

## A NEW DIRECTION IN THE FIELD OF SYNTHESIS OF HIGH-THERMOSTABILITY, RADIOTRANSSPARENT GLASS-CERAMICS

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*The characteristics and technological possibilities of various classes of radiotransparent materials are considered. On the basis of data analysis a new direction in the synthesis of glass-ceramics is proposed and realized. The characteristics of the material obtained by the novel technology are described.*

An important component of modern radar-guided missiles is the aerial fairing. The head aerial fairing not only protects the aerial unit from climatic and aerodynamic factors, but also establishes the tactical-technical characteristics of a missile, forming its aerodynamic efficiency, determining the accuracy of guidance to a target, and taking the basic heat and force loads on itself during maneuvers. With the development of flying speeds and slewability of missiles the requirements placed upon fairings and their materials greatly increased. For missiles of various classes flying at speeds of 5–12 M, the fairing surface temperature can reach 2000°C and the force loads — 10 tons. The glass-reinforced plastics widely used for making fairings no longer satisfy the requirements placed upon them not only because of the insufficient thermostability (refractoriness), but also because of the great changes in the dielectrical characteristics of the material while in use, the inhomogeneity of the material in the shell, and the poor reproduction of the properties from shell to shell.

Since the early 1960s, in the USA and the USSR investigations aimed at developing ceramic materials for the fairings of high-speed missiles have been carried out. A wide assortment of materials has been studied: oxide ceramics based on alumina, magnesium, beryllium oxide, etc., nitride ceramics, as well as pyroceramics — glass-ceramic materials based on glass. By now three kinds of materials — pyroceramics, high-alumina ceramics, and quartz ceramics — have been brought to the stage of wide use. It should be noted that high-alumina materials are being used for making "air-to-air"-class fairings operating at speeds up to 4.45 M. This material is especially widely used in the USA for the fairings of "Sparrow"-type missiles [1].

Pyroceramics (Pirokeram-9606, -9608, AS-418, AS-370, etc.) are being used in both the USA and Russia for making fairings of "ground-to-air" and "air-to-air" missiles flying at speeds from 4 to 7 M. This material has found especially wide use for manufacturing ship- and airdrome-based products. Because of the absence of porosity, the material features a good resistance to sea water and a high humidity even without paint coatings [1].

Quartz ceramics has found wide use for high-speed missiles of various classes flying at speeds from 5 to 10 M [1–3].

In order to determine the direction of investigations within the scope of the present work, it is deemed necessary to perform a more detailed analysis of the above materials.

For high-speed missiles, the main requirement of the fairing material is, undoubtedly, its refractoriness. From this point of view, high-alumina ceramics is preferred. The temperature of change of the aggre-

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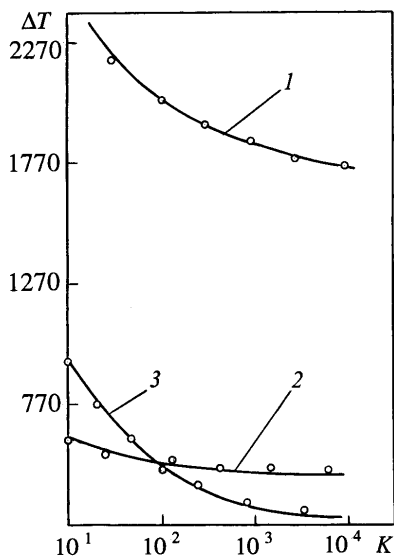


Fig. 1. Resistance of radiotransparent inorganic materials to thermal shock: 1) quartz ceramics; 2) Pirokeram-9606; 3)  $\text{Al}_2\text{O}_3$ -based ceramics.  $\Delta T$ ,  $^{\circ}\text{C}$ .

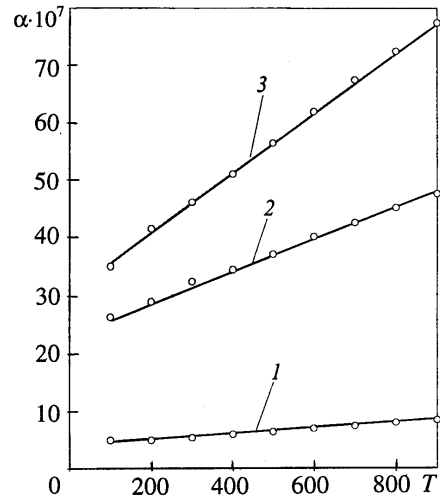


Fig. 2. Temperature dependences of CTLE of inorganic materials: 1–3) notations are the same as in Fig. 1,  $\alpha$ ,  $\text{deg}^{-1}$ ;  $T$ ,  $^{\circ}\text{C}$ .

gate state for it is  $2050^{\circ}\text{C}$ , whereas for pyroceramics it is  $1200\text{--}1350^{\circ}\text{C}$  and for ceramic materials based on quartz glass it does not exceed  $1300^{\circ}\text{C}$ .

However, in one-sided short-term heating, which actually occurs in rocket fairings, the serviceability of a unit is determined by other factors. The most important of them for inorganic refractory materials is the thermostability (resistance to thermal shock and thermocyclic loads). The most common experimental criterion for this quality is the temperature drop the material withstands without destruction. Figure 1 shows the dependence of such a temperature drop  $\Delta T$  for quartz ceramics (1), Pirokeram-9606 (2), and high-alumina ceramics (3) on the value of  $K = a \cdot d / \lambda$ . The value of  $K$  in arbitrary units between  $10^{-3}$  and  $10^{-4}$  corresponds to the thermal loads when a space vehicle enters dense atmospheres. The clear superiority in this parameter of quartz ceramics over other materials is primarily due to the favorable combination of its strength, thermo-physical, and deformation properties [4].

