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Abstract

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APPLICATION OF ELECTRON-MICROSCOPIC AND X-RAY ANALYSIS METHODS TO THE STUDY OF GLASS-CRYSTALLINE MATERIALS

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The production of glass-crystalline materials—sitalls—brings to the fore the problem of deliberately controlling the process of glass crystallization. This problem can be successfully solved by carrying out comprehensive investigations of the structure, phase composition, and properties both of the glass-crystalline materials obtained and of the initial glasses.

The structural features of sitalls—namely, their fine dispersion (the sizes of the crystals are measured in microns and fractions of a micron), multiphase character, etc.—make it impossible to use an ordinary light microscope for their study and require the use of new, more advanced instruments. The methods of electron-microscopic and X-ray phase analyses are the principal methods for studying newly synthesized materials; they provide a clear picture of the crystalline phases that separate out, the size and morphology of the crystals of each phase, and information on the remaining amorphous (glassy) phase.

The electron-microscopic investigation was carried out on a TESLA BS 242A electron microscope at a voltage of 60 kV and magnifications of the order of 4000–6000×, by the method of a carbon replica previously shadowed with chromium. The study was performed on etched surfaces of fresh fractures of the specimens. Etching was carried out with 2% hydrofluoric acid; the etching time was selected empirically for different specimens, depending on their composition and on the relief of the fracture surface, and ranged from 5 to 40 sec. At present a new method of obtaining replicas has been applied, consisting in the simultaneous evaporation of platinum and carbon, which makes it possible to obtain considerably better resolution.

X-ray analysis was carried out by the powder method on a URS-50I X-ray apparatus with ionization recording of the intensity of the X-rays, using CuK_α radiation filtered through Ni foil 2 μ thick.

One of the important results of the combined application of X-ray phase and

electron-microscopic methods of investigation is the possibility of identifying crystals in microphotographs by their appearance. Let us consider several examples. In the microphotograph in Fig. 1*a* (see insert, p. 364), separate crystals, randomly distributed over the entire field in the form of small rods, are visible. X-ray analysis showed that this material contains only one crystalline phase—sphene $CaOSiO_2TiO_2$. In Fig. 1*b*, two crystalline phases can already be seen—sphene and rutile TiO_2, with rutile crystals predominating; they have the characteristic shape of needles. The sizes of the crystals can be judged from the overall magnification (direct and photographic) at which the given electron microphotograph was obtained. The presented photographs for sphene and rutile are especially valuable because they were obtained for different initial glass compositions. The structure of the material, a microphotograph of whose fracture surface is given in Fig. 1*c*, is an aggregate of differently oriented

ribbon-like crystals. The phase composition of this material is very complex. Interpretation of the X-ray diffraction pattern makes it possible to suppose that the separated crystalline compound belongs to the class of amphiboles. In the course of this communication the possibility of identifying other crystalline phases will also be shown.

With the aid of electron-microscopic and X-ray investigations, the dependences of the structure and phase composition of the materials on a number of factors were studied. In the present communication we shall consider the influence of the following factors: crystallization temperature and the initial composition of the glass.

Figure 2a (see inset, p. 364) shows a microphotograph of the initial glass of composition 3P*. As can be seen, already in the initial glass there are zones of inhomogeneity of the order of 500 Å in diameter. According to X-ray analysis, at this stage a crystalline phase has not yet formed. On holding at a temperature of 820° for 1 hour and 850° for 1 hour, the number of inhomogeneity zones increases; they already occupy the entire field of view (Fig. 2b). There is still no crystalline phase. Increasing the holding time at 850° to 2 hours leads to an increase in the size of the microregions of inhomogeneity. With a further increase in temperature (820—1 hour, 850—2 hours, 950—1 hour, 1000—1 hour), crystallization of the material occurs, with the formation first of wollastonite, $CaO \cdot SiO_2$, and then gehlenite ($2CaOAl_2O_3SiO_2$). In Fig. 2c, crystals of definite shape are clearly visible; the size of the separating crystals ranges from tenths of a micron to 1 μ, and the material has a homogeneous close-packed structure.

Analogous structural changes are also characteristic of other glass compositions, in particular lithium compositions. Figure 3 (see inset, p. 364) clearly shows the changes occurring in the structure of the material as the temperature is raised from 830 to 1200°. At temperatures of 1000 (Fig. 3b) and 1200°, for this composition the principal crystalline phase is β-spodumene ($Li_2O \cdot Al_2O_3 \cdot 4SiO_2$) and solid solutions based on it. The characteristic form of the observed crystals is hexagonal plates, closely adjoining one another along an edge.

In the synthesis of new materials based on glass, special attention is paid to the study of the kinetics of crystallization. Of great interest here are the processes preceding crystallization, since heat treatment in the precrystallization period (in the region of relatively low temperatures, 600–800°) substantially changes the subsequent course of crystallization and exerts a significant influence on the properties of the material. There are several different points of view on the nature of the processes occurring in the precrystallization period. One of them, for example, is that the crystallization process is preceded by a process of liquation. And indeed, for certain glass compositions this hypothesis is confirmed. At the Department of Chemistry and Technology of Glass of our institute, studies were carried out on the influence of heat treatment in the precrystallization period, the results of which are reported in another article. These structural changes could be recorded with the aid of an electron microscope, since no crystalline compounds are yet formed.

A great influence on the phase composition of the crystallized material is exerted by changes in the initial composition of the glass. From this point of view, the separation of catalytic additives in the form of one or another crystalline phase is of considerable interest. Various compounds were used as catalytic additives. The introduction of fluorine-containing compounds in individual cases leads to the separation of metal fluorides, in particular calcium fluoride. For example, in materials obtained on the basis of slags, the principal phases are anorthite and fluorite. In the microphotograph one can see massive crystals of anorthite and, against their background, small crystals

* Materials of composition 3P were synthesized by graduate student Z. Zhitkevich.

CaF in the form of pyramids. In no case, when phosphoric anhydride was used as the catalytic additive, was the separation of phosphorus-containing crystalline phases observed. Microphotograph 2a shows the fracture surface of the initial glass containing 5% P_2O_5. The glass already tends toward phase separation. A content of 10% P_2O_5 in the initial glass composition leads to more pronounced phase separation of the glass. When TiO_2 is introduced as the catalytic additive, the separation of titanium-containing crystalline phases is observed, depending on the heat-treatment conditions: rutile, sphene, and magnesium and aluminum titanates. It is believed that the role of titanium in glass is determined by the alkali content. For compositions containing 10–15% TiO_2 and the same amount of alkalis, the liquation process predominates over the crystallization process. The main crystalline phase of such materials proves to be titanium-containing compounds, for example sphene. Heat treatment at temperatures up to 800° inclusive leads to strong phase separation of the glass (the size of the droplet-like liquation regions reaches one micron). The material is completely opaque and in appearance does not differ from a crystallized one.

In conclusion, it should be noted that the application of electron-microscopic and X-ray analysis methods provides extremely valuable information on the structure of new glass-crystalline materials, makes it possible to study the ki-

netics of their crystallization, and to trace the composition–structure–property relationship.

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