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RELATION OF THE OPTICAL PROPERTIES OF BORON COPPER-CONTAINING GLASSES ON THE CONCENTRATION OF LITHIUM

P.S. Shirshnev*, Zh.G. Snezhnaia, E.V. Shirshneva-Vaschenko, A.E. Romanov, V.E. Bougrov

Department of Modern Functional Materials, ITMO University,

Lomonosova str. 9, Saint Petersburg, 191002, Russia,

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

Abstract. In this work, optical properties of a variety of boron host glasses with copper in relation to the lithium content from 0 to 25 % are studied. It is shown that with the increase of the lithium concentration the absorption band of Cu^{2+} increases. This fact is associated with the interaction of lithium ions in the melt with atmospheric oxygen. It is shown that the photoluminescence band shifts by more than 20 nm upon excitation at 320 nm with increasing lithium concentration. This is can be explained by the high splitting of the levels of Cu(I) under the action of lithium ions, and also with the formation of Cu^{+} -Cu^{+} dimers in the glass structure.

Keywords: boron copper-containing glasses, lithium content, optical properties

1. Introduction

The development and investigation of new photonic materials for «down converters» is a new research trend that grows rapidly. These materials convert the UV solar radiation to visible radiation due their luminescence by UV radiation, which allows to improve efficiency of solar cell. Silicon solar cells are not susceptible to the UV radiation. Thus, the converting of UV radiation to visible radiation increases the absorption of solar cell and consequence its efficiency.

There are several types of glass hosts that can be used for down converters. First one, there are borate-barium glasses with ions of rare earth [1]. These glasses production is expensive since the cost of rare earth reagents. Another one type of glass compositions are silicate glass with ions and clusters of silver [2]. The melt temperatures of such glasses are high (1550°C), the requirements for chemical purity of reagents are also high; in addition; cerium ions are present in their composition. Thus, glasses with ions and clusters of silver are also not cheap.

In this work, boron glasses with copper ions are proposed as an alternative to reviewed glasses [3-5]. These glasses have not expensive components, and their synthesis temperatures are 1300-1400°C. In these glasses basic luminescent components are copper ions and clusters. As shown in [6], such type of glasses can be efficient converters of solar UV radiation.

We should say a few words about the states of copper ions in glass. Copper ions can be in three states: atomic (Cu^{0}), Cu(I), Cu(II). When the oxidation-reduction potential of the melt is shifted toward the reduction, an atomic copper [7] occurs in the glass. At the shift towards oxidation the bivalent Cu(II) will be released. Ions of bivalent copper have an absorption band

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at 800 nm. The main factor determining in which state will be the copper ions in the glass is the concentration of oxygen in the melt [8, 9].

Let us consider the luminescent properties of copper ions and clusters more in detail. The absorption bands of Cu^+ ions for different glass hosts can range from 250 to 300 nm [10], and the photoluminescence from 460 to 475 nm, 485-500 nm [11].

It has reason to suppose that the blue luminescence of 485-500 nm corresponds to a transition from the lower triplet energy level ^3E_g" formed by the splitting of the ^{3}Eg level due to the tetragonal stretching of the oxygen octahedron [11]. The change in the level splitting of the ^3E_g level (12) determines the energy of the ^3E_g level, as a result, the blue luminescence band shifts. The 540-nm luminescence band is referred to the Cu^+-Cu^+ dimers (13, 14), as well as to the Cu^+ (15) ions in a planar environment.

In [16] it is shown that lithium in potassium-alumina borate glasses promotes the crystallization and the separation of nanoparticles. Such processes occur at temperatures above the glass transition temperature. As concerns clusters, there may be a separation of copper clusters during the primary cooling of the glass after synthesis. S.A. Stepanov in his work [17] notes that for each type of glass host the pore size is different, that determines the size of the separated clusters [17].

In addition, according to the electronegativity table, lithium ions have a high field strength in comparison with sodium and potassium ions. That can lead to the destruction of covalent bonds in the glass, to the formation of non-bridging oxygens, to the deformation of structural groups in the glass, and thus to change the environment of copper ions. The changes of copper environment contributes to the changes of character of the copper ions luminescence and to the formation of copper clusters.