The high thermostability of quartz ceramics is largely determined by the low, compared to other ceramic materials, thermal expansion coefficient (Fig. 2). Moreover, on heating of quartz ceramics and products based on it a stress relaxation takes place. As the investigations have shown, this phenomenon is observed at temperatures of  $900^{\circ}\text{C}$  and higher, and the effect can be enhanced or weakened by changing the nature of the raw material or the structure of the material [5].

An important characteristic of the fairing is its heat conductivity. At a temperature of the outer surface above  $1000^{\circ}\text{C}$  the aerial unit temperature should not exceed  $300^{\circ}\text{C}$ . Owing to the fact that for a given class of missiles the development of the system of aerial unit forced cooling makes the product design much more sophisticated, the problem is solved by means of the heat-shielding characteristics of the fairing material and its design parameters. Preference is given to materials with a low heat conductivity coefficient. Among the inorganic dielectrics, materials based on amorphous silicon dioxide feature the lowest heat conductivity. Figure 3 shows the temperature dependence of the heat conductivity coefficient for quartz ceramics with a porosity of 8–10% (1), Pirokeram-9606 (2), and zero-porosity high-alumina ceramics  $\text{Al}_2\text{O}_3$  (3). The increase in the strength of quartz ceramics with increasing temperature is also explained by the stress relaxation with the appearance of plastic deformations [8]. Under a prolonged (tens of hours) action of high temperatures the

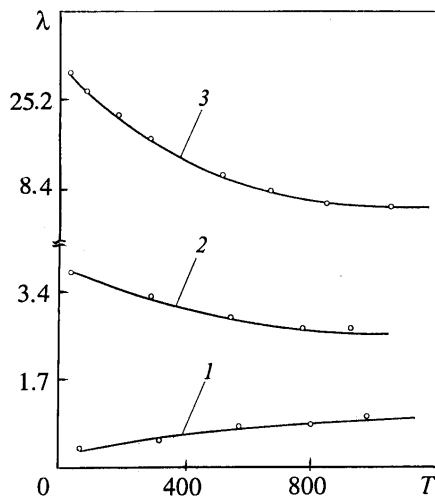


Fig. 3. Temperature dependences of the heat conductivity coefficient of inorganic materials: 1-3) notations are the same as in Fig. 1.  $\lambda$ , W/(m·K);  $T$ , °C.

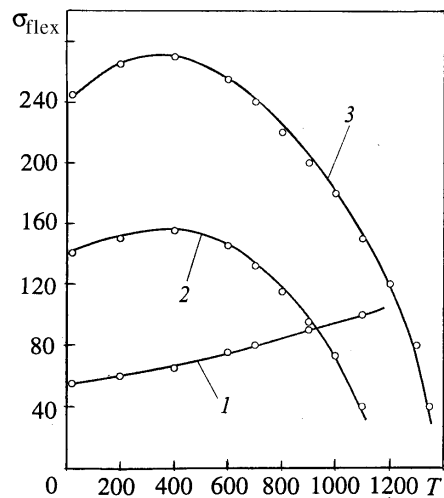


Fig. 4. Temperature dependences of the flexural strength of radiotransparent inorganic materials: 1-3) notations are the same as in Fig. 1.  $\sigma_{flex}$ , MPa;  $T$ , °C.

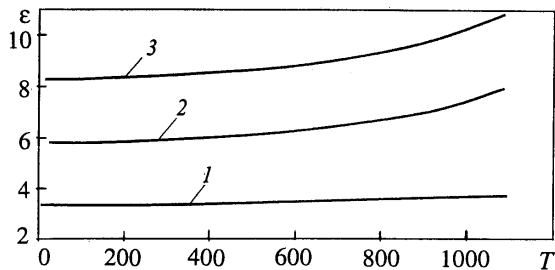


Fig. 5. Temperature dependences of the permittivity of radiotransparent inorganic materials: 1-3) notations are the same as in Fig. 1.  $T$ , °C.

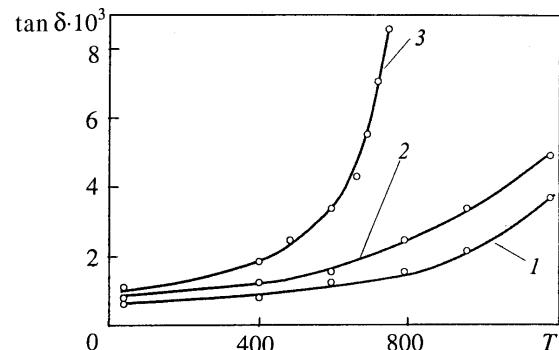


Fig. 6. Temperature dependences of  $\tan \delta$  of radiotransparent inorganic materials: 1)  $\text{Al}_2\text{O}_3$ -based ceramics; 2) quartz ceramics; 3) Pirokeram-9606.  $T$ , °C.

porous quartz ceramics, beginning with a temperature of 900°C, is subjected to additional sintering, then, at a temperature above 1100°C — to crystallization. Sintering is accompanied by compaction and strengthening of the material, and crystallization causes softening of the ceramics. Total loss of strength of the ceramics based on transparent quartz glass occurs upon its being kept in air at  $T = 1200^\circ\text{C}$  for 100–150 hours, at  $T = 1250^\circ\text{C}$  — for 50 hours, and at  $T = 1300^\circ\text{C}$  — for 10–20 hours [9]. However, in the case of short-term heating regimes analogous to the operating conditions of fairings, the material maintains strength at higher temperatures. At one-sided heating the structural strength of the material in a product increases and the service temperatures of the material increase to 1700–2000°C.

