

# Influence of macro- and microcomponent content on the color of $M_2O$ — $PbO$ — $SiO_2$ ( $M = Li, Na, K, Rb, Cs$ ) glasses doped with copper\*

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The dependence of lead silicate glass color, applied using copper(II) ions, on lead content in the glass, the nature of the alkali metal, and copper content was studied. It was shown that the principal contribution to the color is made by the shift of the fundamental absorption edge, which correlates with the amount of lead and copper ions. According to EPR results for glasses with the studied compositions, copper ions have a tetragonally distorted octahedral coordination environment, which does not change considerably with composition. The  $Cu^{II}$  d—d-transition bands also do not undergo considerable changes.

**Key words:** lead glass, color, copper(II) ions, electronic spectra.

Silicate glasses are complex metastable multicomponent systems with properties of wide-gap semiconductors. In industry, d-metal ions have been used to develop colored glasses for a long time. The spectral characteristics of glasses depend both on the nature of the colorant, which can be considered as a dopant due to its low concentration in the glass, as well as on glass phase composition. It is the composition of the glass, primarily its basicity, regulated by the fraction of modifying oxides, which in some cases determines the coordination environment of the d-metal ion. This problem has been studied in detail using cobalt(II) and nickel(II), whose coordination environment geometry changes with increasing basicity of the glass phase, leading to considerable changes in color.<sup>1,2</sup> Many studies show that copper(II) ions in silicate, borate, phosphate glasses have similar coordination environments, which can be described as tetragonally distorted octahedral.<sup>3,4</sup> In the distorted octahedral geometry,  $d^9$  ions correspond to a splitting in which the maximum possible number of d—d-transitions is three. All of them lie in the red region of the visible spectrum or in the near-IR region. This results in a blue color of glasses from copper chromophore. The optical spectra of glasses in a  $Na_2O$ — $K_2O$ — $CaO$ — $SiO_2$  system doped with copper were studied in detail in a recent study.<sup>5</sup> It showed that copper(II) ions have a tetragonally distorted octahedral geometry with a Cu—O bond length equal to  $(1.89–1.91) \pm 0.02$  and  $(2.20–2.24) \pm 0.02$  Å in equatorial and axial positions, respectively. The blue color of these glasses is caused by d—d-transitions.<sup>6</sup>

At the same time, it is known that copper often acts as a green rather than a blue dye in lead silicate glass. A study

of glasses in the  $Na_2O$ — $PbO$ — $SiO_2$  system, which were coloured by copper,<sup>7</sup> showed that the color gradually changes from blue to green with an increasing amount of lead oxide. However, the authors could not explain the observed color change by photoelectron spectroscopy. Other studies examined the behavior of copper chromophore in lead-phosphate<sup>8</sup> and lead-borate<sup>9</sup> systems.

The goal of this work is to study the reasons for the change in color of lead-silicate glasses caused by copper chromophore using optical spectroscopy methods, as well as to characterize the copper coordination polyhedron using EPR.

To accomplish this, we synthesized two series of lead-silicate glasses. In series I glasses, the mass fraction of  $PbO$  of the  $K_2O$ — $PbO$ — $SiO_2$  system containing 0.5 wt.%  $CuO$  was varied. The effect of an alkali metal cation in the  $M_2O$ — $PbO$ — $SiO_2$  ( $M = Li, Na, K, Rb, Cs$ ) system with the same  $CuO$  content was studied using series II glasses. Additionally, two series II glasses with an increased concentration of the colorant (2 wt.%  $CuO$ ) were obtained.

The use of spectroscopic methods made it possible to establish the complex nature of the effect of copper on the color of synthesized glasses, related not only to d—d-transitions of copper(II) ions, but also to the effect of copper(I) and copper(II) on the shift of the fundamental edge by increasing the length of the "tails" of the valence band localized states.

