LAWS OF FORMATION OF THE STRUCTURE AND PROPERTIES OF PYROCERAMIC OF A LITHIUM ALUMOSILICATE COMPOSITION IN THE PROCESS OF THERMAL TREATMENT

E. I. Suzdal'tsev   UDC 666.3.01

This paper considers the laws of formation of the structure and properties of a material in the process of thermal treatment of glass blanks of a lithium alumosilicate composition. The trends for change in the basic properties of materials under thermal treatment in the 700–1200°C temperature range have been determined. The results obtained permit a purposeful approach to the synthesis of a pyroceramic with specified properties.

The purpose of thermal treatment is to transform the source glass into a microcrystalline ceramic. The process of thermal treatment is a critically important stage in the production of pyroceramics which should be thoroughly controlled to guarantee the formation of the desired crystals in the required quantities. The authors of a number of works devoted to the synthesis of pyroceramics note the necessity for the formation of a fine-grained microstructure containing as many small crystals as possible, which provides the realization of high physicotechnical properties of the material [1]. The expedience of obtaining a fine-crystal structure of a material calls for thorough control of the proceeding of the nucleation stage of thermal treatment. After the appearance in the glass of nuclei, it is necessary to increase the temperature in the furnace in order to create the conditions for crystal growth on them. The most general idea about different stages of thermal treatment is given in Fig. 1, where an idealized regime of annealing pyroceramics is depicted [1].

The first stage includes heating of the glass from room temperature to temperature *A* at which nuclei are formed. The heating rate at this stage is not critical for crystallization. Limits on this rate are imposed by the prohibition of the appearance of dangerously high thermal stresses capable of leading to the cracking of articles. The recommended heating rate at this stage is within the limits of 100–300°C/h. In the first approximation, it is thought that the nucleation temperature is between the dilatometric softening point of the source glass and a temperature 50°C higher than it. According to the literature data, the duration of holding glass at the nucleation temperature is normally 0.5–2.0 h [2–4]. After the nucleation stage the glass is heated to the upper crystallization temperature *B*, which is chosen so that crystallization with the maximum rate but without the prohibitive deformation of the material is attained. The rate of crystallization grows rapidly as its upper temperature is approached, but, to prevent deformation of the material at earlier stages where the glassy phase prevails, the heating rate usually does not exceed 300°C/h. The limiting temperature of crystallization is set lower by 25–50°C than the temperature at which a deformation of the material is noted and at which the crystalline phase formed is capable of dissolving again. The upper crystallization temperature *B* (Fig. 1) is maintained for at least 1 h. Holding the material at the upper crystallization temperature for a certain time, it is possible to achieve practically complete crystallization, making the fraction of the residual glassy phase very insignificant. On completion of the holding the material is cooled. This process can be carried out fairly rapidly (up to 600°C/h), since pyroceramics withstand large temperature gradients owing to their high mechanical strength and low thermal linear expansion coefficient (TLEC). As opposed to glasses, pyroceramics do not require annealing for preventing the appearance of residual stresses. The superiority of glass ceramics in this respect can be explained by the very small size of the crystals in them due to which the stresses caused by volume changes remain insignificant.

However, these theoretical ideas about the order of conducting thermal treatment of glass ceramics should be made specific for each particular composition by carrying out a complex of investigations. In this respect, using vari-
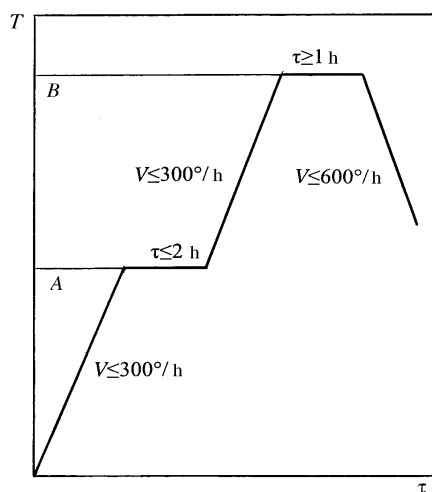
Fig. 1. Theoretical regime of thermal treatment of source glasses for obtaining pyroceramics; *A*, nucleation temperature; *B*, upper crystallization temperature. *T*, °C.
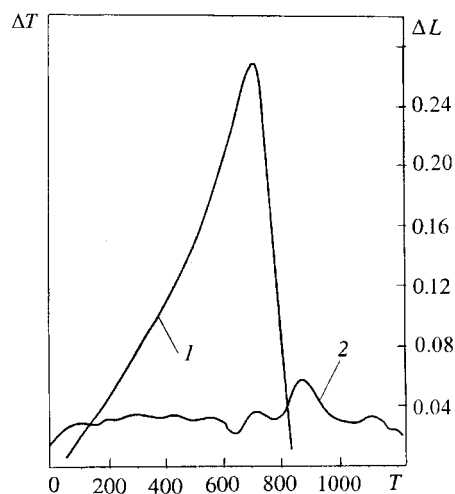
Fig. 2. The dependence of the relative expansion (1) and the curve of differential thermal analysis (2) of lithium alumosilicate glass. ΔL, %; *T*, °C.

