

STUDY OF THE POSSIBILITY OF REDUCING PRELIMINARY CRYSTALLIZATION TEMPERATURE OF LITHIUM ALUMINOSILICATE GLASS AND ITS USE FOR PREPARING COMPONENTS FOR RADIO ENGINEERING PURPOSES

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Translated from *Novye Ogneupory*, No. 6, pp. 49 – 53, June, 2013.

Original article submitted April 2, 2013.

The possibility of using lithium aluminosilicate glass crystallized in a low-temperature furnace (up to 1000°C) for manufacturing components for radio engineering purposes is studied.

Keywords: glass ceramic, lithium aluminosilicate glass, thermomechanical analysis, x-ray phase analysis, microstructure.

Currently some objects for radio engineering purposes operate under conditions of prolonged action of sea water and increased moisture content. As a result of this glass ceramic with high dust and rain erosion resistance become irreplaceable for use in manufacturing such objects.

In ONPP Tekhnologiya ceramic technology has been developed and introduced for preparing objects of glass ceramic OTM-357 (basic phase β -spodumene) [1]. According to this technology objects are formed from amorphous lithium aluminosilicate glass. Results of comprehensive study of glass ceramic OTM-357 have shown that with respect to level of basic physicochemical properties the glass ceramic corresponds to similar overseas materials developed in the USA (Pyroceram 9608) and in the Ukraine (sitall AS-418) by traditional glass technology, and with respect to thermal shock resistance, stability of strength and dielectric properties in the range from 20 to 1175°C, they considerably surpass them.

However, in spite of the indisputable advantages, ceramic technology for manufacturing objects of glass ceramic OTM-357 has a number of disadvantages: a requirement for prolonged heat treatment in high-temperature firing furnaces (more than 70 h), presence of a gradient for physicochemical property indices throughout an object volume (especially throughout the volume of large objects with height up to

1200 mm), which makes object preparation with a prescribed level of radio engineering properties much more difficult.

In order to reduce heat treatment duration for billets in high-temperature firing furnaces and the gradient of physicochemical property indices throughout the volume of an object, technology has been proposed for preparing them from previously recrystallized glass crystalline material OTM-357-O (basic phase β -spodumene) [2]. This makes it possible to reduce heat treatment duration from 70 to 24 – 30 h and to obtain material with more uniform structure. However, use of lithium aluminosilicate glass as a starting material, crystallized at 1170 – 1250°C for 4 – 8 h, requires additional use of a high-temperature firing furnace and an increase in firing time for a single object up to 10 h. The aim of this work is to study the possibility of reducing the temperature for preliminary crystallization of starting lithium aluminosilicate glass and its use for manufacturing objects for radio engineering purposes.

A study of crystallization of lithium aluminosilicate glass was carried out in units for thermal (differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)), dilatometric, x-ray phase (XPA) analyses, and a EVO-40 XVP (SEM) scanning electron microscope. In order to determine ceramic indices (density, water absorption) standard methods, instruments and devices were used, DSC and TGA were performed in a STA 449F1 unit, dilatometric analysis was performed in DKV-5A and DKV-804 type dilatometers, and XPA was carried out in a DRON-6 diffractometer, strength properties were determined in a 9024 DP 100.1500

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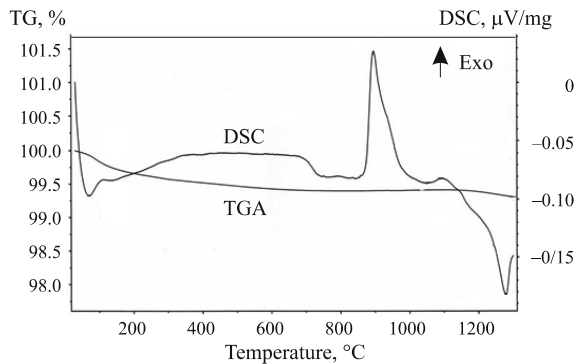


Fig. 1. Thermal analysis of lithium aluminosilicate glass.