## Experimental

Two series of lead glasses  $K_2O$ — $PbO$ — $SiO_2$  were synthesized in this work: series I ( $10K_2O \cdot xPbO \cdot (90-x)SiO_2$ ,  $x = 10–65$  wt.% +  $CuO$  0.5 wt.%); series II (10 wt.%  $M_2O$  + 30 wt.%  $PbO$  +

\* Based on the materials of the 5th EuChemS Inorganic Chemistry Conference (EICC-5) (June 24–28, 2019, Moscow, Russia).

+ 60 wt.% SiO<sub>2</sub>, M = Li, Na, K, Rb, Cs samples); as well as two series **I** glasses with an increased content of copper oxide. The starting substances were quartz sand BC-050-1 (SiO<sub>2</sub> > 99.8%, 0.046% Fe<sub>2</sub>O<sub>3</sub>, 0.144% Al<sub>2</sub>O<sub>3</sub>, humidity 0.01%, average grain size 237 μm), potassium carbonate K<sub>2</sub>CO<sub>3</sub> (reagent grade), potassium nitrate KNO<sub>3</sub> (analytical grade), red lead Pb<sub>3</sub>O<sub>4</sub> (analytical grade), copper oxide CuO (analytical grade) (all Reakhim, Russia). Potassium was introduced as a mixture of carbonate and nitrate during the synthesis to create an oxidizing atmosphere (80 and 20 mol.%, respectively).

Glasses were cooked in alundum crucibles with a capacity of 250 mL in a bottom-loading LHT 02/17LB electric furnace (Nabertherm, Germany) (MoSi<sub>2</sub> heating elements). For annealing and secondary heat treatment, a MF-5 muffle electric furnace (Nabertherm, Germany) was used. Quartz was ground in a Pulverisette 02.102 mortar mill (Fritsch, Germany). The batch in an unglazed porcelain cup was placed into a muffle furnace for 4 h at a temperature of 500–750 °C, which was selected for each composition based on glass softening temperature. The frit was removed from the porcelain cup and ground using a mortar mill for 15 min. The crucible with the batch was heated to 800 °C over 1 h, followed by heating to 1400 °C over 3 h, allowed to stand at this temperature for 4 h, then it was heated to 1450 °C over 15 min, and allowed to stand at this temperature for 30 min. The hot furnace was opened, the crucible was removed and the glass was poured and quenched on a cast-iron plate, preliminarily heated in a muffle furnace to 520 °C. The plate with the glass was placed into a muffle furnace for annealing for 5 min at 400–520 °C, depending on the composition of the glass.

Composition was studied by MS and atomic emission spectroscopy (AES) with inductively coupled plasma (ICP-MS and ICP-AES) using Thermo Scientific X-7 and Thermo Jarrell Ash ICAP-61 spectrometers (USA), respectively, sample preparation and analysis methodologies are described<sup>10</sup> in published literature.

Electronic transmission spectra of the glasses were recorded on a Lambda 950 spectrometer (Perkin-Elmer, USA) in the wavelength range 200–1200 nm. Grinding and polishing of samples for recording electronic spectra were carried out on an MP-2 grinding and polishing bench (Laizhou Huayin Testing Instrument Co, China). Color coordinates were determined in the CIE-Lab system using the Color Master Viewer program.

EPR spectra were recorded on an X-band Varian E-4 EPR spectrometer ( $\nu \approx 9.1$  GHz). The spectra of isolated Cu<sup>2+</sup> ions were modelled using the EasySpin package<sup>11</sup>.

## Results and Discussion

The compositions of the synthesized glasses calculated according to ICP-MS (copper) and AES (potassium, lead) are given in Table 1. The potassium and lead content is lower than the calculated values due to volatilization of components (lead in oxide form (PbO) and potassium in superoxide form (KO<sub>2</sub>)). In Table 1 and hereinafter in the text macrocomponent content is given in terms of oxides.