ous methods of investigations, it is expedient to see how controlled crystallization changes the properties of the source glass throughout the stage of thermal treatment.

In particular, we used standard methods, devices, and units to determine the ceramic indices (shrinkage, density, porosity, and water absorption). The differential thermal analysis of the samples of materials was performed on an OD-102 derivatograph; the TLEC and the deformation temperature (T_d) were determined on dilatometers of the type DKV-5A and -804; x-ray phase analysis of material samples was carried out on a DRON-2.0 diffractometer; petrographic studies of the materials were made on electron and binocular microscopes JSM-35CF and MFS-200, respectively; the dielectric properties were determined on a high-temperature dielectrometer "Kvarts," the strength properties — on a 9024 DP 1000/1500 type unit and a P-0.5 tension testing machine; the microhardness was measured on a PMT-3 type microhardness meter.

In our investigations, we used lithium alumosilicate glass used for obtaining pyroceramics of a β-spodumene composition. Pyroceramics of this class are widely used to manufacture articles with a low thermal linear expansion coefficient in various fields of science and technology. However, there is a lack of systematic investigations on the influence of thermal treatment conditions on the formation of the structure and phase composition of synthesized pyroceramics of this class. The need for investigations in this direction is also associated with the synthesis of glass ceramics of a β-spodumene composition where a better understanding of the processes proceeding in glasses under thermal treatment makes it possible to optimize the technology for manufacturing articles from glass ceramics.

In the present work, we used lithium alumosilicate glass of the following chemical composition (%): SiO_2 = 64–66, Al_2O_3 = 24–26, TiO_2 = 4.0–4.5, and LiO_2 = 3.5–4.0.

We determined the dilatometric softening temperature of the source lithium alumosilicate glass, which is 740°C, and performed a differential thermal analysis of the glass specimen (Fig. 2). Since the structural transformations in the substance at its crystallization are attended by heat release, the differential thermal analysis (DTA) makes it possible to refine the phase transformations in the source glass at high temperatures and establish clear temperature ranges in which crystals are formed. Analysis of the DTA curve (Fig. 2) shows that with increasing temperature a not clearly defined descending portion is noticeable on it. This portion is due to the insignificant absorption of heat as the temperature approaches the glass annealing temperature (~600°C). Then exothermal peaks that are due to the formation of various crystalline phases (temperature of 750, 900, and 1100°C) follow. By the data of the DTA curves we can relate the exothermal peaks to the crystallization of different phases and determine more exactly the nucleation temperature.
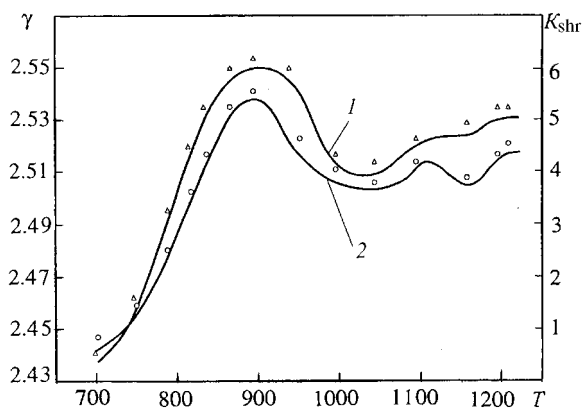
Fig. 3. Behavior of the density (1) and volume shrinkage (2) of lithium alumosilicate glass under thermal treatment in the 700–1200°C range with its holding at final temperatures for 2 h. γ, g/cm^2; K_{shr}, %; T, °C.
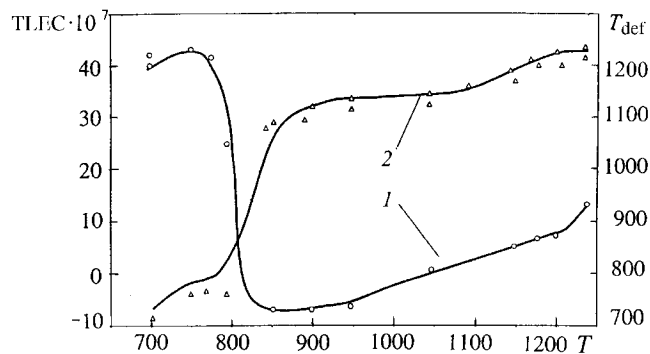
Fig. 4. Behavior of the TLEC mean values in the 20–600°C range (1) and deformation temperature (2) of lithium alumosilicate glass under thermal treatment in the 700–1225°C range with its holding at final temperatures for 2 h. TLEC, deg^{-1}; T_d, °C; T, °C.

