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## Abstract

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# ON THE ROLE OF TITANIUM DIOXIDE IN THE FORMATION OF THE STRUCTURE OF A GLASS-CRYSTALLINE MATERIAL

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The present communication is devoted to the study of the crystallization of glasses in the system $Li_2O$–$Al_2O_3$–$SiO_2$–$TiO_2$. In work ([1]) it was suggested that the centers of crystallization in glasses nucleated by titanium dioxide are rutile in the form of submicroscopic particles; however, in communication ([2]) it was shown that in glasses of analogous compositions no structural groups characteristic of rutile, ($TiO_6$), are observed. It was also suggested that the centers of crystallization in $Li_2O$–$Al_2O_3$–$SiO_2$–$TiO_2$ glasses are structural defects associated with the incorporation of titanium into the structure of the glass ([3]).

To investigate the crystallization properties of the glasses, a series of compositions was melted, listed in Table 1; the same table gives the results of the study of crystallization ability obtained by the polythermal method. In the absence of titanium, or when its amount is insufficient for bulk crystallization (glasses Nos. 48′, 48, 51′, 51, 53′, 53), crystallization begins from the surface. It is characteristic that the crystallization temperature depends only weakly on the presence or absence of titanium dioxide in the glass.

### Table 1

*Compositions of the glasses studied, the character of their crystallization ability, and the composition of residues after crystallization of the spodumene*

| Glass No. | Composition of starting glasses, mol. %: $SiO_2$ | Composition of starting glasses, mol. %: $Al_2O_3$ | Composition of starting glasses, mol. %: $LiO_2$ | Composition of starting glasses, mol. %: $TiO_2$ over 100% | $[Al_2O_3]^*$ | $[Al_2O_3]^*/[TiO_2]$ | Composition of residue after crystallization of spodumene, wt. %: $SiO_2$ | Composition of residue after crystallization of spodumene, wt. %: $Al_2O_3$ | Composition of residue after crystallization of spodumene, wt. %: $TiO_2$ | After crystallization of residue | Character of glass crystallization |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 48′ | 68 | 17 | 15 | – | 2.0 | | | | | | Surface |
| 48 | 68 | 17 | 15 | 1.0 | 2.0 | 2.0 | 64.0 | 25.6 | 10.2 | Mullite | Surface |
| 49 | 68 | 17 | 15 | 2.5 | 2.0 | 0.8 | 53.7 | 21.0 | 25.3 | Aluminum titanate | Bulk |
| 50 | 68 | 17 | 15 | 5.0 | 2.0 | 0.4 | 53.0 | 15.6 | 31.3 | Rutile | Bulk |
| 51′ | 72 | 17 | 11 | – | 6.0 | | | | | | Surface |
| 51 | 72 | 17 | 11 | 2.5 | 6.0 | 2.4 | 69.5 | 23.2 | 7.3 | Mullite | Surface |
| 52 | 72 | 17 | 11 | 10.0 | 6.0 | 0.6 | 58.0 | 18.0 | 24.0 | Aluminum titanate | Bulk |
| 53′ | 66 | 19 | 15 | – | 4.0 | | | | | | Surface |
| 53 | 66 | 19 | 15 | 2.5 | 4.0 | 1.6 | 39.1 | 41.9 | 20.0 | Mullite | Surface |
| 54 | 66 | 19 | 15 | 5.0 | 4.0 | 0.8 | 31.2 | 35.0 | 33.8 | Aluminum titanate | Bulk |
| 65′ | 72 | 13 | 15 | – | – | | | | | (Rutile, lithium titanate) | Coarsely crystalline |
| 65 | 72 | 13 | 15 | 5.0 | – | | | | | | |

**Note.** $[Al_2O_3]^* = [Al_2O_3] - [R_2O]$.

During crystallization of compositions 49, 52, 54, the following regions can be identified: 1) unchanged glass; 2) glass with precrystallization changes; 3) transparent microcrystalline material; 4) opaque microcrystalline material; 5) melt.

In the 1st and 2nd regions the material is amorphous, as shown by the conchoidal fracture of the specimens. In the precrystallization period the material intensely

Fig. 1. Position of glass residues on the $TiO_2$–$SiO_2$–$Al_2O_3$ diagram

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no. In the temperature region for the formation of a transparent glass-ceramic material, the specimens do not have a conchoidal fracture, their color changes, and they crack severely. In the region of comparatively high temperatures, the microcrystalline material changes from transparent to opaque.

In discussing the results obtained, it is necessary to take into account that the glasses investigated, which do not contain titanium dioxide, lie in the crystallization fields of spodumene, eucryptite, and their solid solutions. The phase relationships in these regions have been studied previously (4-8).

It is possible to attempt to determine the composition of the crystalline phase bordering on spodumene, eucryptite, or their solid solutions in the case of glasses with titanium dioxide as follows. Let us suppose that, in the final microcrystalline product, spodumene separates as the principal phase (in the case of separation of solid solutions of eucryptite, the reasoning is analogous). To construct a spodumene molecule, the following are required: one molecule of lithium oxide, one molecule of aluminum oxide, and four molecules of silica. The glass residue will not contain lithium, and titanium dioxide will be added. The calculation of the compositions of the residues is given in Table 1. The data for the $TiO_2$ –$SiO_2$–$Al_2O_3$ system are taken from work (9). Figure 1 shows the position of the compositions on this diagram. The arrangement of the compositions obeys a clear regularity. The compositions of the glass residues that yield a transparent microcrystalline material lie in the crystallization field of the compound $Al_2O_3 \cdot TiO_2$; those crystallizing from the surface lie in the crystallization field of mullite.

