STUDY OF THE SPECTRA OF CRYSTALLINE AND GLASSY SILICATES OF THE PbO–SiO₂ SYSTEM

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To study the structure of glasses by infrared spectroscopy, it is necessary to have information on the spectra of crystalline silicates. Only by direct comparison of the spectra of crystalline and glassy silicates of one and the same system is it possible to obtain data on the structure of the glasses of this system. For instance, the study of the crystalline silicates of lead enables one to obtain some information about the structure of lead silicate glasses which in turn is extremely important for the understanding of the properties of a broad group of optical flint glasses.

We studied some crystalline silicates of the PbO–SiO₂ system in the infrared range. Moreover, we established that the published phase diagrams do not reflect all crystalline silicates existing in this system.

According to one phase diagram [1], two compounds (PbO · SiO₂, 2PbO · SiO₂) exist in the system under consideration; according to another phase diagram [2, 3], three compounds (PbO · SiO₂, 2PbO · SiO₂, 4PbO · SiO₂) exist. The results of our study show that in this system exist either a larger number of modifications of the known systems or a larger number of compounds.

Figure 1 shows the reflection spectra of the crystallization products of the glass system PbO–SiO₂, containing from 36 to 71 mole-% PbO. Curve 9 represents the spectrum of the crystallized glass of lead metasilicate composition.
spectrum is the same as the spectrum of the natural mineral alamosite (PbO \cdot SiO₂). Nevertheless, on crystallization of a glass of the same composition as that of the melt, crystals of another lattice type were discovered in the surface layer of the sample; the spectrum of these is shown by curve 10.

Detailed spectral characteristics in the region of 0.1–25 micrometer for silicates with 50 mole-% PbO and 50 mole-% SiO₂ are shown in Fig. 2. Curve 1 represents the transmission spectrum of alamosite powder in the 6–25 micrometer region which, within the experimental error, coincides with the transmission spectrum of crystallized glass of composition PbO \cdot SiO₂. Curve 4 shows the reflection spectrum of the cortical part of glass of lead metasilicate composition and curve 2 the reflection spectrum of the subcortical part of the same sample in the 0.1–25 micrometer region. Curve 3 also represents a reflection spectrum of the original glass. The difference in the structure of the crystalline lattices (spectra 2 and 4) is confirmed also by electron microscopic analysis. In the known literature we found practically no information on the existence of various lead metasilicate modifications.

Also presented in Fig. 1 are curves 3 and 4 indicating the reflection spectra of the crystallization products of a glass of lead orthosilicate composition at temperatures of 620° and 450° C. Figure 3 shows the reflection and transmission spectra of these two modifications over a broader spectral region (0.1–25 micrometer). Curves 2, 3, and 4, 5 in this figure show in pairs the transmission and reflection spectra of glasses with the composition of lead orthosilicate, which had been crystallized at 450° C (3 and 4) and at 620° C (2 and 5), whereas curves 1 and 6 represent the transmission and reflection spectra of the original glass. It is seen from a comparison of the reflection and transmission spectra of the glasses crystallized at 450° and 620° C that the spectra are not identical for each of these temperatures, e.g., crystals with a different crystalline lattice are formed at different temperatures. As in the case of metasilicate, X-ray analysis supports this conclusion. The existence of two modifications is confirmed also by the thermographic method. Figure 3 (curve 10) shows a thermogram of a glass of orthosilicate composition. As is seen, two exothermal effects appear on this curve, and in the region of crystal volatilization, two endothermic effects arise.

Curves 1 and 2 in Fig. 1 represent the reflection spectra of heavy lead silicates with 70 and 71 mole-% PbO. The reflection and transmission spectra in the region of 0.1–25 micrometer of the same silicates containing 70 mole-% PbO are shown in Fig. 4. It follows from 2, 3, and 4 that the reflection and transmission spectra of crystallized glass with 70 mole-% PbO are not similar to the spectra of the crystallization products of glasses containing 50 and 66.7 mole-% PbO.

It is seen from Fig. 1 that the spectra of crystallized glasses containing 35, 55, and 60 mole-% PbO likewise do not represent superpositions of the spectra of the metasilicate and orthosilicate; this indicates the existence of some unknown silicates in the system.

Let us now compare the spectra of crystalline and glassy silicates with 50, 66.7, and 70 mole-% PbO. It is seen from a consideration of their spectral characteristics that the center of gravity of the bands in the spectra of the original glass is the same as that of the crystallized glasses for each of the compositions studied. It is seen from a careful comparison of the spectra of the original glasses with the spectra of their crystallization products that in some cases this comparison extends also to the fine structure. This indicates that in the microstructure of the glass apparently are atomic groups in which the position of the atoms is similar to the position of the atoms in the lattice of the crystallization products of the glass.

The similarity in the spectra of the glassy and the crystalline states arises not only in the long-wavelength region, but also in the short-wavelength region. This region of the spectrum for silicates with 50, 66.7, and 70 mole-% PbO is represented in the upper left-hand corner of Figs. 2, 3, and 4 at a magnified scale. As is seen, the original and the crystallized glass in the ultraviolet region have an intense band which is a triplet. The position of the maxima for each pair of crystalline and glassy silicates is exactly the same; this confirms once more the similarity in the structures of the glass and of the crystal. The reflection bands discovered in the ultraviolet region of lead glasses indicate an extremely important fact.

It is known that lead glasses have a very high index of refraction and a high dispersion, which increase with increasing lead oxide content in the glass and with increasing temperature. The reason for this had been unknown for a long time. The German physicist Pulfrich [4] proposed the existence of an absorption band in the ultraviolet region of lead glasses, which brings about the special optical properties of flints. This question was not sufficiently studied experimentally in [5, 6]. As follows from the results of this study of silicates with 50, 66.7, and 70 mole-% PbO, such an absorption band is in fact observed in the ultraviolet region.

It is of interest to consider the spectra of crystalline and glassy silicates with 50, 66.7, and 70 mole-% PbO in the ultraviolet region and to explain the spectral changes taking place in the glass with increasing lead oxide content. Figures 2, 3, and 4 show the spectra of the original and crystallized glasses with 50, 66.7, and 70 mole-% PbO in the region of 0.2–0.3 micrometer. As is seen, the positions of the maxima of the triplet coincide; a difference arises only in the value of the reflection coefficient. The band intensity of the selective reflection of the glass is less than that of the crystal. With increasing PbO content in the silicates, the band intensity increases and all bands as a whole are shifted toward higher