In synthesizing glass ceramics, it is expedient to follow the dynamics of changes in the physical and structural properties of the source glass throughout the temperature range of directional crystallization, which would provide the possibility of choosing the optimum conditions for thermal treatment.

To this end, the specimens of the source lithium alumosilicate glass were subjected to thermal treatment at temperatures from 600 to 1225°C with 25 to 50°C intervals, were held at the final temperatures for 2 h and then sharply cooled in order to "freeze" the structure of the material at the given temperature point. Then from annealed glass blanks the required specimens for the investigations were made.

It has been found that thermal treatment causes a change in the glass color from transparent to opaque. Turbidity and the formation of a light-brown color of the glass come to light from temperatures of 750–800°C. Then, as the temperature is increased, the glass takes on a cloudy color, and from thermal-treatment temperatures of 1000°C or higher the glass takes on a light-beige color and loses transparency, which is due to the light scattering by the surfaces between the crystals as well as between the crystals and the residual glassy phase because of the values of the refractive indices of different phases.

It has also been found that the density of the source glass undergoes considerable changes in the process of thermal treatment. They are reduced basically to a decrease in the sizes of specimens with their weight constant (Fig. 3). The maximum volume changes under thermal treatment of the source glass were 5.5% (Fig. 3). It is noteworthy that the changes in the volume of the specimens have a pronounced cyclic character and the volume shrinkage curve has three prominent maxima differing in magnitude by more than 1%. We suggest that these volume changes in the glass under its thermal treatment result from the different specific weights of the crystalline phases formed, which appear to be denser than the source glass, and the crystallization thereby is accompanied by compression of the material. In different temperature ranges, the ratio between the phases formed (β-quartz, corundum, petalite, aluminum titanate, β-spodumene, rutile, and a whole number of solid solutions) becomes different, which determines the complex character of change in the density and volume shrinkage under thermal treatment of the source glass. To support this conclusion, Figure 4 shows the change in the TLEC of the source-glass specimens heat-treated in the 700–1200°C range. As to the absolute value of the TLEC of the specimens measured in the 20–600°C range, there are apparent differences from the TLEC values of the source-glass specimens. X-ray phase analysis shows that in the range of glass annealing temperatures from 700 to 750°C β-quartz, causing an increase in the source glass TLEC, is formed. Then, as the temperature is increased (the 775–850°C range), aluminum titanate and β-eucryptide appear in the glass, causing a sharp decrease in the TLEC. Then, with further increase in the temperature β-spodumene is formed, causing a slight increase in the TLEC of the specimens in the 850–1150°C range; but in the same range there is also a certain amount
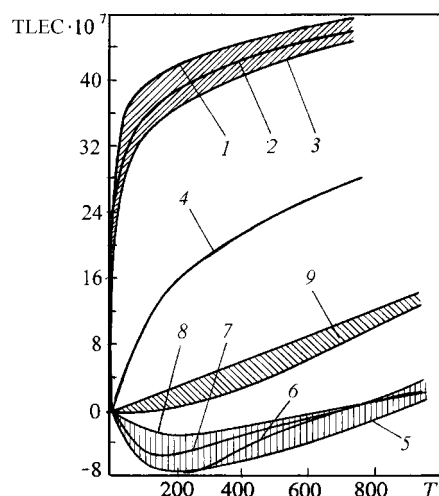
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Fig. 5. Temperature dependence of the TLEC of lithium alumosilicate glass specimens heat-treated at various temperatures with their holding for 2 h: 1, 2, 3, 4, 5, 6, 7, 8) heat-treatment temperatures of 700, 750, 775, 800, 850, 900, 950, and 1000°C respectively, 9) 1100–1200°C temperature range. TLEC, $\deg^{-1}$; T, °C.