2. Experimental

In this work, glasses obtained by standard melting methods in a quartz crucible were investigated. The glasses were melt at 1400°C for 2 hours with a quartz stirrer mixing. Further, the glasses were cooled in a muffle from 400 °C to room temperature for 12 hours. The glass composition was $(25\text{-}x)K_2O\text{-}xLi_2O\text{-}50B_2O_3\text{-}25Al_2O_3$ (molar %). There were additions in excess of 100% of 0.5 Cu_2O and four weight percent of ground coal as a reducing agent. The content of lithium ions was varied from 0 to 25% in steps of 5%.

For further measurements from synthesized glasses, flat-parallel samples were made. The absorption spectra from 300 to 800 nm were measured by the Avaspec 2048 spectrometer complex, photoluminescence spectra were measured on the same complex upon excitation of 320 nm. The quantum yield was measured by the Hamamatsu C9920-02G quantum yield measuring device at the same excitation wavelength.

3. Discussion

The absorption spectra of the samples are shown in Fig. 1. As can be seen, depending on the concentration of lithium, the maximum of absorption in the visible range has the glass, in which the potassium is completely replaced by lithium. It is seen from the Fig. 1 that there is an absorption band at 800 nm due to the presence of bivalent copper in the glass.With an increase in the potassium concentration, the absorption band decreases, which negates the green color of the glass, due to the transition of ions to the Cu^+ state. As can be seen all synthesized glasses have a short-wavelength absorption edge at 350 nm, which is typical for boron glasses with copper [8, 9]. The short-wavelength absorption edge can be coupled with the presence of copper ions in the state of Cu^+, as well as Cu^+ -Cu^+ dimers [10].

Also shown in the figure 2 (left), that at the concentration of 5% of lithium oxide, the absorption band at 600 nm exists, as consequence of copper nanocrystals plasmon absorption. According to [18], it is possible to shift the absorption toward larger wavelengths with an

increase in the refractive index of the surrounding medium. The absorption peak with several absorption bands is possible in the presence of elliptical nanoparticles or particles with dimensions larger than 50 nm. Under this work, this effect was not investigated in details. It should be noted that there is an anomalous formation of these copper nanoparticles just at the announced concentration of lithium ions. One can suppose that the presence of small concentration of lithium contributes to an additional increase of ability of nanoparticle formation in glass, that is, liquation. In this case, lithium exists as a liquation agent [16] rather than the component of a glass net.

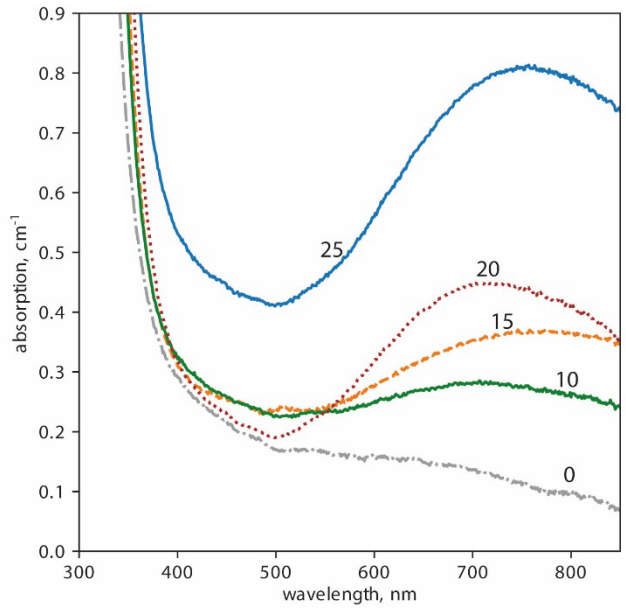

Fig. 1. Optical absorption spectra of glass samples with various concentration of lithium oxide (digits)

In Figure 2 (right), the dependence of the absorption bands of bivalent copper for glasses with different concentrations of lithium ions is shown. As can be seen, the dependence is practically linear, consequently with the increase of lithium concentration the intensity of the absorption band of Cu^{2+} increases. For obvious reasons, there are no results for the glass composition with 5 % of lithium are shown since in this case the plasmon absorption band of copper nanoparticles also appears. Thus, one can say that with an unchanged concentration of the reducing agent (coal) and copper in the glass compositions, an increase in the concentration the lithium content occurs an increase in the concentration of copper ions (II).

