SPECTRAL ABSORPTION OF PHASE-SEPARATING SODIUM BOROSILICATE GLASSES COLORED WITH IRON OXIDES

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In [1], it was determined that the location of the UV transmission boundary in phase-separating sodium borosilicate glasses depends not only on the content of impurity iron in the glasses at low concentrations (the absorption factor), but also on the presence of phase-separation inhomogeneity regions (the scattering factor). It has been assumed that at high iron concentrations (≥ 0.5 wt.% Fe₂O₃) in two-phase glasses, just as in single-phase ones [2-4], clusters are formed, causing a sharp increase in the effect of the iron content on the absorption in the UV spectral region. The spectral behavior of iron ions in the visible and near-IR spectral regions was not considered in [1].

The present paper had as its purpose to elucidate the spectral properties of two-phase sodium borosilicate glasses colored with various iron additives. A glass was studied which was close to industrial glass DV-1, of composition (mole %) 7Na₂O·23B₂O₃·70SiO₂ containing 0.005–1.0 wt.% Fe₂O₃. The procedure for synthesis of the glasses is described in [1]. Absorption measurements were carried out with a Hitachi EPS-3T recording spectrophotometer with polished specimens having dimensions of 20×20×5 mm.

Figure 1 shows the spectral dependence of the specific absorption of glasses containing various amounts of Fe₂O₃ and heat-treated at 600°C for 1 and 4 h. Of interest is the fact that the specific-absorption coefficients did not obey the Bouguer–Lambert–Beer law, as indicated by the increase in the specific absorption, disproportional to the iron concentration. Within the studied concentrations, the specific absorption increased by 600–800%, with it being evident that the increase in the heat-treatment time caused some increase in the specific absorption. We should note that an increase in the treatment temperature from 600 to 650°C did not cause a further increase in ε₇₉* (the curve for 650°C is not shown), although macroscopically there was a structural change expressed in the appearance of opalescence. The specific-absorption coefficients were calculated according to the difference in the absorbance of glasses with and without iron additions, so that the change in the values of ε₇₉ with heat treatment was due exclusively to the behavior of the dye ions, and not to

* The specific-absorption coefficient ε₇₉ is the value of the absorbance calculated per unit concentration of the dye expressed in weight percents and per unit thickness of the glass [5].
the change in the intrinsic structure of the glass. According to a previous electron-microscopic investigation of similar glasses [1], the radius of phase-separation inhomogeneities for a series of specimens which were identically heat-treated did not depend on the iron oxide concentration and was 30-50 nm for glasses heat-treated at 600°C for 4 h. We should note that according to the data of [1] the radius of the inhomogeneity regions strongly depended on the treatment temperature of the glasses for all the FeO3 concentrations and increased in the case of the specimens treated at 650°C for 4 h from 30-50 to 100 nm. At the same time, as was indicated above, such an increase in the size of the inhomogeneities did not cause an increase in the values of ελ.

In considering Fig. 1, we can conclude that on the whole the values of ελ were proportional to the iron content in the entire studied spectral range, indicating that the Fe3+/Fe2+ ratio remained constant in the entire concentration series of the glasses. This same thing is indicated by an analysis of the ESR spectra (the spectra are not shown).

Also of interest is the fact that the specific absorption increased with heat-treatment time mainly only in the short-wave part (400-800 nm) of the studied spectral range. In addition, the greatest increase in ελ occurred for glasses with small FeO3 additions (0.005-0.1%). Thus, whereas for 1-h holding at 600°C the value of ε400nm for the glass with 0.005% FeO3 was 0.2, for 4-h heat treatment it increased to 0.4. For concentrations of 0.05 and 0.1% FeO3, the increase in ε400nm was 0.45-0.60 and 0.70-0.80, respectively.

The observed experimental results can apparently be explained as follows. It is known [6] that the iron in the glass is always in two oxidation states, namely, in the form of ferric oxide (FeO3) and ferrous oxide (FeO), with ferric oxide having insignificant absorption in the long-wave spectral region and great absorption in the short-wave region and with the opposite being characteristic of ferrous oxide. According to [7], in phase-separating sodium borosilicate glasses activated with iron oxides, practically the entire amount of the Fe2+ ions has an octahedral coordination with respect to oxygen and is concentrated in the sodium borate phase. Together with a six coordination, the Fe3+ ions have a partially four coordination and, according to the published data [7], are also predominantly in the sodium borate phase. It is natural that the remaining portion of the Fe3+ ions in the four coordination should be arranged within the high-silica phase or be concentrated along the interfaces. The fact that for our glasses the increase in the absorption coefficient with increasing heat-treatment time was observed mainly only in the region of 400-800 nm is probably due to incomplete of the cluster-formation process under the conditions of the highly viscous high-silica with 1-h treatment and to an intensification of the cluster-formation process with 4-h treatment. For a comparatively low-viscosity sodium borate phase enriched with Fe2+ ions (absorption maximum of 1000-1100 nm), even 1-h holding was sufficient for completion of cluster formation.