TABLE 1. Densities and TLECs of the Main Crystalline Phases Entering into the Composition of Pyroceramics of the β-Spodumene Series

Crystalline phase	Density, g/cm^3	TLEC·10^7, deg^{-1}
β-spodumene (Li$_2$O.Al$_2$O$_3$.4SiO$_2$)	2.38	9 (20–1000°C)
β-eukryptite (Li$_2$O.Al$_2$O$_3$.2SiO$_2$)	2.67	–64 (20–1000°C)
Aluminum titanate (Al$_2$O$_3$.TiO$_2$)	3.62	–19 (20–1000°C)
Rutile (α-TiO$_2$)	4.23	78 (20–1000°C)
Lithium disilicate (Li$_2$O.2SiO$_2$)	2.45	110 (20–600°C)
Corundum (α-Al$_2$O$_3$)	4.00	86 (20–1000°C)
Quartz (SiO$_2$)	2.65	237 (20–600°C)
Cristobalite (SiO$_2$)	2.32	271 (20–600°C)
Petalite (Li$_2$O.Al$_2$O$_3$.8SiO$_2$)	2.42	3 (20–1200°C)

of other phases, and we observe their resultant action. Thermal treatment of the glass in the 1175–1200°C range leads to the formation of the maximum amount of β-spodumene, and at a temperature of 1225°C dissolution of the β-spodumene crystals is most likely to begin, which leads to an increase in the content of the glassy phase and, as a result, to an increase in the TLEC values of the specimens (Fig. 5).

This conclusion is supported by the density and TLEC values of different crystalline phases entering into the composition of glass-ceramics based on lithium alumosilicate glasses (see Table 1).

It should be noted that different chemical compositions of source glasses and different conditions of their thermal treatment in synthesing pyroceramics can lead to the presence of both the whole spectrum of the crystalline phases given in Table 1 and of only some of them. Moreover, under real conditions of glass-ceramic synthesis, as a rule, compounds of particular solid solutions and the presence of the residual glassy phase at the boundaries of crystals (though in small quantities) take place. Therefore, the results presented in Table 1 can only serve as indirect evidence of the formation of particular phases in the synthesis of pyroceramics.

The investigation of the temperature dependences of the TLEC of heat-treated specimens has shown that the selection of a particular regime of thermal treatment of the source glass makes it possible to synthesize a material with
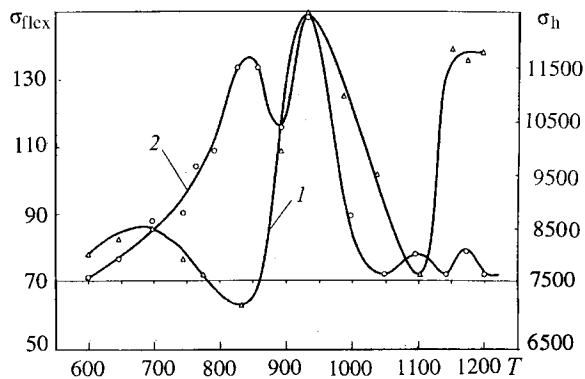
Fig. 6. Behavior of the flexural strength (1) and microhardness (2) of lithium alumosilicate glass under heat treatment in the 600–1200°C range. σ_{flex}, MPa; σ_h, MPa; T, °C.
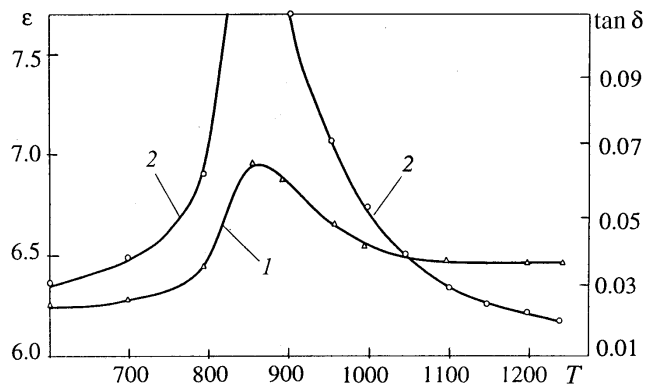
Fig. 7. Behavior of the permittivity (1) and dielectric loss tangent (2) of lithium alumosilicate glass in the 600–1200° range with its holding at final temperatures for 2 h. T, °C.