As numerous investigations in our country and abroad have shown, owing to their high thermostability and low thermal conductivity, products from quartz ceramics retain their bearing capacity even at a partial loss of the shell thickness due to the fusion and sublimation of the material [10–13].

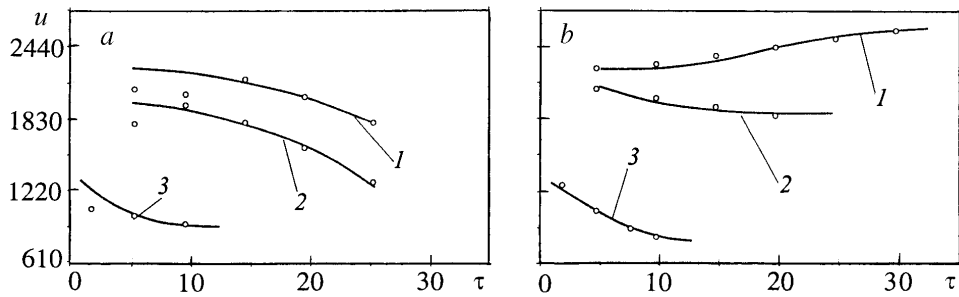


Fig. 7. Limiting possibilities of ceramics as to the combination of dielectric properties [a) launch angle  $\varphi = 20^\circ$ ; b)  $80^\circ$ ]; 1–3) notations are the same as in Fig. 1.  $v$ , m/sec;  $\tau$ , sec.

The deciding factor in choosing the material for a real fairing is the stability of the dielectric constant and the relatively low value of the dielectric loss tangent (Figs. 5 and 6) [4]. The change in the former for quartz ceramics, Pirokeram-9606, and high-alumina ceramics  $\text{Al}_2\text{O}_3$  constitutes, respectively, 1.0, 2.7, and 4.8% for the 25–500°C temperature range and, respectively, 3.0, 6.2, and 18.0% for the 25–1000°C temperature range (Fig. 5).

In the temperature range up to 1200°C, the change in the dielectric constant of quartz ceramics does not exceed 4%, and even in the case where the material is brought up to the quartz glass melt ( $T = 1800$ –2000°C), the dielectric constant does not exceed 4.1 unities [14]. The low heat conductivity of quartz ceramics for one-sided short-term heating regimes prevents the shell from being heated to a large depth and the high temperature is localized in a surface layer up to 0.5 mm thick, which considerably increases the serviceability of the fairing in terms of the radiotechnical characteristics.

The absolute value of the dielectric constant is also of great importance for providing radiotechnical characteristics. It is the lowest in quartz ceramics (Fig. 5), and this fact not only decreases distortions in the aerial directivity diagram and superreflection SHF losses, but also simplifies the technological process of mechanical treatment of shells, since the standard wall thickness tolerances are lower than for other materials.

L. B. Weskesser et al. [15] reported on investigations to find the limiting possibilities of various materials and to combine their dielectric properties as applied to aerial fairings with a half-wave thickness of the wall. Limitations for different materials are characterized by the maximum permissible speed as a function of the flight altitude and time. Evaluation of the limiting possibilities of materials was carried out with regard for the change in  $\epsilon$  and  $\tan \delta$  in the process of aerodynamic heating. The limiting possibilities of materials according to [15] for two launching angles are presented in Fig. 7. Quartz ceramics compares favorably with materials based on  $\text{Al}_2\text{O}_3$  and Pirokeram-9606 in the combination of dielectric characteristics.

A number of works present the results of calculations of the limiting possibilities of radiotransparent materials also for the half-wave wall of fairings by their fusion temperatures and simultaneous action of temperature and aerodynamic and inertial loads. As the limiting speed values for the fusion temperature, the speed at which the temperature of the outer surface of the fairing at a distance of 100 mm from the nose reaches the fusion temperature of the material was taken. Quartz ceramics with a fusion temperature of 1700°C and a high melt viscosity can also perform well at temperatures up to 2500°C.

Under a simultaneous action of temperature and aerodynamic and mass loads, as is observed under real operating conditions of aerial fairings,  $\text{SiO}_2$ -based materials are also preferable. It is noted that for  $\text{Al}_2\text{O}_3$  fairings the maximum speed is 4–5 M, for fairings from Pirokeram-9606 — 5.5–6.5 M, and for quartz ceramics — 8–10 M. Of course, the estimation made does not exclude widening of the field of application of the materials under consideration due to the upgrading and stabilization of the physicotechnical properties of the materials and improvement of the fairing design, but it reflects fairly well the qualitative characteristic of the serviceability of fairings from the materials under consideration.