This can be explained by the high chemical reactivity of the lithium. In a melt during the glass synthesis, lithium easy interacts with oxygen from the atmosphere above the melt, and thereby displaces the oxidation-reduction equilibrium in the melt toward the oxidation, and therefore also increases the content of bivalent copper in the melt.

The photoluminescence spectra of the samples are shown in Fig. 3. It should be taken into account that these spectra only the structure of the bands should be determined. It can be seen that all the bands have a half-width of 125 nm and have one maximum. The dependence of the magnitude of the maximum on the concentration of lithium ions is shown in Fig. 4 (left).

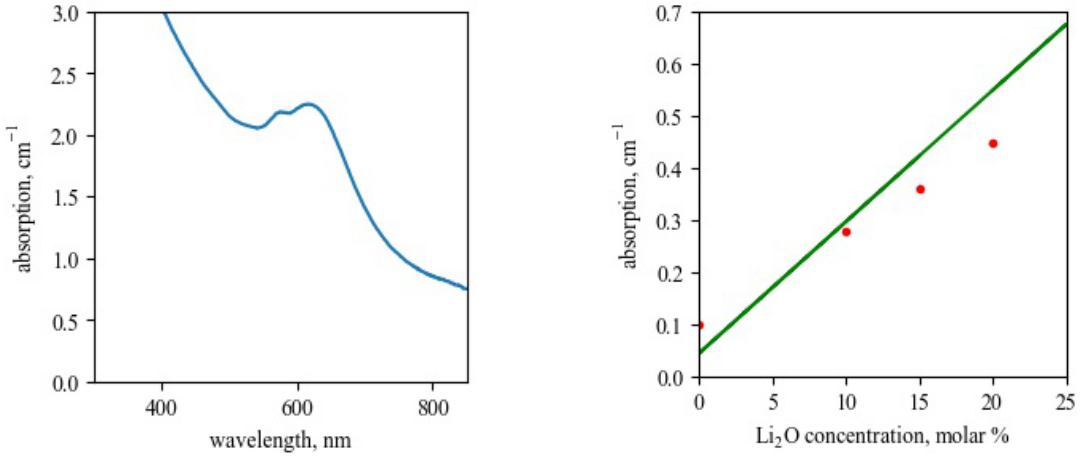

Fig. 2. Opticalabsorption spectra of a glass with 5 % Li_2O (left) and dependence of intensity of optical absorption Cu(II) from the Li_2O concentration (right)

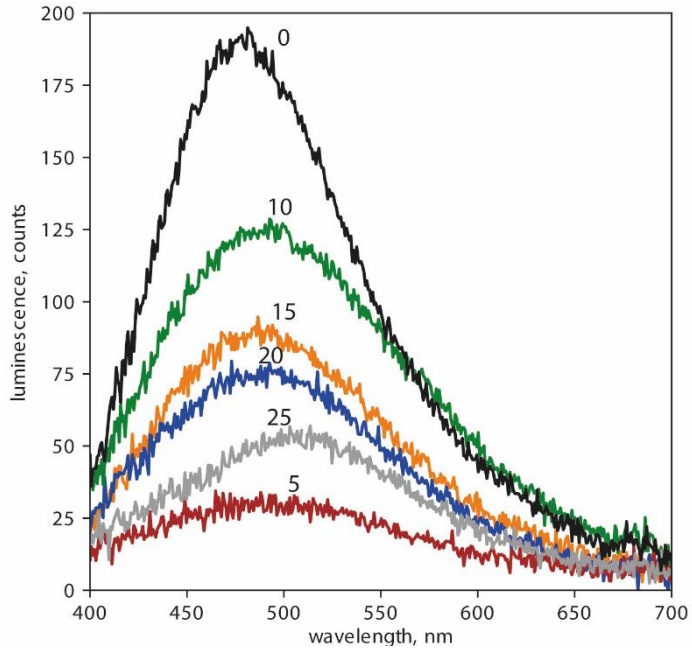

Fig. 3. Photoluminescence emission spectra of glass samples with various concentration of lithium oxide (digits)

