Nanostructured Magnesium-Aluminosilicate Glass-Ceramic Materials for Electronics and Engineering

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***Abstract*—The prospects for the use of glass-ceramic materials as electrical products are analyzed. The priority of the formation of a self-organized macro- and nanostructure, glass-ceramic materials under conditions of low-temperature heat treatment to ensure their high physical and chemical properties is characterized. The effect of crystallization catalysts on the formation of the structure and viscosity of magnesium aluminosilicate glasses during their heat treatment is analyzed.**

The composition of magnesium aluminosilicate glass is optimized by using a combined crystallization catalyst in its composition, and an optimal heat treatment mode is established. The features of structure formation in magnesium-aluminosilicate glass-ceramic materials are analyzed, which consist in the sequential course of the following stages: phase separation of glass by the spinodal mechanism (T = 800-850 °C); nucleation of crystals of μ-cordierite (T = 850 °C) and the formation of prismatic crystals of mulite (T = 1100 °C), which are tightly connected. The formation of the nano- and submicron structure of the developed glass-ceramic material containing 80 vol. % mulite allows obtaining high physicochemical and electrical properties, which, along with its reduced weight, makes it promising for development as substrates in the design of a hybrid integrated circuit, vacuum-tight shell and capacitor dielectrics.

***Keywords*—glass-ceramic, nanostructure, magnesium-aluminosilicate glass, viscosity, electrical properties.**

I. INTRODUCTION

Today, the development and production of nanostructured glass-ceramic materials with a self-organized structure is a promising direction for the development of innovative technologies in the leading branches of science and technology: mechanical engineering and instrument making, medicine, electronics, electrical engineering, aviation and rocketry, etc.). Glass-ceramic materials for electrical purposes have found wide application in radio and high-frequency technology as materials for producing radar housings, electrical insulators, vacuum-tight shells, substrates for microcircuits and electronic devices, information carriers, capacitor dielectrics, and vacuum tubes [1]. Due to the formation of a self-organized micro- and nanostructure, glass-ceramic materials are characterized by special electrical properties (dielectric constant 5.5–23.8; electrical resistivity, at a temperature of 20 ºC, log ρ = 10–16 Ohm·m; dielectric loss tangent, at a frequency of 1 MHz and a temperature of 25 ºC, tg = 0.0003–0.0030).

The main problem in the introduction of glass-ceramic materials is the implementation of their polyfunctionality along with the provision of difficult-to-match properties (high transparency, strength, certain electrical properties and low density) along with reduced cost and manufacturability [2]. This can be solved by choosing the optimal glass composition, changing the amount and type of crystallization catalysts and heat treatment modes.

In the process of developing and obtaining glass-ceramic materials with a programmed structure, it is especially important to select the type and amount of crystallization catalysts (CC) in their composition. The use of crystallization catalysts traditional for glasses and their combination can radically change the mechanism and course of crystallization and, as a consequence, the structure of materials [3, 4]. Of particular interest is the study of the effect of CC on the structure of magnesium aluminosilicate glass-ceramic materials (Table 1).

TABLE I. Influence of crystallization catalyst on the structure of magnesium aluminosilicate glasses

CC	The mechanism of influence on the structure	Content, wt. %
TiO_2	phase separation of glass, increase in the content of α-cordierite crystals	1.0–10.0
ZrO_2	increase in the content of α-cordierite crystals	3.0–5.0
ZnO	phase separation of glass, providing fine crystallization	2.0–8.0
CeO_2	phase separation of glass, increase in the content of α-cordierite crystals	0.5–2.5
P_2O_5	phase separation of glass, increase in the content of μ-cordierite crystals	0.5–8.0

For glasses of the $MgO–Al_2O_3–SiO_2$ system, the formation of a structure during heat treatment is complex and is realized through the formation of solid solutions with a variable composition. It is the sequence of precipitation of crystalline phases that makes it possible to form the dissipative structure of glasses and ensure the designed properties of glass-ceramic materials based on them.