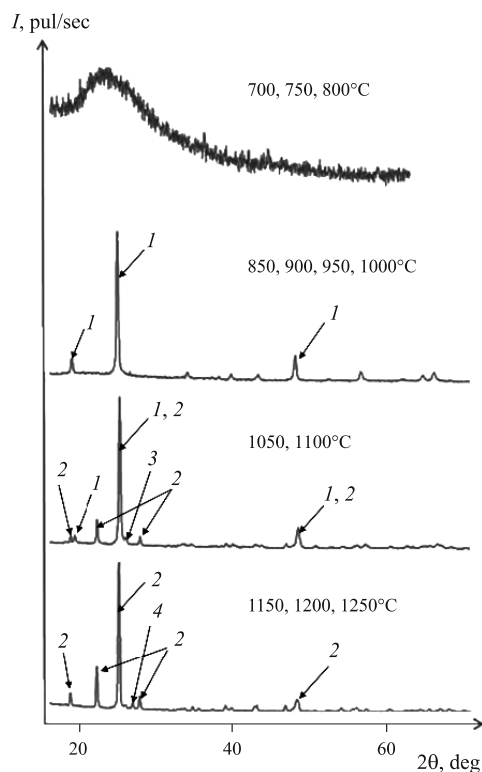


Fig. 2. X-ray diffraction pattern of lithium aluminosilicate glass specimens after heat treatment at 700 – 1250°C (shown on diagram) with soaking for 2 h: 1) solid solution with hexagonal lattice; 2) β -spodumene solid solution; 3) aluminum titanate; 4) rutile.

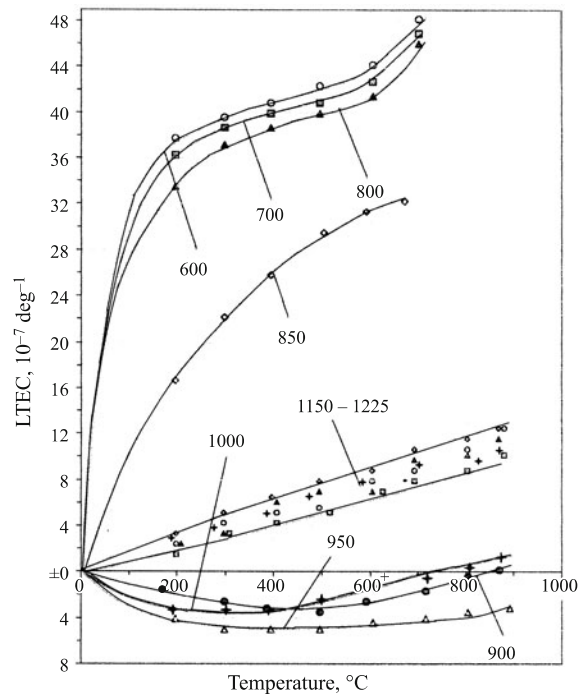


Fig. 3. LTEC temperature dependence for lithium aluminosilicate glass specimens fired without soaking at different temperatures (shown on curves, °C).

type unit, and dielectric properties were determined in a Kvartz high-temperature dielectrometer.

The original lithium aluminosilicate glass of β -spodumene composition was used as specimens for DSC and TGA. For dilatometric analysis specimens of lithium aluminosilicate glass were heat treated at from 600 to 1225°C without soaking, and with soaking at the maximum temperature for 2 h. For XPA lithium aluminosilicate glass specimens were heat treated at 700 – 1250°C with soaking at the maximum temperature for 2 h.

In order to study material microstructure and properties test batches of specimens were prepared, fired at 1250°C for 6 h. The starting billets for specimens were prepared from amorphous lithium aluminosilicate glass, from glass ceramic fired at 1250°C for 6 h, and from glass crystallized at 850°C for 2 h and 1180°C for 6 h.

TABLE 1. Properties of Glass Ceramic Materials Prepared from Different Starting Raw Material and Fired at 1250°C for Six Hours

Specimen	Billet starting materials	Apparent density, g/cm ³	Water absorption, %	Ultimate strength in bending, MPa, at 20°C	Dielectric permittivity at 20°C	Dielectric loss angle, tg δ , 10 ⁻⁴
1	Amorphous glass	2.49	0.05	125	7.00	115
2	Glass ceramic fired at 1250°C, 6 h	2.48	0.03	126	6.92	117
	Original glass, crystallized at:	2.50	0.04	128	6.95	116
3	1180°C, 6 h					
4	850°C, 2 h	2.51	0.05	129	7.10	114

TABLE 2. Material Density Over Lithium Aluminosilicate Glass Material Billet Height Prepared from Different Starting Raw Materials and Fired at 1250°C for Six Hours

Zone over billet height from base with 120 mm interval	Billet starting material density, g/cm ³ (see Table 1)			
	1	2	3	4
1	2.49	2.48	2.51	2.50
2	2.49	2.48	2.51	2.51
3	2.49	2.48	2.50	2.51
4	2.48	2.49	2.51	2.51
5	2.48	2.48	2.51	2.51
6	2.48	2.48	2.51	2.50
7	2.47	2.48	2.50	2.50
8	2.46	2.49	2.50	2.49
9	2.46	2.49	2.51	2.49
10	2.45	2.48	2.49	2.48

TGA (Fig. 1) showed that with a high temperature there is insignificant specimen weight loss, i.e., less than 0.5%. DSC (Fig. 1) established presence of two exothermic peaks at 900 and 1100°C. Exothermic peak data may be connected with crystallization and phase transformations in specimens.