a wide spectrum of TLEC values. For instance, thermal treatment of the source glass in the 700–800°C range permits obtaining a material with fairly high TLEC values, thermal treatment in the 850–1000°C range enables one to obtain materials with negative TLEC values, and the same process at 1100–1200°C makes it possible to obtain materials with low TLEC values (Fig. 5). These results are important and useful, because they permit a purposeful approach to the synthesis of a material with given properties.

Another characteristic feature of the change in the physical characteristics under thermal treatment of the source glass in the 700–1225°C range is an increase in the refractoriness of the material (Fig. 4). In this case, the maximum increase in the deformation temperature is exhibited by glass specimens heat-treated at temperatures above 850°C, where rather low TLEC values of the material and the formation of a structure of the β-spodumene series are noted.

A spectacular proof of the relationship between the physical properties of the source glass and the heat-treatment temperature is provided by the changes in the strength and dielectric characteristics.

Considerable interest is attracted by the striking difference in the character of changes in the flexural strength and microhardness at the final stage of glass crystallization, where the strength sharply increases as the formation of the crystalline structure of the material approaches its final stage while the microhardness remains unaltered at the level of the source-glass values. There has been no conclusive explanation of these data so far, but it may be suggested that they are associated with a particular structure of the material that has formed, since analogous effects have also been observed at other temperatures of heat treatment. For example, at 850°C the strength decreases and the microhardness increases, at 900°C the strength increases and the microhardness decreases, and at 950°C the maximum values of both the strength and the microhardness are observed (Fig. 6).

An increase in the amount of the crystalline phase in the source glass with increasing heat-treatment temperature and the formation of a stronger ionic bond within a perfect crystal lattice lead to an increase in the permittivity values (Fig. 7). However, in the region of 900°C there is a fairly sharp increase in tan δ, which is due to the formation in the structure of the material of β-eucryptite having a higher density and higher dielectric characteristics.

To refine the temperature ranges of nucleation and of the final stage of crystallization, we used the methods of electron microscopy and x-ray phase analysis. However, they have certain limitations. X-ray phase analysis reveals the presence of the crystalline phase in the material when its content is no less than 2% and the minimum size of the crystals exceeds 0.2 μm. The use of scanning electron microscopy makes it possible to detect crystallization centers of very small size, but this method permits obtaining only a number of photographs of the structure of the material and, as x-ray phase analysis, does not provide continuous recording of the changes taking place, thus excluding the possibility of observing the formation of particular individual nuclei and the evolution of the crystal growth on them. Nevertheless, both methods, together with the results of the investigation of the physical properties of the material, provide
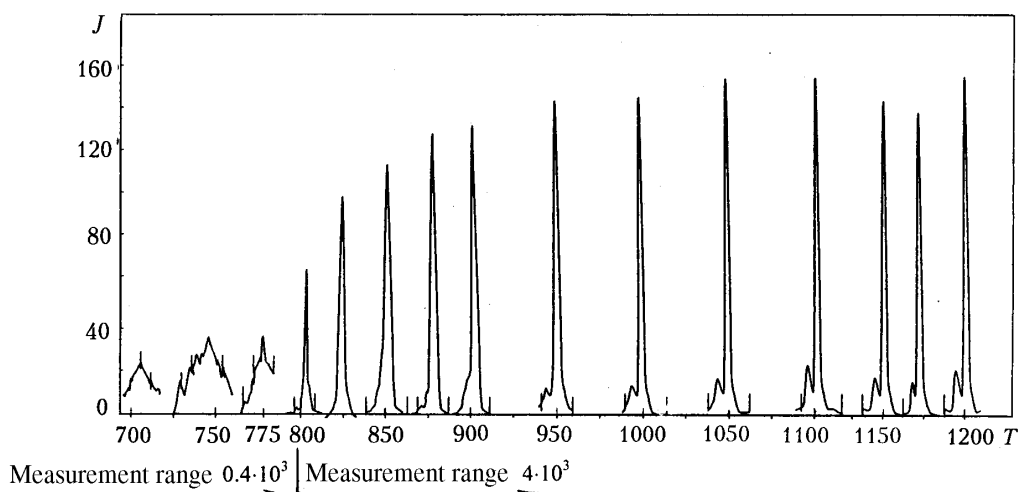
Fig. 8. Behavior of the 100% line of β-spodumene of lithium alumosilicate glass depending on the heat-treatment temperature (duration of holding at final temperatures — 2 h). *J*, mm; *T*, °C.

the possibility of obtaining valuable information in synthesing the material and explaining the processes proceeding under thermal treatment.