**Fig. 1.** Position of glass residues on the $TiO_2$–$SiO_2$–$Al_2O_3$ diagram

It is of interest that, in glasses where $[Al_2O_3]^*/[TiO_2] < 1$, where $[Al_2O_3]^*$ is the concentration of aluminum oxide present in the position of $(AlO_6)$ units, the characteristic change in coloration inherent in the iron–titanium complex (10) is observed, and only such glasses can be transformed into a transparent polycrystalline material.

The behavior of titanium in the glasses investigated can be described as follows. Aluminum oxide in glass, according to modern concepts, may occur in the form of $(AlO_4)$ and $(AlO_6)$ units. For the formation of $(AlO_4)$ tetrahedra, additional oxygen is required, which can be obtained from lithium oxide. The excess aluminum oxide not associated with lithium oxide is present in the position of $(AlO_6)$ units; such a picture is apparently also observed in our glasses. When titanium dioxide is added to such a glass, titanium tends to complete its coordination sphere with six oxygen atoms at the expense of oxygen atoms of the

Fig. 2. Proposed form of the quaternary diagram $Li_2O$—$Al_2O_3$—$SiO_2$—$TiO_2$ in the region of low $TiO_2$ concentrations

Figure 2: Fig. 2. Proposed form of the quaternary diagram $Li_2O$—$Al_2O_3$—$SiO_2$—$TiO_2$ in the region of low $TiO_2$ concentrations

$(AlO_6)$ octahedra; the resulting structure $Al_2O_3 \cdot TiO_2$ (of the pseudobrookite type) contains $(TiO_6)$, $(AlO_6)$ units and the $(AlO_4)$ units linking them (11). According to thermodynamic calculations carried out by A. S. Berezhnoi (12), the compound is stable at a temperature of 1500°. It may be assumed that it separates in the form of submicroscopic liquation droplets in the low-temperature region and is the future center for the onset of crystallization.

When titanium dioxide is introduced into the glass in excess of the amount of aluminum oxide in octahedral coordination, a process of incorporation of titanium into the network of spodumene composition is indicated, with the formation of $(TiO_4)$ units. This position of titanium corresponds to a metastable equilibrium established at the high melting temperatures. On heating the glass, titanium tends to decrease the oxygen deficit, in particular at the expense of $(FeO_6)$ units,

and the reaction $(TiO_4) + (FeO_6) \rightarrow (FeO_4) + (TiO_6)$ proceeds, which leads to darkening in the precrystallization period [13].

At the sites where $(TiO_4)$ is introduced, the local dielectric permittivity $\varepsilon$ increases greatly, which leads to a weakening of the interaction between polar structural groupings, i.e., to a decrease in the autosolvation effect [14]. Polar groupings in the precrystallization period will be broken up even more strongly, thereby facilitating their further ordering. The $(TiO_4)$ units, as it were, "warm up" the aluminosilicate structure, bringing it closer to the future polycrystalline one.

**Fig. 2.** Proposed form of the quaternary diagram $Li_2O$—$Al_2O_3$—$SiO_2$—$TiO_2$ in the region of low $TiO_2$ concentrations

A further increase in the concentration of titanium dioxide in the glass may lead to titanium beginning to reduce the oxygen deficiency at the expense of the $TiO_2$ molecule. This will lead to the separation of rutile already during cooling, and the principal phase crystallizes on the rutile particles; such a phenomenon is observed, apparently, in glass No. 50. In the absence of $(AlO_6)$ units as crystallization centers, lithium titanates may possibly separate, and crystallization proceeds spontaneously during cooling, with the formation of a comparatively coarse structure.

The proposed form of the system $Li_2O$—$Al_2O_3$—$SiO_2$—$TiO_2$ in the region of low titanium dioxide concentration is shown in Fig. 2. According to the work [15], the line of formation of structural units $(AlO_6)$ does not coincide with the line $SiO_2$—$Li_2O$—$Al_2O_3$, but occupies some position $XY$. The glasses studied lie in the hatched region of the diagram. In the quaternary system, the region of mullite separation is bounded by the side $SiO_2$—$Al_2O_3$, and also by the curves $M_1M_2M_3$ and $K_1K_2KK_3$. The regions of separation of spodumene, eucryptite, and their solid solutions are bounded on one side by the surface $K_1K_2K_3M_3M_2M_1$; on the other side it is intersected by the surface $N_1N_2N_3M_3M_2M_1$, which, in our opinion, is the boundary surface separating one-phase and two-phase systems. Above the surface $N_1N_2N_3M_3M_2M_1$ the melt system is two-phase; moreover, it is possible that the completion of the liquation process occurs in the precrystallization period, i.e., the liquation is partly latent in character.

On the basis of the foregoing, the nucleation process by titanium dioxide may ...

can be described as follows. The compounds $Al_2O_3 \cdot TiO_2$ formed at high temperature separate out on cooling in the form of submicroscopic liquation products. In the temperature region of the precrystallization period, liquation is completed and the $Al_2O_3 \cdot TiO_2$ liquation products crystallize. At the same time, the aluminosilicate structure is fragmented by $(TiO_4)$ nodes. It is possible that the number of $Al_2O_3 \cdot TiO_2$ particles is considerably smaller than the number of aluminosilicate crystallites. The separation of new crystallites takes place on those that had separated earlier.

The dual role of titanium dioxide in the formation of the structure of transparent glass-ceramic materials indicates that this process is not ordinary, generally accepted heterogeneous crystallization. The mechanism of formation of such a structure may be called submicroscopic polymerization.

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