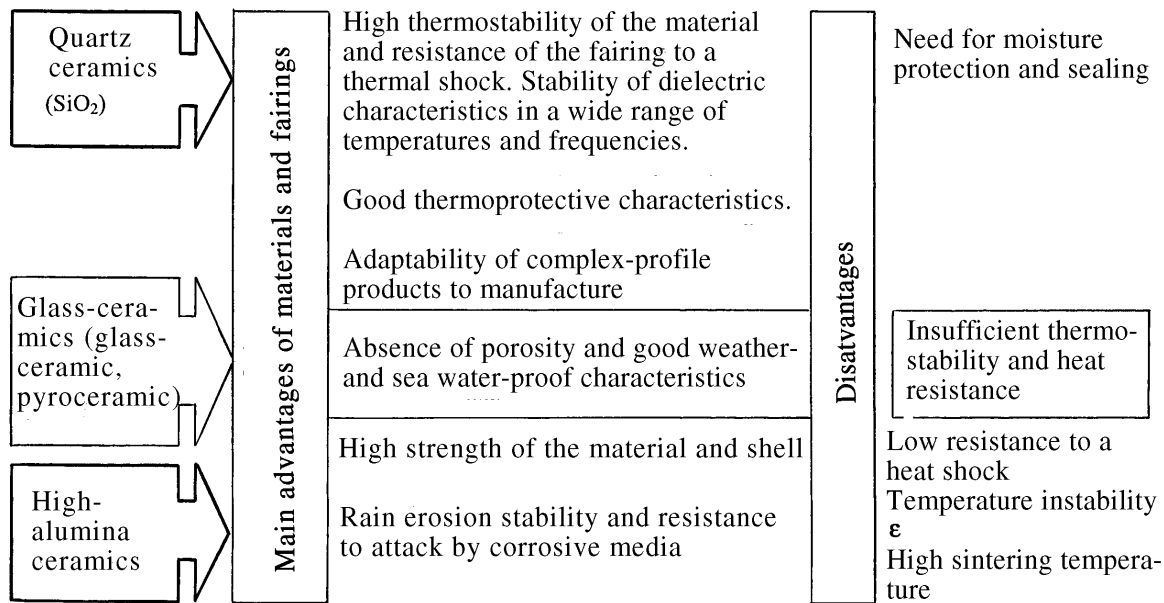


Fig. 8. Integrated comparative characteristics of radiotransparent, high-thermostability inorganic materials

An important advantage of quartz ceramics is its workability. Organization of the manufacture of products from it requires no expensive equipment, and as source materials, quartz materials widely distributed on the earth's surface — vein quartz and glass sands — are used. Various silica glass production wastes are also used. If we take for comparison molding of articles from high-alumina ceramics, pyro- and quartz ceramics, in the first case molding is carried out by hot slip casting with the addition of more than 10% of organic binder, which is then burnt, releasing harmful substances. In the second case, products are molded from glass melt at high temperatures under the conditions of hot production, whereas products from quartz ceramics are easily molded by the method of water slip casting in normal plaster molds. The annealing temperature of quartz ceramic products is 1240–1270°C, for which instead of the high-temperature gas furnaces for annealing articles from Al<sub>2</sub>O<sub>3</sub> with a temperature of 1650°C simple-to-operate electric furnaces are used. Because of their small hardness, articles from quartz ceramics are relatively easy to work. It should be noted that because of the small annealing shrinkage (up to 1.5% for quartz ceramics versus 10% for high-alumina ceramics) and convenience of slip casting molding as compared, for example, to the centrifugal molding of pyroceramics, the conditions for manufacturing quartz ceramics with a small machining allowance are created. This significantly simplifies the manufacturing process and reduces the labor content and consumption of raw and other materials. The technology of obtaining highly concentrated casting slips as well as dense and strong castings developed by the Obninsk specialists [5] has made it possible to master the manufacture of large-sized (up to 1.5 m) articles, which is still impossible to do with pyroceramics by the traditional glass technology and with high-alumina ceramics.

Analysis of the level of the physicochemical properties and technological possibilities of these materials (Fig. 8) shows that in the world's experience there is no single material or composition capable of satisfying the requirements placed upon fairings. Because of this fact scientists and practical workers are compelled to establish a line of demarcation between the fields of application of materials as applied to the conditions of creating fairings of particular systems.

For instance, quartz ceramics with a porosity of 8–10% is widely used in fairings of S-300 rocket complexes of various modifications (Russia), "Patriot" missiles (USA), and other systems whose operation calls for the use of protective transport-launch containers. At the same time, due to the comparatively low

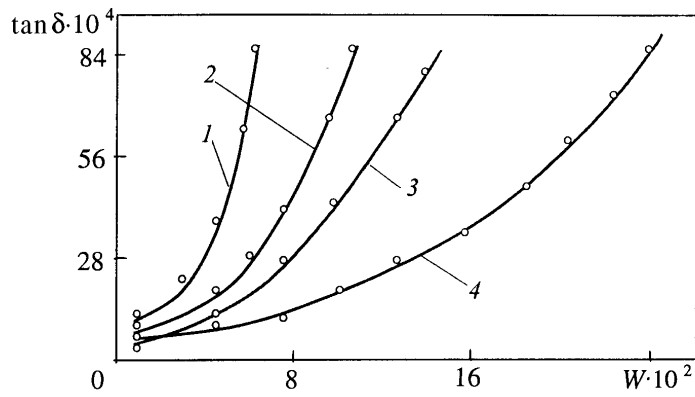


Fig. 9. Dielectric loss tangent  $\tan \delta$  of quartz ceramics of different porosity versus moisture absorption: 1)  $\Pi = 6.8$ ; 2) 11.5; 3) 16.3; 4) 18.7%.  $W$ , %.

