Crystallography

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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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STUDY OF THE STRUCTURE OF GLASSES OF THE SYSTEM

$RO–Al_2O_3–B_2O_3–SiO_2$

(Presented by Academician N. V. Belov, February 9, 1970)

Glasses of composition 20.2% RO–11.4% Al_2O_3, 11.4% B_2O_3–57% SiO_2 (molecular percentages) were studied; CaO, MgO, SrO, BaO, ZnO, CdO, and PbO were used as RO. The structure of the initial and crystallized glasses was investigated by DTA, forced crystallization, X-ray phase analysis, and IR spectroscopy.

Almost all the glasses studied possess high crystallization stability. The exception is the glass with zinc oxide. On the DTA curve in the temperature region up to 950°, an exothermic effect (the maximum corresponds to 860°) is observed only for the glass with zinc oxide. The crystalline phase in such a glass is readily determined by X-ray structural analysis after holding the zinc-containing glass in a gradient furnace with a temperature gradient of 500–1150° for 2 h. In the remaining glasses, with such heat treatment, it was not possible radiographically to detect crystalline phases. In glasses containing calcium, magnesium, strontium, and barium, crystalline compounds were recorded only after treating the glasses in the powdered state at 1050° for 6 h. In glasses containing cadmium and lead, X-ray structural analysis detects no crystalline formations at all.

The study of infrared spectra showed that in the calcium-containing glass there is glassy silica (bands at 1100 and 800 cm^{-1}) and a calcium-borate compound (Fig. 1, curve 1). Upon crystallization, the calcium-borate phase remains unchanged. Silica separates out in the form of cristobalite—the bands at 800 and 620 cm^{-1} are sharply expressed. Boron in the glass is found predominantly in fourfold coordination. This assumption was made on the basis of the low intensity of the band near 1400 cm^{-1}, characteristic–

Fig. 1. Infrared spectra of glasses of composition 20.2% RO–11.4% Al_2O_3–11.4% B_2O_3–57% SiO_2, where RO–CaO *(1, 2)*, MgO *(3, 4)*, PbO *(5)*, SrO *(6, 7)*, BaO *(8, 9)*, CdO *(10, 11, 12)*, ZnO *(13, 14)*. Heat-treatment conditions: *1,*

Fig. 2. Infrared spectra of minerals: 1 –anorthite, 2 –cordierite, 3 –gahnite

Figure 2: Fig. 2. Infrared spectra of minerals: 1 –anorthite, 2 –cordierite, 3 –gahnite

3, 5, 6, 8, 10, 13–untreated glasses; *2, 4, 7, 9*–1050°, 6 h; *11*–700°, 2 h; *12*–950°, 2 h; *14*–850°, 2 h.

for threefold coordination. From the low intensity of the band at 800 cm^{-1} (Fig. 1, curve 2) it follows that part of the silica is used for the formation of calcium aluminosilicates, as indicated by the presence of the bands 930 and 570 cm^{-1}, which are characteristic in the spectrum of anorthite (Fig. 2, curve 1).

In the series of Ca-, Pb-, Sr-, and Ba-containing glasses, a shift of the principal band from 1100 to 1020 cm^{-1} is observed in the spectra (Fig. 1, curves 1, 5, 6, 8). This is probably due to the fact that divalent cations not bound to the borate component are used for the formation of aluminosilicate glasses. This supposition is confirmed by the spectra of crystallized strontium- and barium-containing glasses (Fig. 1, curves 7, 9), in which the separation of free silica is not recorded. According to X-ray structural analysis, during crystallization of strontium- and barium-containing glasses, strontium and barium aluminosilicates, respectively, are separated.

Fig. 2. Infrared spectra of minerals:
1 –anorthite, *2* –cordierite, *3* –gahnite

Glasses with cadmium, magnesium, and zinc, in contrast to those considered, have an increased tendency toward liquation, the degree of which increases from CdO to ZnO. In the composition of the cadmium-containing glass, during heat treatment, silica is separated in the form of α-quartz, which accounts for the appearance of the doublet 810-785 cm^{-1}, which is especially clearly visible in the spectrum of the glass treated at 950° (Fig. 1, curve 12).

In the crystallized magnesium-containing glass (Fig. 1, curve 4) there is a series of characteristic bands that exactly coincide with the bands of the cordierite spectrum: 965, 775 cm^{-1} and the doublet 620-580 cm^{-1} (Fig. 2, curve 2). The presence of cordierite in the magnesium-containing glass is also confirmed radiographically.

An interesting feature in the crystallization of the zinc-containing glass is the significant increase in it of three-coordinated boron, which is evident from the strengthening of the intensity of the band near 1400 cm^{-1} (Fig. 1, curve 14). According to X-ray phase analysis, gahnite ($ZnAl_2O_4$) is separated in the glass. This is in full agreement with the noted increase in intensity of the 1400 cm^{-1} band, since the accumulation of boron in threefold coordination is apparently accompanied by the liberation of Zn^{+2} cations, which form the indicated compound with aluminum. At the same time, bands at 675 and 520 cm^{-1}, characteristic of gahnite, appear in the spectrum of the crystallized glass (Fig. 2,

curve 3). The other gahnite bands coincide with the silicates: 1100 and 480 cm^{-1}. The presence of the 920 cm^{-1} band indicates the possible presence of willemite (Zn_2SiO_4) in the crystallized zinc-containing glass ([1]).

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REFERENCES

1. A. M. Shevyakov, Doctoral dissertation, Leningrad, 1968.

Note: Figure translations are in progress. See original paper for figures.