The decisive influence on the formation of the structure of magnesium aluminosilicate glasses (M–A–S) is distinguished by titanium dioxide, the cations of which will replace silicon in the structure of silicate glass. At high temperatures, Ti^{4+} replaces Si^{4+}, and as the temperature decreases, the solubility of these cations decreases and, as a consequence, the glass becomes oversaturated with respect to them. During heat treatment, an excess amount of coordination polyhedra formed by these cations leaves the glass frame, forming microinhomogeneities. Depending on the type of coordination polyhedron, either crystallization or separation of glass can take place. If the cation itself can be a glass former, then the microheterogeneities increase and form a second glass phase, that is, a stratification is formed. If the cation is not a glass former, then the enriched zone becomes unstable with respect to crystallization and is the nucleus of crystallization [5].

When analyzing the mechanism of action of P_2O_5 as CC in the structure of M–A–S glasses, it was confirmed that it promotes their separation into two rare phases [6]. Embedded in the glass network, P_2O_5 creates conditions for breaking the Si–O–Si bonds, since the requirement of electroneutrality determines the double bond of the phosphorus ion with oxygen. Such a change in bonds in the glass network promotes the release of phosphorus-containing groups under certain temperature conditions even at the stage of melting. It is the appearance in the structure of glass materials of secondary separation as a stage of heterogeneous nucleation of crystals that will make it possible to form crystalline phases, the structure of which, from the point of view of short-range order, is most akin to the structure of glass. This will lead to a decrease in energy barriers during the nucleation of crystals, which can be easily overcome at relatively low temperatures at which the initial crystallization of glass is carried out.

The authors of [7] found that the introduction of P_2O_5 into the composition of magnesium aluminosilicate glasses promotes the intensification of the crystallization of μ-cordierite, and B_2O_3 – of α-cordierite. The temperature effect of P_2O_5 in glasses is less than that of B_2O_3, because the growth rate of μ-cordierite is lower than that of α-cordierite with increasing temperature. A positive effect of P_2O_5 in the structure of glasses of the M–A–S system is observed upon the formation of a single aluminophosphoric oxygen framework, which affects an increase in the chemical resistance of the glass and a decrease in thermal expansion coefficient [8]. The role of the Al^{3+} cation in increasing the chemical resistance of glasses containing both P_2O_5 and B_2O_3 is that it, in the presence of RO, it promotes the transition of the BO_3 to BO_4 groups.

To ensure the occurrence of nucleation and the formation of crystalline phases in the region of lower temperatures, CCs of ZnO and CeO_2 are introduced into the glass composition, which, simultaneously with P_2O_5, contribute to the phase separation of glass and the formation of a nanodispersed glass structure during its heat treatment. Also, the introduction of zinc oxide into the composition of glass-ceramic materials, along with the presence of CCs of Cr_2O_3 and CaF_2, will promote the formation of a fine structure [9] with a crystal size of about 1 μm, which, in turn, will increase the mechanical properties of materials. The crystallization ability of glasses with a CeO_2 content of 0.5–2.5 wt. % is significantly enhanced by the presence of Al_2O_3, CaO, MgO or ZrO_2 in their composition.

To ensure the formation of a high-strength structure of glass-ceramic materials based on glasses of the M–A–S system, it is important to ensure metastable phase separation that occurs under conditions of increased viscosity in the glass transition range. It is the high viscosity of the glass that makes an important contribution to the kinetics of the process: at a certain time, the glass cannot separate into two layers, the precipitated glassy phase forms fine droplets, which leads to the formation of a developed droplet two-frame structure in a short time. The viscosity of a glass melt of the M–A–S system increases with an increase in the concentration of CeO_2 [10, 11] and ZrO_2, while an increase in the content of CeO_2 can lead to a decrease in the content of cordierite [12]. In general, the addition of oxides of rare earth elements to cordierite glass ceramics of nonstoichiometric composition will reduce the sintering temperature to 900–950 °C, improve the compaction process, and reduce the activation energy of sintering [12]. It should be noted that the tendency to crystallization when some oxides are replaced by others decreases with increasing glass viscosity in the temperature range of crystallization. To reduce the viscosity at high temperatures and melting points, to increase the tensile strength in compression and bending, calcium and strontium oxide are used along with B_2O_3. The introduction of antimony oxide [13] also helps to reduce the viscosity of the melt, improve the illumination conditions of the molten glass, and create additional crystallization centers. Therefore, it is important in the development of high-strength magnesium aluminosilicate glass-ceramic materials with specified electrical properties under conditions of low-temperature heat treatment: the choice of a certain content of CCs and phase-forming components, the optimal viscosity and character of crystallization of magnesium aluminosilicate glasses during the formation of their structure.