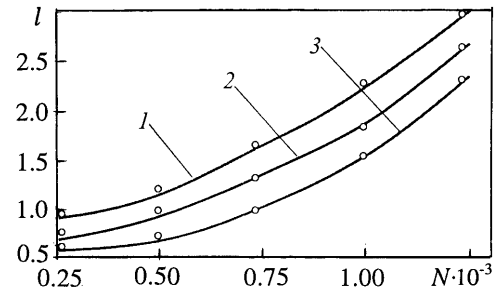


Fig. 10. Damage depth of quartz ceramics with a porosity of 8.5% versus the droplet load intensity at various impact velocities (m/sec): 1) 120; 2) 150; 3) 180.  $l$ , mm;  $N$ , imp/min.

mechanical strength, the ability to absorb environmental water (Fig. 9), and the low dust and rain erosion resistance (Fig. 10) the use of quartz ceramics for fairings of airdrome and ship-based missiles becomes practically impossible [16, 17]. For these types of missiles in the USA pyroceramics and alumooxide ceramics are widely used. In Russia, airdrome and ship-based missiles are mainly furnished with pyroceramic fairings, since this class of materials, having obvious advantages in a number of physicochemical properties over alumooxide ceramics, features a better workability than the latter.

However, in the former USSR the development and manufacture of radiotransparent pyroceramic fairings for missiles made under the order of the Defence Ministry were concentrated at the only enterprise which is now outside of Russia. Taking into account the political and foreign economic situation that has formed in the relations between the CIS countries as well as the fact that the materials developed in the 1960–70s, including pyroceramics (AS-418, AS-370, AS-023, etc.), are obsolescent and no longer satisfy the requirements for fairings, the need for investigations on the synthesis of new materials capable of replacing imported pyroceramic fairings for furnishing the Russian military machinery and providing the possibility of making prospective missiles is becoming obvious.

Taking into account the important properties of quartz ceramics and pyroceramics, attempts were made time and again to combine them into a single complex and create a material featuring simultaneously high thermostability and permittivity, high strength and low porosity, and stability of dielectric and strength characteristics in a wide range of temperatures.

For instance, in [18] the possibility of obtaining quartz ceramics with zero water absorption due to the introduction into the  $\text{SiO}_2$  matrix of sintering activators is shown. The technology enabled us to obtain fairings, but we failed to increase the strength of the material compared to the quartz ceramics.

In [9], an attempt was made to bring the permittivity value of quartz ceramics to the level of the known pyroceramics Pirokeram-9606 and -9608 by introducing into the material up to 25% of  $\text{TiO}_2$  admixtures. And although the author managed to increase the permittivity value to 6.5 unities, the strength and structural characteristics of the material were greatly impaired. For instance, the bending strength decreased to 35 MPa and the material porosity increased to 25%. In [20, 21], owing to the change of the nature of the  $\text{TiO}_2$  admixture, we managed to synthesize a quartz ceramic with a permittivity of up to 5.5 unities and a bending strength of up to 65 MPa but failed to obtain a nonporous material of the type of pyroceramics.

TABLE 1. The Main Characteristics of Ceramic Radiotransparent Materials Based on Amorphous Silicon Dioxide

Characteristics	Brand of material						
	TSM-109	TSM-107	Niacite	OTM-920	OTM-921	OTM-607	OTM-605
Density ( $\gamma$ ), g/cm <sup>3</sup>	2.10–2.15	2.15–2.18	1.94–2.05	1.70–1.75	1.26–1.33	0.5–0.6	0.3–0.4
Porosity ( $\Pi$ ), %	5–10	≤0.5	8–10	21–25	40–43	70–80	82–86
Flexural strength ( $\sigma_{\text{flex}}$ ), MPa	65	55	45	28	20	9	3
Heat conductivity ( $\lambda$ ), W/(m·K)	1.8	1.5	0.7	0.6	0.4	0.1	0.07
CTLE ( $\alpha \cdot 10^7$ ), deg <sup>-1</sup>	≤9.5	≤7.5	≤7.5	≤7.5	≤7.5	≤7.5	≤7.5
Permittivity ( $\epsilon$ ) at $f = 10^{10}$ Hz, 20°C	5.5	3.7	3.5	2.9	2.5	1.5	1.3

The authors of [22] managed to make a moisture-protective, erosion-resistant layer on a totally treated shell from porous quartz ceramics by fusing its outer surface to a depth of 0.05–0.5 mm. But the inner surface of the fairing remained unprotected against moisture, which gave no guarantee against ingress of moisture into the fairing.

Analysis of the results of the investigations to modify quartz ceramics by oxides and compounds in order to obtain particular new properties of the material shows that this method is only good for solving particular local problems, although they are also important, and the results are demanded by industry, but it was impossible to solve the problem as a complex by this method. On the one hand, as a result of quartz glass crystallization, the material is not sintered to zero porosity on the addition of a large amount of modifying admixtures and, on the other hand, the obtained nonporous quartz ceramics cannot replace the pyroceramic fairing because of the relatively low permittivity value — 3.72 — which causes an increase in the fairing wall thickness [19] and weight. Moreover, the industry is oriented to the production of control means proceeding from the properties of pyroceramics. Therefore, a simple replacement of one material by another would call for a change in the design of missiles and complete restructuring of missile control systems, which is an extremely difficult, time-consuming, and expensive problem. The principal properties of the materials based on amorphous silicon dioxide with a porosity from zero to 85% are presented in Table 1.