As can be seen from the luminescence bands, with a change in the lithium concentration, the maximum of the luminescence intensity shifts by 30 nm from 480 nm to 510 nm. According to the data we can suppose [6] that the peak at 480 nm in the spectrum corresponds to the luminescence of Cu^+. For the abnormal shift more than 30 nm of the luminescence maximum in spectrum both the Cu^+-Cu^+ dimer bands and the above-mentioned tetragonal stretching of the oxygen octahedron under the action of lithium ions [11] can be responsible. Therefore, in an increase of lithium ions concentration occurs to an increase in the concentration of copper dimers and to the splitting of the levels of univalent copper.

Figure 4 (right) shows the dependence of the quantum yield on the concentration of lithium ions in the glass. It can be seen that the quantum yield decreases by more than 3 times. It can be explained by increasing of the absorption band of bivalent copper ions with the concentration of lithium increases. In this case, part of the copper ions, which could be univalent, became divalent, thereby reducing the number of luminescent centers. The

absorption centers of Cu^{2+} block the luminescence of the remaining univalent copper ions. Owing to these two factors, shown above, the quantum yield of glasses decreases as the concentration of lithium ions increases.

Thus, we can detail the basic results of this work:

1. There is an increase in the concentration of bivalent copper in glass at the transition from lithium to potassium.
2. The quantum yield decreases at the transition from potassium to lithium.
3. The maximum of the luminescence spectra changes by 30 nm - a shift to a longer wavelength occurs.
4. An increase in the concentration of lithium ions in boron glass leads to the transition of Cu^{+} ions to the state of Cu^{+}-Cu+ dimers, as well as to anomalous stretching of bonds of oxygen-containing octahedral groups, into which univalent copper ions enter.

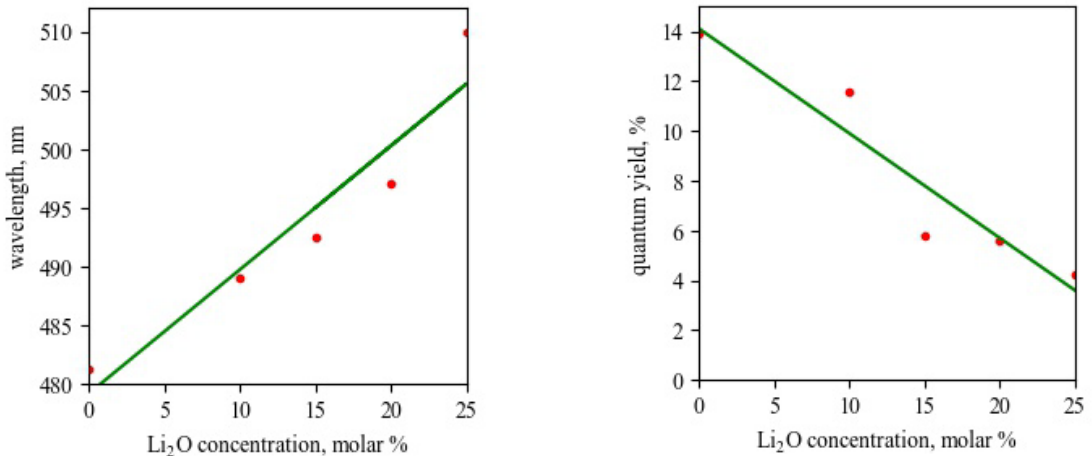

Fig. 4. Photoluminescence peak wavelength dependence from lithium oxide concentration (left) and quantum yield dependence from lithium oxide concentration (right)

4. Conclusions

With an increase in the concentration of lithium in the borate glass with copper, the concentration of bivalent copper ions increases, and the luminescence band shifts from 480 to 510 nm. We suppose that lithium ions contribute to an increase in the content of oxygen groups in the melt, and contribute to a high degree of splitting of the energy levels of univalent copper ions in the glass and, possibly, to the formation of Cu^{+}-Cu^{+} dimers.

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