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Abstract

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INVESTIGATION OF THE PROCESS OF CATALYZED CRYSTALLIZATION BY THE METHOD OF RAMAN LIGHT-SCATTERING SPECTRA

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The objects of the investigation carried out were samples of a complex glass-forming system having the composition of spodumene with a small addition of titanium dioxide.* This oxide is usually assigned an important role in the formation, from samples of the indicated system under the influence of heat treatment, of a new material with specific properties (^{1}). An attempt to elucidate this role was the aim of the work. The spectra were interpreted on the basis of an earlier investigation, in which it was established that the characteristic bands for structures formed by the combination of titanium-oxygen octahedra lie in the frequency region $\sim$ 600–630 cm^{-1}, and those of titanium-oxygen tetrahedra in the frequency region $\sim$ 875–960 cm^{-1} ($^{2-6}$). The main experimental material is presented in Fig. 1 in the form of spectra pertaining to samples of the initial glass that had undergone various heat treatments.

Spectrum 1 of the initial glass very much resembles the spectra obtained earlier from normal three-component silicate glasses with a small amount of TiO_2 (^{2}). As before, the presence of TiO_2 is manifested in the band $\sim$ 900 cm^{-1}. On the high-frequency side there adjoins it a band of approximately the same intensity, which is undoubtedly connected with vibrations of the aluminosilicate framework. This is indicated by the analogy with the spectra of two-component silicate glasses.

Prolonged holding of the sample at a temperature of 600° led to a certain relative weakening of the bands under consideration (spectrum 2). Further heat treatment of the sample, carried out at ever higher temperatures, weakens these bands still more; ultimately they practically disappear entirely in spectrum 4. At the same time, other interesting details are also observed. First, at $\sim$ 600 cm^{-1} a rather broad band is traced more and more distinctly; second, a fine structure is indicated in the band $\sim$ 500 cm^{-1}; third, a weak band appears in the region $\sim$ 220 cm^{-1}; finally, fourth, an intense band appears in the region of low frequencies (120 cm^{-1}).

Spectrum 5 in Fig. 1 pertains to a sample that had completely undergone

Fig. 1. Raman spectra of the samples studied. 1 —initial sample; 2, 3, 4 —samples heated, respectively, to 600, 630, and 660°; 5 —sample that has fully undergone heat treatment; in the last case the spectrum was recorded at two amplification settings

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heat treatment, as a result of which it acquired a number of new macroscopic properties. As can be seen, its spectrum is a set of more or less narrow lines and bands. In the region of internal vibrations (approximately from 200 cm^{-1} and above) it is very similar to the spectra of crystals with octahedral coordination of titanium (2–6). The fact deserves special attention that the line in the low-frequency region becomes extremely narrow and intense. It is also interesting that the weak band ~ 220 cm^{-1} is not manifested in the spectrum of the sample under consideration. Consequently, there is no monotonicity in the structural changes of the sample as its heat treatment is intensified.

The behavior of the Raman spectra of the samples studied admits the following preliminary interpretation.

Since, when the sample is heated, the spectra show a systematic weakening of the band at ~ 900 cm^{-1}, which is assigned to vibrations of linked TiO_4 tetrahedra, and at the same time a band appears at ~ 600 cm^{-1}, characterizing vibrations of TiO_6 octahedra, one may draw the convincing conclusion that titanium gradually passes from tetrahedral to octahedral coordination. This structural rearrangement is completed after prolonged heat treatment of the sample at a temperature near 660°, as evidenced by the practically complete disappearance of the high-frequency band. At the same time, the appearance of these bands does not change: they remain, as before, broad, which is highly characteristic of the glassy state of a substance. On this basis it may be asserted that, in the bulk of the sample at this stage of heat treatment, crystallites—understood as geometrically ordered regions of definite composition—are absent.

In connection with the foregoing, the question arises: do glassy bodies built of octahedra linked to one another exist at all? As Brady showed by the X-ray method, a two-component tellurite glass has such a structure (7). However, the TeO_6 octahedra in this glass, in contrast to crystalline TeO_2, are connected mainly by corners, which provides flexibility of its structural network—the condition for vitrification of the substance. It may be assumed that the glassy titanium-containing phase also has an analogous structure.

* The melting technology and heat-treatment regimes of the samples were developed by E. V. Podushko. The author expresses gratitude to E. V. Podushko for providing the samples for the investigation.

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If this is so, then the transfer of titanium in the glass to octahedral coordination requires a source of oxygen ions. It is not excluded that such a source is

lithium oxide passing into the titanium-containing structural network; or a small part of aluminum oxide, in which the aluminum was initially in an octahedral oxygen environment and, under the influence of heat treatment, changed its coordination to tetrahedral. Both assumptions agree with the fact that the highest-frequency band itself is weakened, although the latter contradicts the generally accepted idea that oxygen ions are released, on the contrary, when the coordination number of aluminum increases. However, it must not be forgotten that the donor-acceptor properties of different compounds with respect to oxygen are determined entirely by the character of their initial and final structures.

Thus, from analysis of the Raman spectra two possible mechanisms emerge for the formation of a glasslike titanium-containing structural network: one based on the participation of Li_2O as a modifier, the other on that of a small part of Al_2O_3. The simultaneous action of both mechanisms is not excluded.

The formation of a comparatively unstable two-phase glasslike system completes the first stage of the process. Further heating of the sample, apparently, first of all causes the removal from the titanium-containing network of alumino-oxygen and lithium-oxygen radicals. The TiO_6 octahedra are partially joined by edges. This means nothing other than the ordering of their geometric arrangement. Crystallites are formed that are entirely analogous to rutile or are of more complex composition. These crystallites, or the liberated alumino- and lithium-oxygen radicals (most likely joined together in the form of crystals of submicroscopic dimensions), become crystallization centers initiating the subsequent process. Intensive crystallization of the main part of the glasslike phase, approximately having the composition of spodumene, begins. This second stage of crystallization of the substance is expressed in a sharp narrowing of the spectral lines, which is precisely an inalienable property of Raman spectra in crystalline bodies.

Noteworthy here is the disappearance of the weak band at ~ 220 cm^{-1}. It should probably be correctly assigned to deformation vibrations of the lattice. Ordering of the latter should have the strongest effect precisely on such vibrations. Moreover, it is obvious that when octahedra are joined predominantly by corners, there are more degrees of freedom for various deformation vibrations. Therefore the fact under discussion—the disappearance of the band at ~ 220 cm^{-1}—may serve as an additional argument in favor of the point of view put forward.

Let us note, in conclusion, that the appearance in the spectrum of a sample that has undergone complete heat treatment of a very intense and narrow line in the low-frequency region is not yet amenable to interpretation. Indeed, in the spectra of rutile ([5]) and powdered TiO_2 there is no such line. Its presence in the spectra of more complex titanium-containing crystals, in which titanium can in principle segregate, is unlikely. The attribution of this line to vibrations of crystallizing spodumene is also doubtful, although such a possibility cannot be completely rejected; thus the question of the origin of the line under consideration remains open. It is possible that the small sizes of the crystals are responsible for its appearance. The narrowness of the lines may mean that the crystal sizes have not reached the critical dimensions at which the lines begin to broaden.

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