Analogously to the works on unification of the properties of quartz ceramics, investigations with the aim of improving the properties of the previously developed radiotechnical-purpose pyroceramics were also made. They were primarily directed at increasing their thermostability and mechanical strength and at stabilizing the dielectric characteristics. The factors preventing the realization of this complex of important properties of pyroceramics, namely, the presence of bubbles and cavities, surface and bulk defects, the structure and phase composition, and the technological regimes, were subjected to thorough analysis [23–26]. As a result, methods for increasing the mechanical strength and thermostability and for stabilizing the dielectric characteristics of pyroceramics were developed. For instance, in [27–32] it is shown that it is possible to increase significantly the mechanical strength, the impact elasticity, and the thermostability of pyroceramics of the cordierite and  $\beta$ -spodumene series as a result of etching in HF and H<sub>2</sub>SO<sub>4</sub> solutions to a depth of up to 300  $\mu\text{m}$  followed by ion exchange treatment of the materials in NaNO<sub>3</sub> and KNO<sub>3</sub> melts. In the first case, the surface defects of the materials are stripped and in the second case compressive stresses are formed.

In [33, 34], it is shown that the technological procedures in making pyroceramics (correction of the chemical composition of the source glass, increasing the holding time at the crystallization temperature to 10 h) make it possible to stabilize the dielectric characteristics of pyroceramics in the range of temperatures up to 600–700°C.

The above works and a number of other investigations point to an extensive search for ways and means of improving the properties of radiotechnical-purpose pyroceramics, but there is a lack of advanced means for radically improving the properties of pyroceramics. This is largely due to the technology of obtain-

TABLE 2. The Main Characteristics of Glass-Ceramics Used for Making Aerial Fairings

Characteristics	Brand of material			
	Pirokeram-9606 (USA)	AS-370 (Ukraine)	Pirokeram-9608 (USA)	AS-418 (Ukraine)
Density ( $\gamma$ ), g/cm <sup>3</sup>	2.60	2.6–2.7	2.5	2.5–2.6
Water absorption ( $W$ ), %	0	≤0.02	0	≤0.02
Flexural strength ( $\sigma_{flex}$ ) at 20°C, MPa	120–260	170–210	110–130	100–145
Elastic modulus ( $E_{st} \cdot 10^{-4}$ ), MPa	12.3	13.2	8.8	9.0
CTLE ( $\alpha \cdot 10^7$ ) at 20–600°C, deg <sup>-1</sup>	15–57	20–40	4–20	5–22
Heat conductivity coefficient ( $\lambda$ ) at 20–600°C, W/(m·K)	3.0–2.2	3.1–2.1	1.8–2.0	1.8–2.0
Specific heat capacity ( $c$ ) at 20–600°C, kJ/(kg·K)	0.8–1.3	0.9–1.3	1.75–1.2	0.5–1.1
Permittivity ( $\epsilon$ ) at $f = 10^{10}$ Hz, 20°C, unities	5.7	6.7	6.9	7.5
Dielectric loss tangent ( $\tan \delta$ ) at $f = 10^{10}$ Hz, 20°C	0.0002	0.0012	–	0.015
Thermostability ( $\Delta T$ ), °C	350	400	550	600

ing pyroceramics when it is exceedingly difficult and at times impossible to considerably change the initial chemical composition of glasses.

The classical (glass) technology of obtaining pyroceramics provides limited compositions of pyroceramics and impedes their development in the direction of raising the level of their properties.

First, the necessity of providing the capacity of a pyroceramic composition for glass formation and the required technological properties of the melt makes it impossible to obtain pyroceramics on the basis of the majority of crystalline phases and generates a need for introducing into the glass composition, apart from oxides, a large group of additional components corresponding to the composition of a given crystalline phase, which can impede the separation of a given phase or sharply decrease its content.

Second, the limitation of the upper bound of the boiling temperature ( $\sim 1600^\circ\text{C}$ ) makes it impossible to synthesize pyroceramics on the basis of refractory phases and thus obtain heat-resistant materials.

Third, the lack of knowledge of the laws of relationships between the properties of multiphase materials and their structure and of the processes of catalyzed crystallization of glass on the whole impedes control of the pyroceramic manufacturing process and optimization of this technology.

With all its visible drawbacks, the classical (glass) technology of obtaining pyroceramics including the following stages — preparation of a mixture of a given chemical composition, making of glass, molding of articles by centrifugal casting, compacting or rolling, annealing of articles, crystallization and mechanical treatment of articles — is the main technology used both in our country and abroad in making aerial fairings of airdrome and ship-based missiles. The theory and practice of manufacturing articles from technical pyroceramics by the above technology are described in [36–40].

By now, hundreds of pyroceramic compositions have been synthesized. However, not many of them have been introduced into production, and for manufacturing aerial fairings of missiles only a few are being used. The most promising pyroceramics for aerial fairings are those in the  $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MgO}$  system (Pirokeram-9606 (USA), AS-370 and AS-023 (Ukraine)) and in the  $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--Li}_2\text{O}$  system (Pirokeram-9608 (USA) and AS-418 (Ukraine)). The pyroceramics of the first system contain no ions of alkali metals, which endows them with low dielectric losses. However, because of the high coefficient of thermal linear expansion (CTLE) their thermostability is not high. The pyroceramics of the second system have worse values of the dielectric loss tangent, but because of the low CTLE values their thermostability is higher. The main crystalline phases of the pyroceramics of the first group are cordierite ( $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ ), rutile ( $\alpha\text{TiO}_2$ ), and