**Electronic spectra.** The electronic spectra of series **I** glasses (Fig. 1) have bands only in the UV range. The maxima found in the spectra are related to lead(II) transitions <sup>1</sup>S<sub>0</sub>–<sup>3</sup>P<sub>1</sub> (305–315 nm) and <sup>1</sup>S<sub>0</sub>–<sup>1</sup>P<sub>1</sub> (240–250 nm). The transition with the lower energy undergoes a batho-

**Table 1.** Composition of glasses according to ICP-MS and ICP-AES

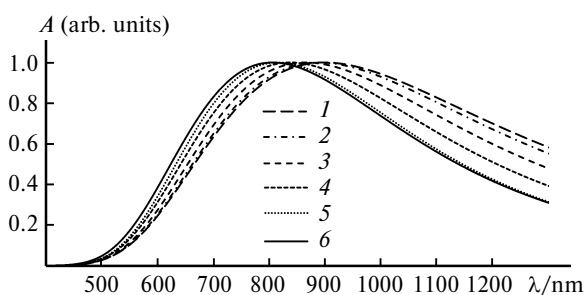
Sample	M	Composition (mol.%)			
		M <sub>2</sub> O	PbO	SiO <sub>2</sub>	CuO
1	K	7.05	3.03	89.50	0.42
2	K	7.35	6.13	86.07	0.45
3	K	8.29	10.45	80.76	0.50
4	K	8.59	14.81	76.06	0.54
5	K	9.63	20.34	69.43	0.60
6	K	10.72	23.89	64.75	0.64
7	K	11.28	27.60	60.44	0.68
8	K	11.53	31.69	56.06	0.72
9	Li	8.54	10.42	80.57	0.46
10	Na	8.55	11.03	79.94	0.49
11*	K	8.29	10.45	80.76	0.50
12	Rb	8.54	10.68	80.23	0.55
13	Cs	8.50	10.70	80.20	0.60
14	K	7.25	6.04	84.91	1.79
15	K	7.53	9.25	81.30	1.92

\* Identical to sample 3.

chromic shift with an increasing amount of lead. Band broadening is explained by the presence of lead ions with different coordination environments in the glass.

*The position of the fundamental absorption edge.* The fundamental absorption edge, also located in the UV range, is superimposed with the transition bands in lead ions, and an increase of their concentration considerably shifts the edge toward the red region of the spectrum. This shift is so substantial, that for samples with a high lead concentration it partially covers the violet part of the visible spectrum.

Two types of electronic transitions are observed near the fundamental absorption edge: direct and indirect. The band gap for both types of transitions was determined by analyzing the linear part of the spectrum near the fundamental absorption edge.<sup>12</sup> The analysis of the adjacent exponential part of the spectrum made it possible to determine the Urbach energy characterizing the defectiveness of the glass and the length of the tails of the conduction and valence bands<sup>12</sup> (Table 2).



**Fig. 1.** The sum of two Gaussians approximating d–d-transitions in series **I** glasses.



It is known that in glasses with a high lead content, impurities have a stronger effect on color than in glasses with a low lead content, even when their content in the glass phase is negligible.<sup>13</sup> In this work this considerable effect of impurities on the color of glasses with a high lead content is explained by the increasing number of defects. Tricharged cations, such as chromium, have an even stronger effect on the shift of the Urbach edge.<sup>14</sup>

The number of non-bridging oxygen atoms also contributing to the valence band does not change with an increasing ionic radius of the alkali metal for constant concentrations of lead and silicon oxides. Accordingly, the valence band tail of series I glasses does not change, but the band gap increases.

A bathochromic shift of the fundamental edge with respect to series I glasses with the same basic composition is observed for glasses 14 and 15, which indicates a correlation with dye content. This leads to glasses 14 and 15 with 2% CuO having a green color, while the corresponding series I samples (1 and 4, 0.5% CuO) are blue and turquoise, respectively. This is explained by a consistent decrease of the energy gap due to an increase of defectiveness. It is known<sup>15</sup> that a further increase in the concentration of copper in glass to 40 mol.% CuO leads to the active participation of copper electrons in the formation of the valence band. The ratio of Cu<sup>II</sup> and Cu<sup>I</sup> in this case determines the electronic state of the system. According to published data,<sup>16</sup> bands of forbidden transitions 3d<sup>10</sup>—3d<sup>9</sup>4s<sup>1</sup> in Cu<sup>I</sup> are also located in the UV region, and their probability increases due to interaction with the lattice. Due to the low Cu<sup>I</sup> content, these bands do not appear individually, but contribute to the redshift of the fundamental edge.