II. PURPOSE AND METODOLOGY OF RESERCH

The aim of this work is to study the effect of crystallization catalysts on the formation of the structure of magnesium aluminosilicate glasses in relation to the change in viscosity under heat treatment and to determine their electrical properties.

To study the structure and phase composition of materials, we used complementary methods of physicochemical analysis: X-ray phase (diffractometer DRON-3M), petrographic (optical microscope NU-2E), differential thermal analysis (derivatograph Q-1500D of the Paulik-Paulik-Erday system). The viscosity of the glass was determined by the method of stretching the thread of the test material during heat treatment.

Resistance, dielectric constant, and dielectric loss tangent at 10^6 Hz were measured using an E6-13A teraometer on a trielectrode system at a temperature of 29 °C and a DE-5000 RLC meter.

III. EXPERIMENTAL PART

A. Selection of Glass Compositions

The previously developed glass-ceramic material (GCM) CGC-10, which was synthesized in the M–A–S system using a combined crystallization catalyst (TiO_2, ZrO_2, CeO_2, P_2O_5), was chosen as a basis (Tab. 2). This material is characterized by the formation of a sitalized structure based on solid mulite solutions under conditions of low-temperature two-stage heat treatment and high physicochemical (Vickers hardness 10.4 GPa, fire resistance 1350 °C, density 2800 kg/m^3) and electrical (dielectric loss tangent tg $\delta = 0.006$ and $\varepsilon = 8.5$ at a frequency of 10^6 Hz, lg $\rho_v = 14.5$ at a temperature of 20 °C, dielectric strength $E_m = 40$ MV/m) properties. However, it has insufficient fracture toughness $K_{1C} = 3.5$ MPa·m$^{1/2}$ and a significant duration of the heat treatment regime (10 hours). To improve these disadvantages while maintaining electrical and physicochemical properties, its composition was optimized and a sample CGC-10.1 was obtained (Tab. 2).

TABLE II. Differences in the chemical composition of the developed glasses

The role of components		**Marking GCM**	
		CGC-10	**CGC-10.1**
Phase-forming components, wt. %	MgO	9	9
	Al_2O_3	29	28
	SiO_2	51	50
	Σ(CaO, SrO, B_2O_3)	5	5
Crystallization catalysts, wt. %	TiO_2	2	2
	ZrO_2	1.5	1
	CeO_2	0.5	0.4
	P_2O_5	2.0	3.0
	Sb_2O_5	–	0.1
	ZnO	–	1.5

The electrical losses of the experimental GCM are due to the presence of a complex of dielectric losses of both amorphous and crystalline phases. The content of the glass phase determines the main share of dielectric losses for materials, since free ions of alkali metals, which are mainly contained in the glass phase, are the main carriers of the current arising due to the migration of ions. The crystalline phase of the developed materials has a low electrical conductivity, and an effective decrease in the electrical conductivity of the glass phase of the experimental materials was achieved due to the simultaneous introduction of several glass-formers SiO_2, B_2O_3, Al_2O_3 and Ti^{4+} cation into their composition [1].

The introduction of zirconium dioxide as a glass component contributing to an increase in the chemical and thermal stability of silicate glasses containing B_2O_3 [12] will significantly enhance their crystallization ability, especially when combined with TiO_2 and P_2O_5. It should be borne in mind that the presence of such components as Al_2O_3, ZnO and MgO reduces the solubility of ZrO_2 in glass and enhances the crystallization ability, which can lead to a decrease in the strength of the glass structure during prolonged high-temperature heat treatments.

To enhance the nucleation process and the formation of crystalline phases in the region of low temperatures, ZnO was additionally introduced, which along with P_2O_5 will promote the phase separation of CGC-10.1 glass and the formation of its nanodispersed structure during heat treatment. To reduce the viscosity in the glass composition, 0.1 wt. % CeO_2 was replaced by Sb_2O_5. To increase the content of μ-cordierite (quartz-like solid solution of MgO·Al_2O_3 in SiO_2), the content of P_2O_5 was increased.

Optimization of the composition of CGC-10.1 made it possible to reduce its melting temperature from 1550 °C for CGC-10 to 1500 °C, which is an essential aspect of the implementation of energy-saving technology in the development of high-strength glass-ceramic materials for electronic equipment.