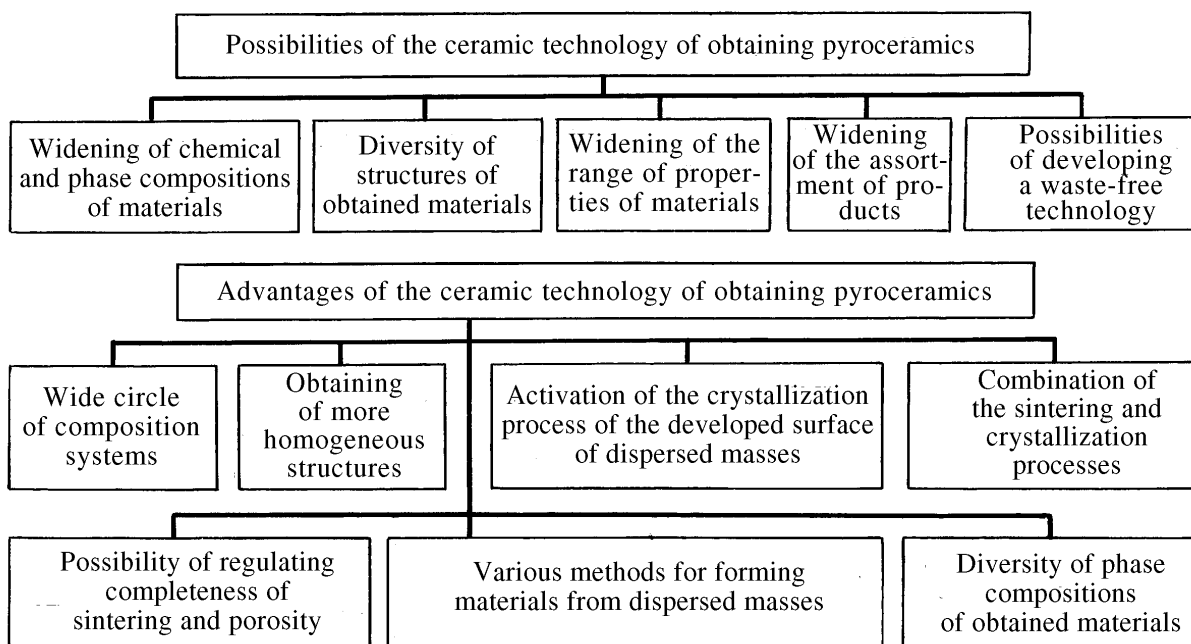


Fig. 11. Possibilities and advantages of the ceramic technology of obtaining pyroceramics compared with the classical technology

solid solution of  $\beta$ -quartz. The main crystalline phases of the second group pyroceramics are solid solutions of  $\beta$ -spodumene ( $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ ), rutile ( $\alpha\text{TiO}_2$ ), and solid solution of  $\beta$ -eucryptite ( $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ). The basic physicochemical characteristics of these pyroceramics, according to domestic and foreign sources, are reported in Table 2.

The values of the characteristics (Table 2) of materials belonging to one system are close in their indices, which points to the possibilities of these systems. This is why in recent times more and more consideration is being given to the ceramic technology of synthesizing glass ceramics. The procedure consists of granulating a melted glass mass by a water jet, powdering the granules, postforming of blanks by the dry-press process of molding or thermoplastic pressure casting with the use of binders (paraffin plasticizers, polyvinyl alcohol or silicon-organic binders) followed by sintering and crystallization of the material [35, 41–51]. The integrated data on the possibilities and advantages of the ceramic technology of obtaining pyroceramics as compared with the classical (glass) technology are given in Fig. 11.

The traditional (glass) technology restricts the possibilities of obtaining a given phase composition and, therefore, the properties of the material because of the necessity of using for synthesis only materials with glass-forming compositions. At the existing temperatures of glass founding ( $\sim 1600^\circ\text{C}$ ) the range of such compositions does not include a number of crystalline phases such as mullite, spinel, zircon, and many other phases capable of providing a complex of radically new physicochemical properties of materials, including the ability to dramatically increase the temperature of using articles from them. Under normal (traditional) conditions of synthesis, the content of these phases in pyroceramics is relatively small and an increase in their number can only be attained by increasing the glass founding temperature (to  $1800\text{--}1900^\circ\text{C}$ ), which is highly problematic. With the use of the ceramic technology these difficulties can be overcome by correcting the composition of the molding mass due to the addition of admixtures activating the formation of a desirable phase. In this case, the phase composition and structure of the material are formed not only due to the glass crystallization (which is characteristic of classical pyroceramics), but also as a result of the proceeding of a reaction between the admixtures and the glass components. The properties of the thus-obtained glass-ceramics will be determined by the chemical composition in general. For instance, in [52] a glass-ceramic containing

TABLE 3. The Characteristics of Glass-Ceramics According to the Data of [52]

Characteristics	Admixtures		Characteristics	Admixtures	
	MgF <sub>2</sub>	AlF <sub>2</sub>		MgF <sub>2</sub>	AlF <sub>2</sub>
Density ( $\gamma$ ), g/cm <sup>3</sup>	2.31	2.02	CTLE ( $\alpha \cdot 10^6$ ), deg <sup>-1</sup>	2.33	2.0
Porosity ( $\Pi$ ), %	0.8	12.7	Impact elasticity ( $\sigma_{imp}$ ), kg·cm/cm <sup>2</sup>	3.3	1.4
Compression strength ( $\sigma_{comp}$ ), MPa	150	234	Softening temperature ( $T_{soft}$ ), °C	1600	1600

in its structure up to 80% mullite obtained by the ceramic technology is reported. The material was made from aluminosilicate glass (45% SiO<sub>2</sub> and 55% Al<sub>2</sub>O<sub>3</sub>) with the addition of fluorides. Some of its characteristics are reported in Table 3.