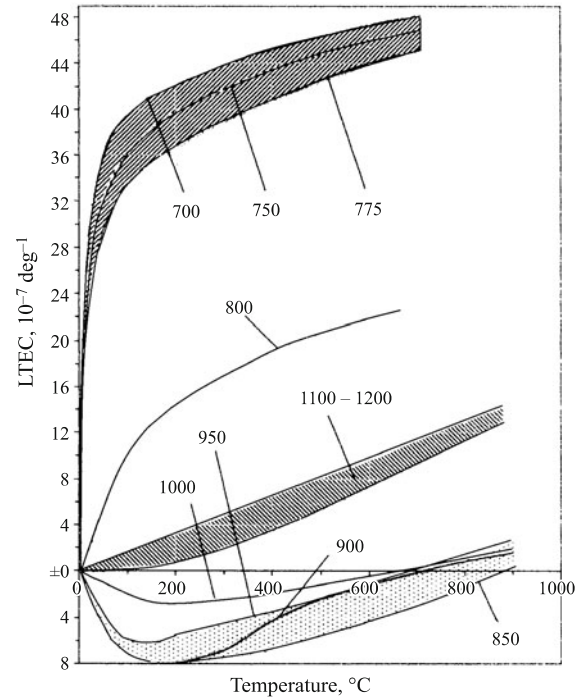
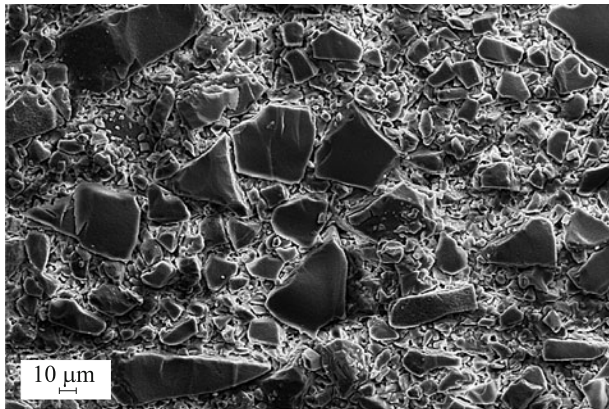
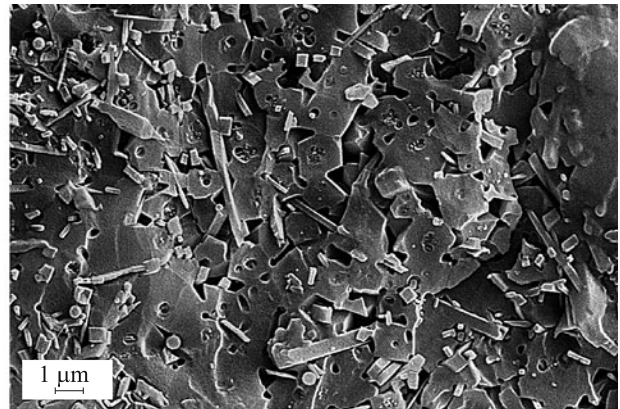


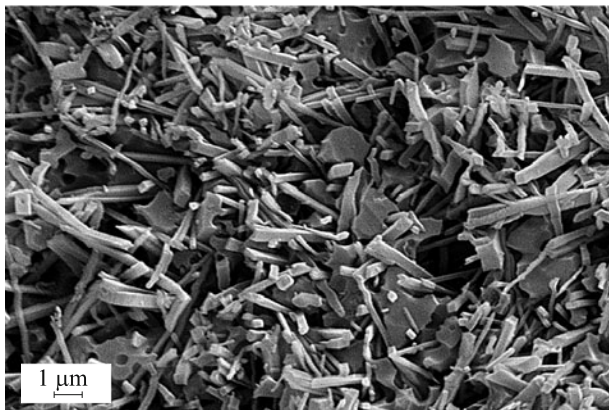
Fig. 4. LTEC temperature dependence for lithium aluminosilicate glass specimens heat treated at different temperatures (shown on curves, °C) with soaking for 2 h.