*d—d-Transitions.* A wide band with a maximum in the red and near-IR regions corresponds to a set of d—d-transitions in the Cu<sup>II</sup> ion. It can be decomposed into Gaussians corresponding to individual d—d-transitions.<sup>5</sup> The number of bands in the spectrum can vary from one

to four, depending on the degree of distortion of the octahedral coordination environment of the copper ion in the glass. The calculation of the spectra using the Kubelka—Munk equation shows that all polyhedra actually have C<sub>1</sub> symmetry, characterized by the maximum degree of distortion, which in some cases can be formally raised to C<sub>s</sub> or C<sub>2v</sub>.<sup>17</sup>

For d—d-transitions in series I glasses, two Gaussians can be singled out. The position of the low-energy (940 nm) Gaussian remains practically unchanged with increasing lead oxide concentration; the position of the high-energy Gaussian shifts toward the blue region (880 → 700 nm) (Table 3). At the same time, the relative intensity of the high-energy band decreases considerably (see Fig. 2), which shifts the envelope function maximum in the opposite direction. If we assume that copper in each glass has a distorted octahedral environment, then it is logical to link this hypsochromic shift with increasing distortion, which leads to the disappearance of elements of symmetry.

The relationship between the macrocharacteristics of glasses and optical absorption described for the NCS system<sup>18</sup> suggests that an increase of lead oxide concentration results in a change of the non-radiative relaxation mechanism, which then leads to an increase in the intensity of d—d-transitions in glasses.

The spectra of series II samples also contain one broad peak, the maximum of which depends on the nature of the alkali metal (Table 4). In the Li—Cs series, the maximum undergoes a gradual shift toward the high-energy spectral region. The shift of the maximum in the studied samples repeats the trend observed for calcium silicate glasses doped with CuO.<sup>19</sup> When going from lithium to cesium, the intensity of the lower-energy band increases, which leads to the hypsochromic shift of the single maximum in the absorption spectrum. Based on calculations, it can be determined that tetragonal distortion in the [CuO<sub>6</sub>] octahedron decreases when going from lithium to cesium glass. This can be explained by a greater covalent contribution

**Table 3.** Absorption band maximum and color coordinates for series I glasses

Sample	Band maximum/nm	Gaussian maxima/nm		Ratio of intensities I : II	$n_D$	Color coordinates in the CIE-Lab system			
		I	II			$L$	$a$	$b$	$RGB$
<i>1</i>	874	916	879	1.92	1.50	79.34	−29.11	−27.37	85 213 246
<i>2</i>	872	935	826	1.83	1.53	81.32	−26.64	−20.82	115 217 240
<i>3</i>	871	979	820	0.57	1.55	83.16	−25.32	−13.08	133 221 234
<i>4</i>	869	927	801	0.51	1.59	77.04	−35.46	−17.77	70 209 222
<i>5</i>	819	959	751	0.52	1.64	76.96	−38.95	−7.30	77 210 202
<i>6</i>	808	991	744	0.53	1.67	77.25	−36.28	−5.37	93 210 199
<i>7</i>	811	907	629	1.24	1.69	79.58	−32.67	−1.87	118 214 199
<i>8</i>	802	934	728	0.53	1.72	86.85	−16.83	1.15	183 227 215
<i>14</i>	875	940	830	1.80	1.53	90.90	−22.78	−12.07	166 242 251
<i>15</i>	870	985	815	0.71	1.55	90.01	−26.50	−11.83	153 242 248