In obtaining high-quality articles from pyroceramics by the classical (glass) technology, the problem of providing homogeneity of the glass mass and articles is particularly complicated. The high temperatures of glass founding and manufacturing cause a considerable amount of spoilage and lower the useful output of melted glass mass. The formation of glass into granulate and the averaging of the characteristics while grinding and preparing molding masses eliminates this drawback. The process of shaping products, in particular, fairings from a glass mass, is also very complicated for technical reasons: sophisticated equipment, high temperatures, and the inevitability of large technological allowances. The ceramic technology compares favorably in this respect, since it permits obtaining blanks with minimum variations in thickness, and the configuration and shape of an article are practically not specified. An important distinguishing feature of the ceramic technology of obtaining pyroceramics is a considerable shortening and simplification of the thermal treatment regime. This is explained by the fact that the developed surface of fine glass powders can successfully act as a catalyst [41, 44]. The properties of porous and high-porosity pyroceramics is another advantage of the ceramic technology. In [47, 50], the possibility of obtaining  $\beta$ -spodumene ceramics by the method of thermoplastic casting followed by blank sintering at temperatures of 1000–1250°C with a porosity from 1 to 40% and a strength up to 90 MPa is shown.

The ceramic technology of obtaining glass-ceramics makes it possible to combine the process of material sintering and glass crystallization and use different methods of molding from dispersed masses, including water slip casting of blanks [51]; it also provides the possibility of reclaiming technological wastes and is indispensable at small volumes of production as well as in the cases of frequent and quick change of the assortment of articles.

The use of the latest achievements of the present technology — matrix reinforcement, sol-gel processes, reaction formation of phases, and other methods — opens up wide prospects for developing glass-ceramics with a qualitatively new level of properties.

In general, the analysis of the state of the art of synthesis of glass-ceramics shows that novel methods and directions in the field of pyroceramic technology are being developed intensively.

To develop works on replacement of imported pyroceramic fairings, for the Obninsk scientific-production enterprise "Tekhnologiya" the ceramic method of synthesizing materials and technologies is the most advantageous and technologically justified, since the enterprise has more than 30 years of experience in developing and producing fairings from SiO<sub>2</sub>- and Al<sub>2</sub>O<sub>3</sub>-based ceramics. Works on the development and production of fairings are carried out as a complex: from agreeing upon the technical assignment for a fairing to its production, including the electrodynamic and heat resistance calculations of the design, the development of the material and technology needed for these purposes, the production of prototypes and their land trial followed by their production in quantities and delivery of products to the customer.

TABLE 4. The Main Characteristics of Pyroceramics Based on Lithium Aluminum Silicate Glass Obtained by the Ceramic Technology with the Use of the Method of Slip Casting from Water Suspensions

Characteristics	Values of indices	Characteristics	Values of indices
Density ( $\gamma$ ), g/cm <sup>3</sup>	2.47	Microhardness ( $\sigma_{\text{hard}}$ ), MPa	8000
Water adsorption ( $W$ ), %	0.1	CTLE ( $\alpha \cdot 10^7$ ) at 20–700°C, deg <sup>-1</sup>	4–8
Flexural strength ( $\sigma_{\text{flex}}$ ), MPa:		Heat conductivity coefficient ( $\lambda$ ) at 20–500°C, W/(m·K)	1.7–2.0
at 20°C	90–110	Permittivity ( $\epsilon$ ) at $f = 10^{10}$ Hz,	6.9–7.3
at 1150°C	90–110	20°C, unities	
Elastic modulus ( $E_{\text{st}} \cdot 10^{-4}$ ), MPa)	5.6	Thermostability ( $\Delta T$ ), °C	≥1200

As the basic variant in conducting investigations, we used lithium aluminum silicate glass, since pyroceramics based on it display satisfactory technical characteristics and are used in making fairings for furnishing the Russian military machinery.

As the base technology, we used water slip casting, which permits obtaining high-density, large-sized complex-profile blanks, which in turn can provide the obtaining of nonporous fairings. The basic characteristics of one of the materials obtained by the ceramic technology are reported in Table 4.

## NOTATION

$\Delta T$ , temperature difference, °C;  $M$ , speed in Mach numbers;  $d$ , thickness of the product wall, mm; SHF, superhigh frequency;  $a$ , heat-transfer coefficient;  $T$ , trial temperature, °C;  $\alpha$ , coefficient of thermal linear expansion (CTLE), deg<sup>-1</sup>;  $\lambda$ , heat conductivity coefficient, W/(m·K);  $\sigma_{\text{flex}}$ , ultimate flexural strength, MPa;  $\sigma_{\text{comp}}$ , ultimate compression strength;  $\sigma_{\text{imp}}$ , impact strength, kg·cm/cm<sup>2</sup>;  $\sigma_{\text{hard}}$ , microhardness, MPa;  $\epsilon$ , permittivity;  $\tan \delta$ , dielectric loss tangent;  $W$ , moisture absorption, %;  $\Pi$ , porosity of samples, %;  $\gamma$ , density, g/cm<sup>3</sup>;  $c$ , specific heat capacity, kJ/(kg·K);  $T_s$ , softening temperature, °C;  $l$ , damage depth, mm;  $N$ , droplet load intensity, imp/min;  $v$ , flying speed, m/sec;  $\varphi$ , launch angle, deg;  $\tau$ , flight time, sec;  $E_{\text{st}}$ , elastic modulus, static, MPa.

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