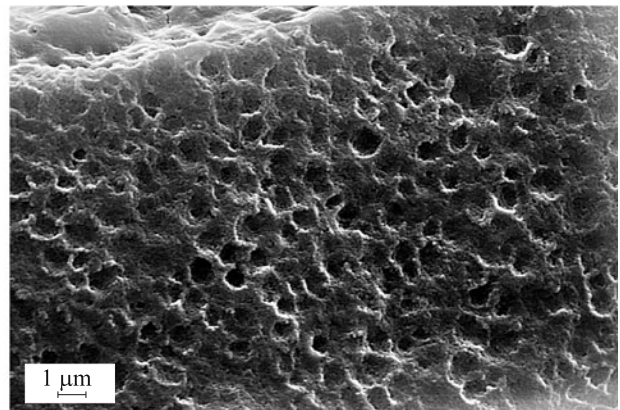
1



2



3



4

Fig. 5. Microstructure of specimens 1 – 4 (see Table 1): 1) ×500; 2 – 4) ×10000.

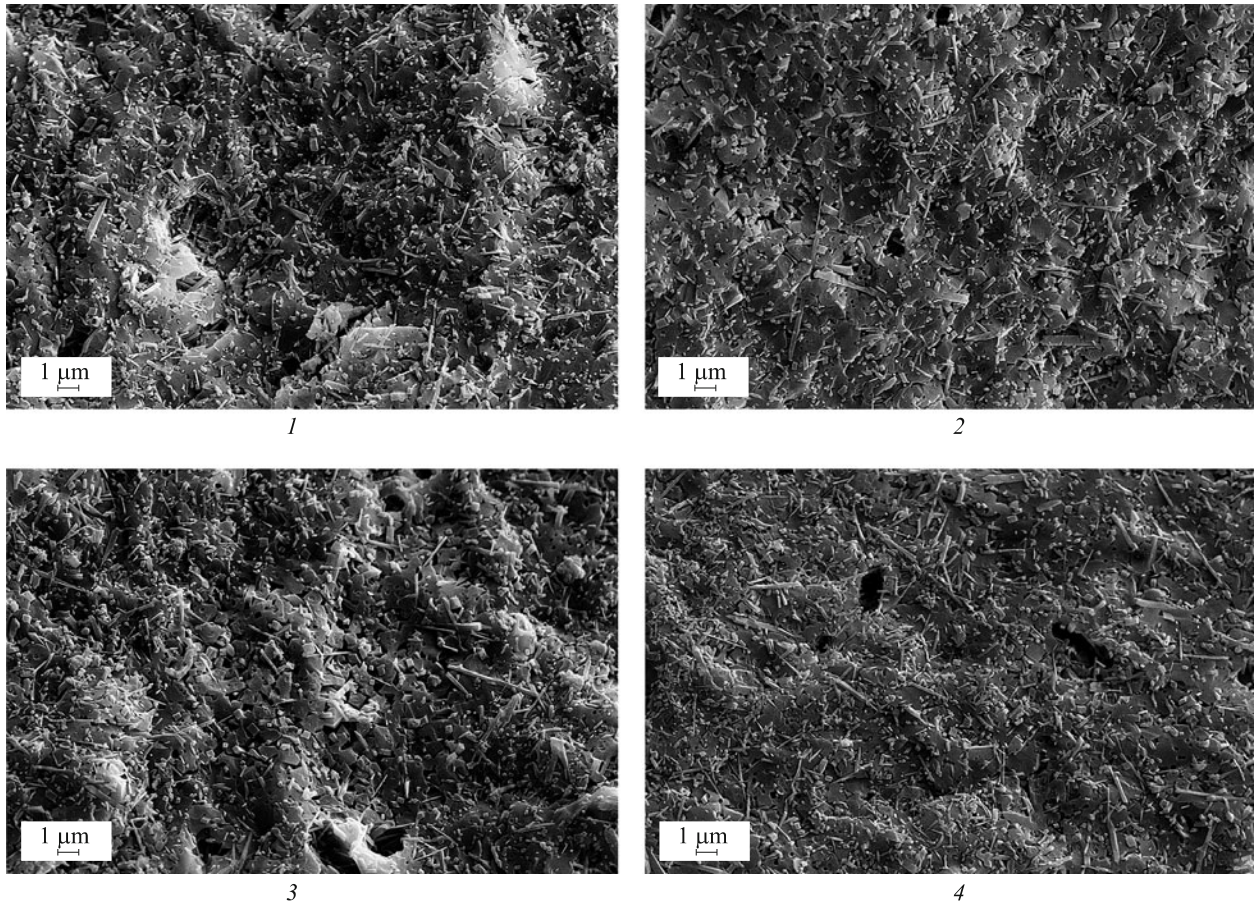


Fig. 6. Microstructure of specimens 1 – 4 after firing at 1250°C for 6 h, prepared from different starting material (see Table 1). $\times 4000$.