**Table 4.** Absorption band maximum and color coordinates of series **II** glasses

Sample	Band maximum/nm	Gaussian maxima/nm		Ratio of intensities I : II	Color coordinates in the CIE-Lab system			
		I	II		<i>L</i>	<i>a</i>	<i>b</i>	<i>RGB</i>
9	758	940	727	0.37	86.22	−20.61	−9.30	162 228 232
10	803	940	745	0.72	85.11	−20.65	−12.29	156 225 235
11	871	979	820	0.57	83.16	−25.32	−13.08	133 221 234
12	877	943	766	0.40	91.29	−9.47	−4.26	207 236 238
13	907	910	676	0.08	89.08	−13.57	−9.66	187 232 242

to the Li—O bond, due to which the interaction between the oxygen atom and the copper cation becomes weakened. A more accurate interpretation of the change in the geometry of the copper coordination polyhedron in the studied glasses when going from lithium to cesium is beyond the scope of this study, the purpose of which is to determine the reasons for the change of the color of glasses depending on their composition. The color coordinates of the series **II** glasses have similar values, corresponding to their blue color.

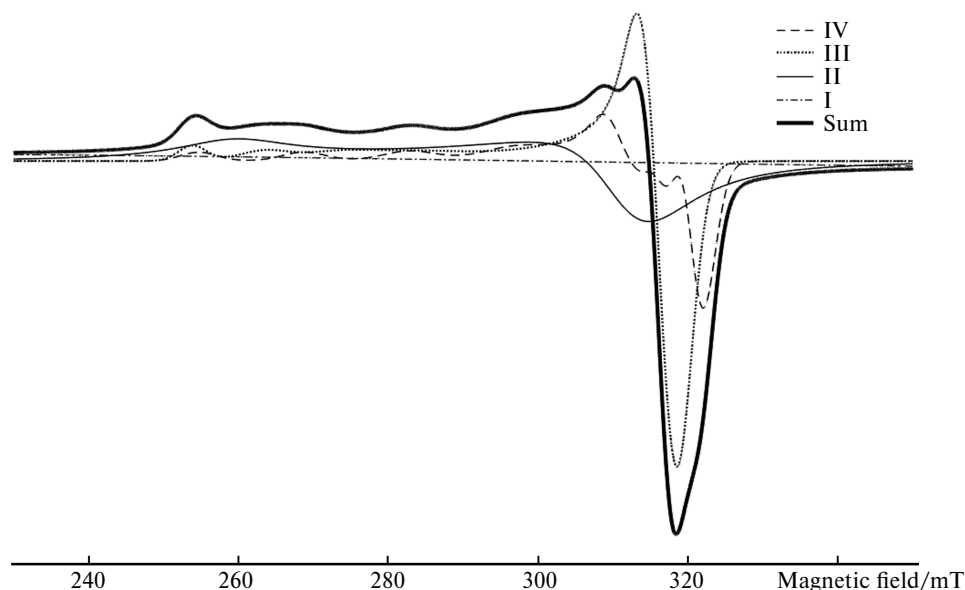
In glasses *14* and *15*, the d—d-transition band intensity increases without changing its shape and position of the maximum.

Thus, an increase in dopant concentration (CuO) in lead-silicate glass results in changing color in two ways: 1) the intensity of d—d-transitions in the red region (Cu<sup>II</sup>) increases; 2) the redshift of the fundamental absorption edge (Cu<sup>I</sup>) increases. Along with a decrease of the band gap, the increasing concentration of lead ions leads to a change of the glass color from blue to green, obtained

from a simultaneous absorption of light in the red and violet spectral regions.

**Electron paramagnetic resonance.** The EPR spectra of copper(II) ions in glasses have<sup>20–28</sup> a characteristic shape (Figs 3 and 4). In the studied glasses, copper(II) ions are in an axially symmetric environment, the lines are broadened due to large differences in the local environments of copper ions in the disordered matrix. Since  $g_{\parallel} > g_{\perp}$ , it can be suggested that oxygen atoms in the local environment of copper ions lie at the vertices of a tetragonally distorted, elongated octahedron, and the distances in the plane for a specific copper ion can vary, but their average values are similar.

When lead content is varied, the line shape changes insignificantly, which indicates that the copper environment remains the same, however, the broad linewidth makes a detailed analysis impossible. To describe the real line shape, a superposition of several signals (I—IV) from various paramagnetic centers was used by analogy with the work.<sup>18</sup>

**Fig. 3.** Typical decomposition of the EPR spectrum of series **I** glasses. Theoretical (sum) line shape and individual spectra (I—IV).