It is known that a crystalline substance appears in x-ray photographs as clear diffraction spectra which can be used to identify crystalline phases by comparison with standard values. In our case, the presence of crystalline phases in the material under thermal treatment in the 600–1225°C range was determined on a DRON-2 diffractometer. It has been found that the glass specimens heat-treated to temperatures of 750°C contain no crystalline phase. Then, beginning with a heat-treatment temperature of 775–800°C, in the specimens there is a clear increase in the content of β-spodumene in the form of a solid solution and traces of β-quartz are possible (Fig. 8). At a heat-treatment temperature of 950–1000°C the β-spodumene line intensity reaches its maximum value and with increasing temperature only a more clearly defined formation of crystals proper takes place. X-ray phase analysis under these conditions of thermal treatment reveals the presence in the material of rutile, aluminum titanate, petalite, and corundum. It is noteworthy that as the temperature is increased to 1200°C, the peaks of rutile and corundum somewhat increase and those of aluminum titanate and petalite decrease.

In performing the electron-microscopic analysis of heat-treated specimens, the metallographic sections were subjected to etching in a 3% solution of hydrofluoric acid in order to reveal the grain boundaries and make more prominent the structure of the material, since different crystalline phases and the residual glassy phase are etched at different rates. Specimens with a large content of the crystalline phase were subjected to longer etching for revealing the crystal boundaries. Thermal treatment of the source glass specimens at various temperatures enabled us to follow the dynamics of nucleation of crystalline phases and crystal growth (Fig. 9).

In thermal treatment at 700°C, homogeneous formation of the crystalline phase throughout the bulk of the specimen is observed. The crystalline phase shows up in the form of spherical particles with smeared boundaries and sizes of 800–1000 Å (in the photographs they are located against a gray background). There are also larger crystals with sizes up to 0.1–0.2 μm forming in some places a kind of aggregate, which is most likely a consequence of the source-glass inhomogeneity. The x-ray phase analysis revealed no crystalline phases.

Thermal treatment at 750°C causes an increase in the great bulk of the crystals up to 0.1–0.2 μm. The volume fraction of 0.3 μm crystals increases and individual crystals with a size of 1.0 μm appear. The x-ray phase analysis revealed the presence in the specimens of traces of β-spodumene. The 100% line of β-spodumene has a low intensity because of the imperfect shape of the crystals and their small size. We did not manage to reveal other crystalline phases.

Thermal treatment at 775°C did not reveal any special differences in the microstructure formation or in the sizes and shapes of the crystals and their position from the structure of the specimens annealed at 750°C. The x-ray phase analysis revealed an insignificant content of β-spodumene in the glass specimens.
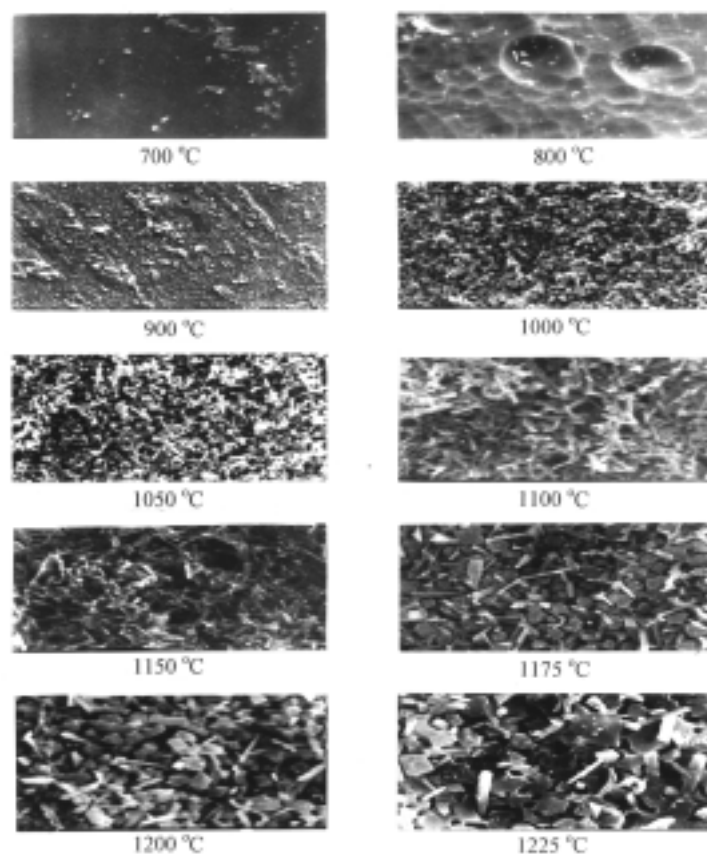
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Fig. 9. Changes in the structure of lithium alumosilicate glass under thermal treatment in the 700–1225°C range with its holding at final temperatures for 2 h.