B. Investigation of the Effect of Viscosity on the Formation of the Structure of Magnesium Aluminosilicate Glass

For experimental glasses, an anomalous increase in viscosity with increasing temperature in the glass transition range T_g–T_f for test glasses is associated with a high rate of temperature rise, preceding an increase in viscosity, which leads to a dip in the viscosity curve (Fig. 1). This state is quickly eliminated and a more intense increase in the crystalline phase occurs due to a decrease in the amount of the glassy phase, which determines the repeated increase in viscosity before the end of heat treatment [14].

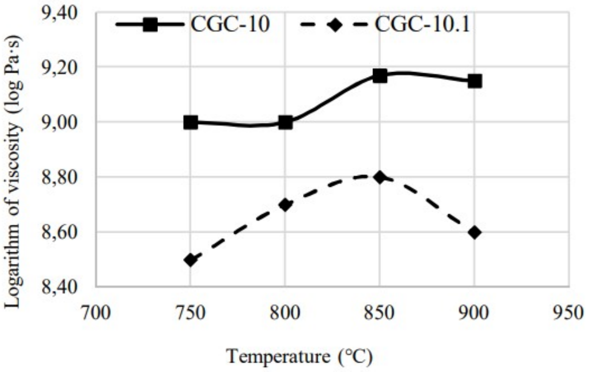


Fig. 1. Dependence of the viscosity of the test glasses on temperature

In general, the effect of viscosity on the crystallization ability of glasses of the M–A–S system upon cooling from the melting point is rather complex, since along with the structural viscosity caused by the formation of a spatial framework, there is crystallization viscosity due to an increase in the number of crystals. A feature of the formation of a sitized structure of magnesium aluminosilicate glasses is: high viscosity of glass melt (10^9 Pa·s), significant temperatures of nucleation (900–1000 °C) and crystallization of 1250–1300 °C, duration of heat treatment processes (total duration about 10 h). This not only increases the cost of materials and limits the methods of forming products, but also significantly reduces the strength of materials due to the intensive growth of the crystalline phase during high-temperature long-term heat treatment.

A feature of the structure of magnesium aluminosilicate glasses is that, along with the occurrence of diffusion processes, it is important that at low temperatures the high viscosity of the melt leads to a decrease in the size of the liquation regions, an increase in their number and a shift in their appearance to the region near T_g. These data not only determine the dependence on the change in the viscosity of the sample as a function of crystallization, but also determine the direction of control of the thermal history of glass during crystallization.

The difference in the nature of the viscosity curve for CGC-10.1 glass when compared with CGC-10 is that intense formation of fluctuations is observed at a viscosity of $10^{8.5}$ to $10^{8.8}$ Pa·s in the range of lower temperatures 750–850 °C (Fig. 1), which is realized due to the introduction of Σ(CaO, SrO, B_2O_3, Sb_2O_5) in an amount of 6 wt. %.

For CGC-10.1 glass, the course of the viscosity versus temperature curve is optimal for the formation of crystallization nuclei, since its maximum is rapid and is in the temperature range below the softening point, that is, in the range of viscosity values above 10^8 Pa·s. It is the decrease in the viscosity of the CGC-10.1 glass and the shift of the intensive growth to the region of lower temperatures that is an important factor in ensuring the intensive course of phase separation and the formation of a high-strength glass structure.

Confirmation of the shift of the T_g–T_f interval to the temperature range of 800–850 °C and the temperatures of exothermic effects to the lower temperature range is provided by the data of differential thermal analysis (DTA) (Fig. 2).