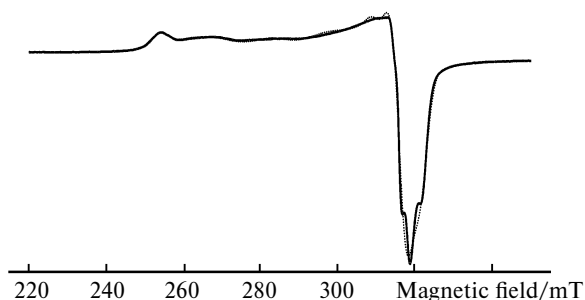


Fig. 4. The solid line represents the EPR spectrum of sample I, and the dashed line corresponds to the theoretical spectrum.

In the range of fields studied in this work, it is not possible to reach the zero line, *i.e.*, the registered first derivatives of the absorption signal in minimum and maximum fields do not overlap, which indicates the presence of a broad signal, whose width is greater than the studied range. The nature of such a signal is, as a rule, a magnetic phase with a strong exchange (signal I).

There is a clear signal with a hyperfine structure (HFS) from copper nuclei ( $I = 3/2$ ),  $g_{\parallel} \approx 2.35$ ,  $g_{\perp} \approx 2.07$ ,  $A_{\parallel} \approx 400$  MHz (Table 5). The signal was described by a Lorentzian with a variable linewidth, taking into account broadening due to the normal distribution of the spin Hamiltonian parameters ( $g$  and  $A$ ) with a negative correlation (signal IV).

For the description of the real line shape it is not sufficient to use only these two signals, because it is not possible to satisfactorily describe the signal amplitude in the model spectra, and, as a result, additional signals have to be introduced for compensation. Two more signals were added for a more suitable description. The choice of the starting parameters was carried out by analogy with the work,<sup>27</sup> *i.e.*,  $g_{\text{iso}}$  remained constant and  $g$ -tensor parameters were changed. One of them "degenerated" into an axial tensor with  $A \approx 0$  during optimization; hereafter, its HFS was not taken into account to reduce the number of variable parameters (signal II).

The calculated parameters of the spin Hamiltonian are in agreement with those found in published literature for copper ions in silicate, borate, and phosphate glasses.<sup>20–28</sup>

Signal broadening is observed in glass samples with a higher copper content (14 and 15), which can be at-

tributed to strong exchange interaction between the paramagnetic centers, as a result, interpreting these signals is even more difficult, because even the hyperfine signal structure expresses itself very weakly.

Thus, we have shown that copper(II) ions in the glass phase can affect the color of silicate glasses both by absorbing light through  $d-d$ -transitions and by causing a bathochromic shift of the fundamental edge by increasing the number of defects of the valence band tails. According to electronic spectra and EPR spectra, copper ions in all the studied glasses are in a distorted octahedral environment. The shift of the fundamental edge is the main contribution to the color change accompanying an increase of the amount of lead in the glass. Although they are caused by a decrease in the symmetry of the environment, changes in  $d-d$ -transitions do not lead to a noticeable change in color coordinates. Varying the alkali metal does not have a substantial effect on glass color. It does not result in considerable changes in the position of the fundamental edge, but leads to a slight shift of the  $d-d$ -transition band toward higher energies. Copper ions in the glass affect the color irrespective of the oxidation degree. With increasing dye concentration, the color changes due to a shift in the position of the fundamental edge. It is shown that varying macro- and microcomponents in the  $\text{K}_2\text{O}-\text{PbO}-\text{SiO}_2$  system allows one to change the structure, which creates the conditions for the directed synthesis of glasses with the desired color.

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Table 5. EPR signal parameters

Signal	$g_{\perp}$	$g_{\parallel}$	$A_{\perp}$	$A_{\parallel}$
			MHz	
I	2.170	2.170	0	0
II	2.094	2.516	0	0
III	2.062	2.435	25	316
IV	2.065	2.368	86	454

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