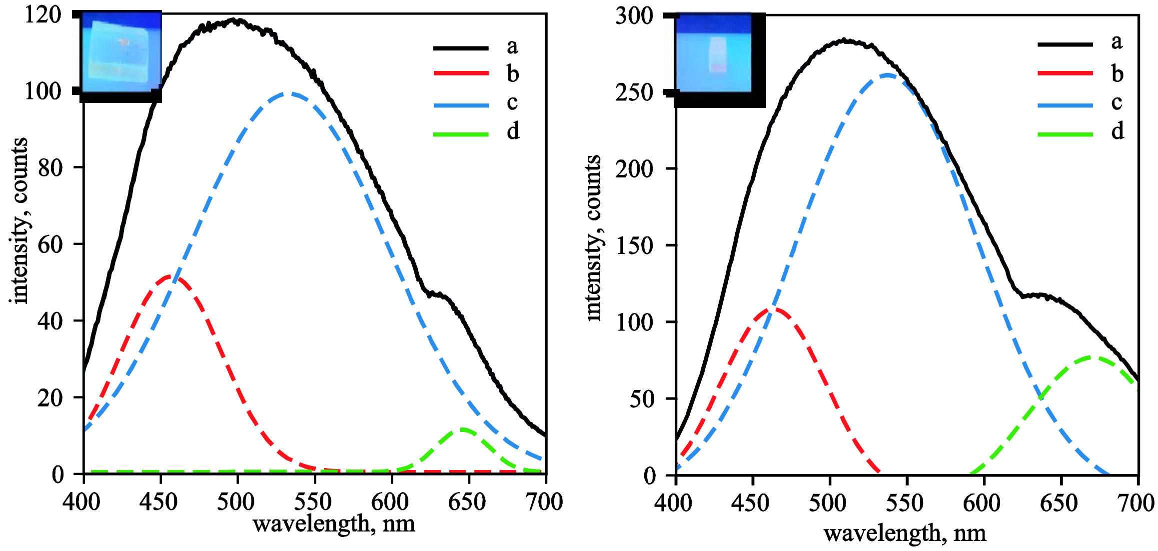

Fig. 1. Luminescence spectra upon excitation wavelength of 360 nm. left – before gamma rays irradiation, right – after gamma rays irradiation. Solid curves (a) – measured spectra, dashed curves (b, c, d) – decomposition by Gaussians

Figure 2 presents the luminescence spectra of the reference and irradiated by gamma rays samples for excitation wavelength 405 nm. The reference sample before gamma rays irradiation has a luminescence spectrum with a maximum at 584 nm. The half-width of the band is 116 nm. After gamma rays irradiation, the luminescence band shifts to 100 nm, and its half-width changes almost one and a half times to 79 nm. The luminescence color changes visually from yellow-orange to red, which is also shown in the insert (Fig. 2). It should be noted that the luminescence band at 685 nm is an order of magnitude higher than the luminescence band at 584 nm. In Fig. 2 these bands are given in proportion for understanding their structure.

4. Discussion

The luminescence band at 450–460 nm upon exciting copper-containing borate glass at 360 nm corresponds to the monovalent copper ion luminescence [14, 15]. As it can be seen from the literature, the excitation band edge of monovalent copper is 360 nm. The luminescence band may vary depending on the degree of tetrahedral distortion of the copper environment [16]. The gamma ray irradiation causes a slight shift in the copper luminescence band, which can be explained by a slight change in the structure of the glass around the ion.

According to [17–21], the luminescence band at 530 nm upon excitation wavelength of 360 nm can correspond to Cu^+ –Cu^+ dimers [8]. After gamma ray irradiation, the Cu^+ –Cu^+ dimers band, as well as luminescence band of copper ions, shifts by 10 nm to the long wavelengths, which also indicates a change in the structure of copper dimers environment.