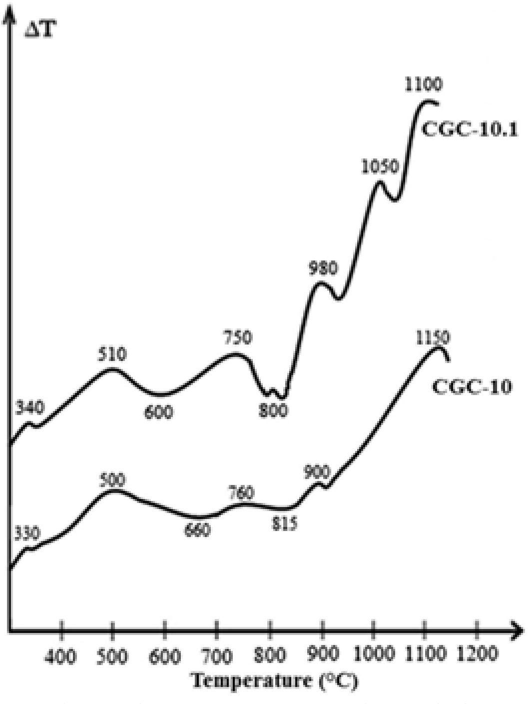


Fig. 2. Thermograms of experimental glasses

A characteristic feature of the DTA curve for CGC-10.1 glass is the presence of a phase separation process in the temperature range T_g–T_f, which manifests itself in an insignificant change in the endo- and exoeffects at temperatures of 800 °C and 820 °C, respectively. Phase separation coincides with the opalescence region of this glass during heat treatment according to the data of gradient thermal analysis [14]. It is characterized by an increase in viscosity (Fig. 1) as an indicator of changes in the glass structure.

Theoretically, it can be assumed that if, upon heating, several liquid phases are formed in glass, then the DTA curve in the separation region changes its direction in accordance with the number of phases. The rapidity of the DTA curve for CGC-10.1 glass as compared to CGC-10 glass indicates a significant growth rate of fine crystals at temperatures of 850–900 °C (Fig. 2). It should be noted that, in view of the high viscosity of magnesium aluminosilicate glasses and the peculiarities of the formation of solid solutions, an important condition for the formation of a nanoscale structure is to ensure a high rate of nucleation and limit the rate of linear crystal growth. The presence of a rapid peak of the exoeffect at a temperature of 980 °C indicates a more intense formation of saturated and supersaturated homogeneous solid solutions and labile solid solutions based on α-cristobalite and spinel. The latter, when heated, react with the formation of α-cordierite at a temperature of 1050 °C and then react to mullite at 1100 °C, which is confirmed by the data of petrographic analysis. The intensification of crystallization processes in CGC-10.1 glass at a temperature of 1100 °C, which is determined by a high peak on the thermogram, is evidence of the occurrence of bulk fine crystallization of glass-ceramic.

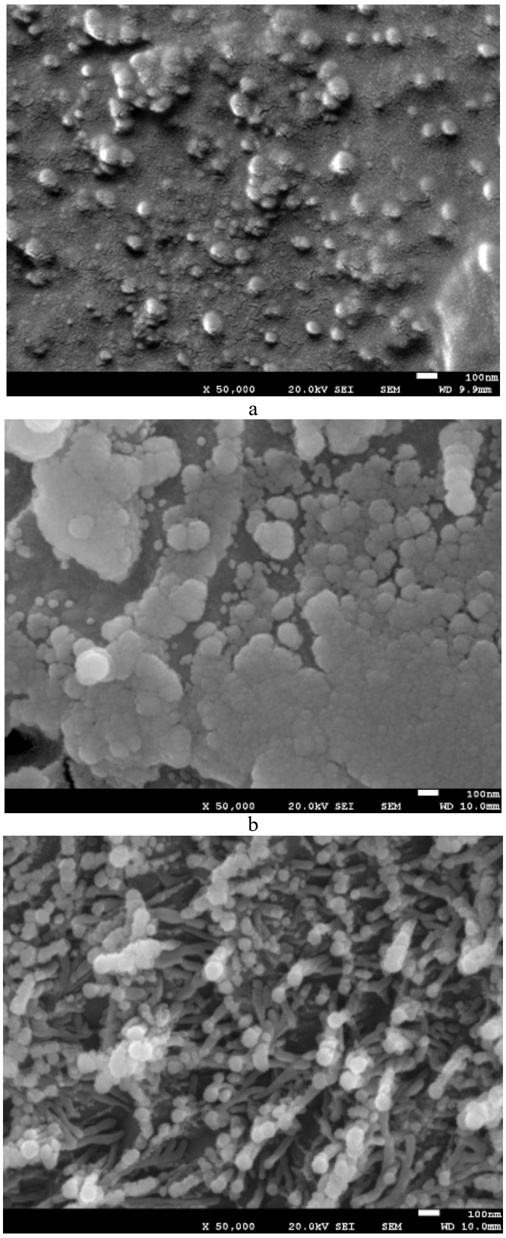
C. Investigation of the Structure and Properties