XPA (Fig. 2) showed that specimens heat treated at 700 – 800°C are amorphous, and at 850 – 1000°C there is glass crystallization in the form of solid solution of variable composition with a hexagonal lattice, at 1050 – 1100°C phase transition is accomplished for solid solutions with a hexagonal lattice into solid solutions of β -spodumene, and 1150 – 1250°C solid solutions of β -spodumene are observed. Rutile and aluminum titanate are detected with XPA of specimens.

It was established by dilatometric analysis (Figs. 3 and 4) that specimens of lithium aluminosilicate glass, crystallized at 900 – 1000°C in the form of solid solutions with a hexagonal lattice (according to XPA results) have a linear thermal expansion coefficient (LTEC) close to zero, which provides a possibility of specimen rapid heating and cooling during heat treatment. Heat treatment duration at 900 – 1000°C does not lead to marked changes in LTEC. This provided the possibility of developing technology for separate object firing.

There is formation by this technology of amorphous lithium aluminosilicate glass objects heat treated in two stages: first in a low-temperature furnace at 850 – 900°C for 1.5 h with a temperature increase rate of 20 – 60°C/h, and then in a high-temperature furnace at 1230 – 1250°C for 4 – 7 h with a temperature increase rate up to 500 °C/h. Multioperation

technology requires additional operation for transfer of objects from a low- to a high-temperature furnace, as a result of which defects may form within objects. In order not to move objects from a one furnace to another and have a possibility for rapid heating with a rate of temperature increase up to 500 °C/h, it is necessary first to carry out crystallization of lithium aluminosilicate glass, then to form objects from it only by firing.

Crystallization of lithium aluminosilicate glass may be accomplished at 1180 – 1250°C [2]. At these temperatures within specimens there is formation of β -spodumene solid solutions. Crystallization of lithium aluminosilicate glass may also be accomplished at 850 – 1000°C in the form of solid solutions with a hexagonal lattice, and formation of β -spodumene solid solution will proceed during final object firing at 1230 – 1250°C [3 – 6].

A study of test batches of specimens prepared from different starting material showed that they have similar phase composition (β -spodumene solid solution, rutile), comparable values of strength and density, absorption and dielectric properties (Table 1). Use of crystallized lithium aluminosilicate glass for forming billets promotes an increase in their uniformity and reduction in gradient for physicochemical

property indices throughout the volume of an object, particularly large objects with height up to 1200 mm (Table 2) [7].

A study of the microstructure of original materials showed that a specimen of amorphous glass is a combination of grains of lump morphology with a size from ~ 2.5 to 10 and from 10 to 120 μm , which are distributed uniformly among themselves (Fig. 5, specimen 1). The microstructure of a specimen of fired glass ceramic consists of blocks, penetrated by elongated prismatic crystals (Fig. 5, specimen 2). The microstructure of a specimen of lithium glass crystallized at 1180°C for 6 h consists of elongated prismatic crystals and blocks between them (Fig. 5, specimen 3). The microstructure of a lithium glass specimen crystallized at 850°C for 2 h has fine grained aggregates at the surface, pointing to crystallization (Fig. 5, specimen 4).

The microstructure of specimens prepared from the given starting materials after firing at 1250°C and soaking for 6 h consists of elongated prismatic and block crystals, and uniformly distributed pores (Fig. 6). The microstructure of fired specimens requires more profound study.

Thus, the possibility has been demonstrated of using material previously crystallized at 850 – 900°C in order to prepare billets of lithium glass, which provides a reduction in the level of glass heat treatment temperature from 1180 – 1250 to 850 – 900°C. As a result of this the possibility develops of carrying out heat treatment not within high-temperature firing furnaces, but in low-temperature (up to 1000°C) furnaces with shortening of heat treatment time in high-temperature furnaces.

The results obtained point to a possibility of more profound study in the area of original glass crystallization in the

temperature range 850 – 900°C, determining the level of properties, the possibility of preparing objects, and also performing comprehensive tests by regimes similar to those existing in operating conditions.

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