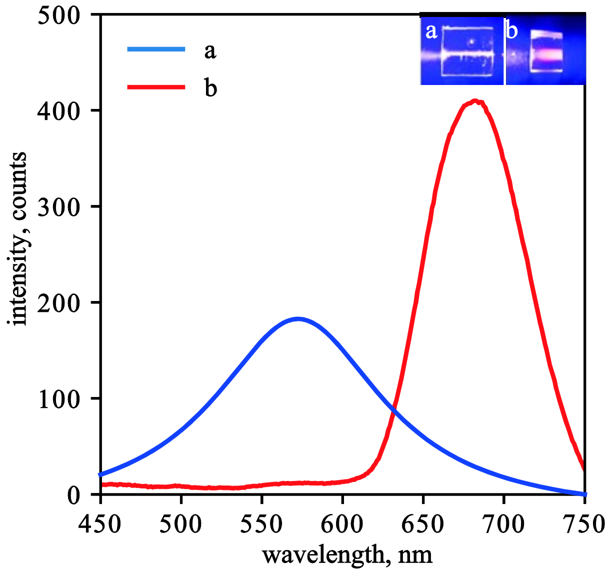

Fig. 2. Photoluminescence spectra and photos of samples upon excitation wavelength of 405 nm: a – before gamma rays irradiation, b – after gamma rays irradiation

The 635 nm band most definitely corresponds to $(Cu_2O)_n$ clusters. In [9], the luminescence band with a maximum at 600 nm was indicated for copper oxide clusters. However, it can varied depending on the cluster size.

We assume that the band with a maximum at 635 nm for the excitation wavelength 360 nm is related to the band of copper oxide [17, 8] and Cu_4 [9].

It should be pointed out that, in [8], molecular clusters in borate copper-containing glass were obtained after a long time (20 hours) heat treatment at high temperatures (480°C). In our glass, the clusters are obtained "immediately", as it is evidenced by the luminescence peak at 635 nm. This result can be explained by the fact that the lithium-borate matrix has unique segregation properties [22]. Therefore, the formation of clusters during the synthesis of glass is already possible at the stage of its cooling after melt.

The existence of the luminescence band at 671 nm that appears after gamma rays irradiation can be explained similar to [13]. There it was demonstrated the appearance of the third luminescence band in copper-containing phosphate glass, which is similar by its structure to our band for the excitation wavelength 360 nm. In both cases the same "broadening" of the right wing of the luminescence band occurs. However, in the phosphate glass, such band appears after X-ray irradiation and heat treatment. In [13], luminescence is excited by shorter-wavelength light sources (320 nm) and luminescence band itself is also at a shorter-wavelength 570–580 nm.

The question of the 671 nm band belonging to luminescent structures will be discussed below.

Let us analyze the luminescence bands for the excitation wavelength 405 nm. As it can be seen from the luminescence spectra, there is a luminescence band at 584 nm in the reference sample (before gamma ray irradiation) for the excitation wavelength 405 nm. According to [17, 8], the edge of the excitation band of $(Cu_2O)_n$ clusters passes through 405 nm, with luminescence at 600 nm.

Consequently, considering the results of the sample irradiation, it can be said that the "abnormal" band is at 685 nm, which is not described in the literature concerning copper-containing borate glasses.

We will try to explain its origin. It was revealed in [23] that copper ions surrounded by organic complexes had luminescence spectra with a maximum at a wavelength 680 nm for the excitation wavelength 405 nm.

In the case of the above-mentioned phosphate glass [13], irradiation was carried out with less energy X-ray radiation. The X-ray wavelength in [13] was 0.15 nm, in our experiment it was 0.000992 nm, that is 150 times smaller, respectively. Thus, the irradiation energy in our study is 150 times more than in [13].

It can be assumed that at such radiation energies, the covalent bonds of a part of boron ions are destroyed in such a way that the configuration of the environment, where copper ions are located, changes. Consequently, the system of levels is modified, which ultimately gives the above-mentioned effect of the appearance of the luminescence at 685 nm for the excitation wavelength 405 nm, as well as a band of 671 nm for the excitation wavelength 360 nm.

5. Conclusion

It has been shown that, upon gamma rays irradiation with dose of 360 Henry, a new intense luminescence band appears in lithium borate glass. The luminescence band at 685 nm corresponds to the exciting wavelength 405 nm, the luminescence band at 671 nm corresponds to the exciting wavelength 360 nm. The effect has not been previously mentioned in the literature and can be useful from a practical point of view for creating fluorescent dosimeters of gamma radiation. In order to understand exactly which structures luminesce in glass, a detailed study of the samples structure by other methods is necessary.

Acknowledgments. *We glad to Igor Arkadievich Gladskih for photoluminescence spectra corrections. Research was conducted under the support of the Russian Science Foundation, Grant no. 17-72-10216.*

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