The formation of a dissipative nanostructure for CGC-10.1 glass in the pre-crystallization period is an important stage in the formation of unsaturated and saturated solid homogeneous solutions with the structure of hightemperature quartz even at a temperature of 850 °C. Investigation of the structure of CGC-10.1 glass using scanning electron microscopy (Fig. 3) made it possible to establish the occurrence of phase separation according to the spinodal mechanism. It manifests itself in the enlargement and combination of crystals in stable conglomerates with a content of more than 50 vol. % in the area of the nucleus at 800 °C (Fig. 3 a). At a temperature of 850 °C, the presence of spherical inhomogeneities 50–100 nm in size is observed (Fig. 3 b), which coalesce and form a dense structure of μ-cordierite crystals. This is a prerequisite for the formation of a mutually permeable sitalized structure of the CGC-10.1 material with the presence of mulite crystals of about 80 vol. % at a temperature of 1100 °C (Fig. 3 c), which is characterized by high self-organization.

According to the research results, the optimal heat treatment mode was selected: Stage I – temperature (T) 800 °C, duration (τ) 2 hours; Stage II – T = 980 °C, τ = 2 hours; Stage III – T = 1100 °C, τ = 1 hour, characterized by lower temperatures and duration in comparison with the known glass-ceramics based on mulite [15].

Formed by ceramic technology glass-crystalline material CGC-10.1, obtained according to the specified heat treatment mode, differs from CGC-10 in higher indicators of mechanical properties (K_{IC} = 6.5 MPa·$m^{1/2}$ and E = 350 GPa) and a little bit higher density (ρ = 2850 kg/m^3). A sharp increase in the fracture toughness coefficient is explained by a decrease in the average crystal size and, as a result, by a decrease in the value of the breaking stress.

For the developed sitals, the tg δ losses are explained by dipole relaxation losses associated with thermal ion polarization at a frequency of 10^6 Hz, which are insignificant due to the absence of relaxing elements (alkali metals) in the composition of both materials and are associated with structural defects. However, the difference between the compositions is the provision of "homogenization" of the structure in the composition of CGC-10.1, which manifests itself in uniform intergrowth of crystals in the bulk of the material, and the alignment of property gradients on the phase limits, which changes the electrical properties (tg $\delta = 0.005$, $\varepsilon = 8.0$, lg $\rho_v = 14.8$, $E_m = 38$ MV/m). Ensuring the formation of a dense homogeneous nano- and submicron structure of the CGC-10.1 material is of decisive importance for reducing the indicated electrical properties.



a

b

c

Fig. 3. The structure of the experimental material CGC-10.1:
a – 800 ºC; b – 850 ºC; c – 1100 ºC

IV. CONCLUSION

The necessity of development of high-strength polyfunctional nanostructured glass-ceramic materials for electronic engineering is shown. The effect of crystallization catalysts on the formation of the structure and viscosity of magnesium aluminosilicate glasses during their heat treatment is analyzed.

The composition of magnesium aluminosilicate glass is optimized by using a combined crystallization catalyst in the composition, and the optimal mode of its thermal treatment is established. The features of structure formation in magnesium-aluminosilicate glass-ceramic materials are analyzed, which consist in: phase separation of glass by the spinodal mechanism (T = 800–850 °C), nucleation of μ-cordierite crystals at viscosity $\eta = 10^{8.8}$ Pa·s (T = 850 °C) and the formation of prismatic mulite crystals (T = 1100 °C), which are tightly connected. The formation of the nano- and submicron structure of the developed glass-ceramic material with a content of 80 vol. % mulite allows to provide high indicators of physical and chemical properties (K_{1C} = 6.5 MPa·m$^{1/2}$, E = 350 GPa, ρ = 2850 kg/m^3) at preservation of the necessary electrical properties. Due to the combination of dielectric properties (tg $\delta = 0.005$, $\varepsilon = 8.0$, lg $\rho_v = 14.8$, $E_m = 38$ MV/m), manufacturability and high mechanical strength, the developed CGC-10.1 sample is promising in the development of materials for electrical purposes (for the manufacture of substrates for microcircuits and electronic devices, storage media, capacitor dielectrics, flasks of electric vacuum devices), capable of withstanding significant thermal, mechanical and electrical loads.

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