Thermal treatment at 800°C leads to the layering of the glass. Inside individual "droplets," an intense growth of crystals up to 0.3 μm is observed. Besides the main crystalline phase of β-spodumene, the x-ray phase analysis revealed the presence of aluminum titanate and β-quartz in the form of solid solution.

Thermal treatment of the source glass at 825, 850, and 875°C leads to further formation of the microstructure of the material. Crystal growth up to 0.3 μm is noted, the volume fraction of crystals with sizes up to 0.5 μm increases, and individual crystals with sizes up to 1–3 μm are detected. X-ray phase analysis confirms this fact by an increase in the 100% line of β-spodumene.

Thermal treatment at 900 and 950°C is accompanied by homogeneous volume crystallization and a crystal growth up to 0.8–0.9 μm. According to the x-ray phase analysis, the main crystalline phase is β-spodumene.

Thermal treatment at 1000–1050°C leads to the formation of the first small needle-shaped crystals with a ratio of $c/a = 10$. The fraction of such crystals is not large so far — within the limits of 5%. The other crystals have no marked boundaries. According to the x-ray phase analysis, the main crystalline phase is β-spodumene.

Thermal treatment at 1100–1150°C causes the formation of a structure of the material with a chaotic arrangement of needle-shaped and prismatic crystals. The specimens reveal a still fairly large quantity of the residual glassy phase whose composition is apparently different from the source glass. The needle-shaped crystals acquire dimensions with a mean ratio of $c/a = 10$–12, and the prismatic ones — with 2–4. The appearance in the material of petalite, aluminum titanate, rutile, corundum, and solid solution with the structure of β-quartz, although in small amounts, is noted.

Thermal treatment at 1175–1200°C causes further growth of needle-shaped and prismatic crystals. There appear tablet-shaped crystals measuring 1.2–1.5 μm. It has been found that on β-spodumene crystals fine-grained prismatic crystals measuring up to 0.3 μm are formed. These are, most probably, rutile crystals. In the photograph, they are seen either in the form of faceted "holes" or in the form of light inclusions. X-ray phase analysis reveals the presence in the specimens of solid solution of β-spodumene, aluminum titanate, α-quartz, corundum, rutile, and petalite.

Thermal treatment at 1225$^{\text{o}}$C increases the sizes of crystals to 5 μm with a mean value of 3 μm. At this temperature, however, a considerable deformation of the source-glass specimens is noted, which points to the inexpediency of increasing the temperature in investigating the source glass.

Thus, the complex investigations carried out under heat treatment in the 600–1225$^{\text{o}}$C range have revealed the tendency towards the formation of the phase composition, the structure, and some of the physicotechnical properties of the material, which makes it possible to purposefully approach the syntheses of pyroceramics with a given level of properties.

NOTATION

T, temperature, $^{\text{o}}$C; ΔT, temperature difference in the weighted sample of the material with respect to the furnace temperature; γ, density, g/cm^3; K_{shr}, volume shrinkage, %; σ_{flex}, flexural strength, MPa; σ_{h}, microhardness, MPa; ε, permittivity; tan δ, dielectric loss tangent; c, crystal length, μm; a, crystal width, μm; V, rate of temperature rise, $^{\text{o}}$C/h; τ, holding at a particular temperature, h; ΔL, relative expansion, %; J, intensity of the 100% line of β-spodumene, mm.

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