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*O.V. Zaichuk, A.A. Amelina, Y.S. Hordieiev, D.V. Filonenko, Y.R. Kalishenko, O.S. Khomenko*

## HEAT-RESISTANT RADIO-TRANSPARENT CERAMICS IN THE $\text{SrO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ SYSTEM MODIFIED WITH $\text{BaO}$

**Ukrainian State University of Science and Technologies, Dnipro, Ukraine**

Strontium anorthite ceramics modified with barium oxide were synthesized using glasses of composition  $(37.4-x)\text{SrO}-x\text{BaO}-7.8\text{Al}_2\text{O}_3-10.5\text{B}_2\text{O}_3-44.3\text{SiO}_2$ , where  $x$  ranged from 0 to 20 mol.%. The crystallization of the strontium anorthite phase was achieved through reaction-based structure formation, incorporating crystalline fillers to supply any deficient components. The ceramics demonstrated zero water absorption at a low firing temperature of 1250°C. The primary crystalline phase identified was monoclinic strontium anorthite, forming a uniform structural matrix. Strontium anorthite formed a solid solution with barium owing to the similar ionic radii and charges of  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ , preserving the integrity of the basic structural units. The ceramics demonstrated excellent thermal characteristics, including thermal stability up to 800°C and refractoriness of 1460°C. Dielectric characterization at  $10^{10}$  Hz showed a relative permittivity of 4.9–5.0 and low dielectric losses ( $\tan\delta=0.001$ ), which allows the developed ceramics to be used in the aerospace and rocket industries.

**Keywords:** radio-transparent ceramics, firing, microstructure, strontium anorthite, thermal characteristics.

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### Introduction

The improvement of and aerospace and rocket technologies demands the development of novel dielectric materials, particularly glass-ceramic and ceramic materials with diverse and robust functional properties. Materials used in radar systems and in the protective components of onboard radio equipment for guided missiles must meet a stringent set of performance requirements. Chief among these are high transparency in the radio frequency range ( $10^5$ – $10^{12}$  Hz), resistance to erosion, and the ability to endure extreme thermomechanical stresses [1].

Relatively cost-effective, heat-resistant, and radio-transparent materials include silicon dioxide ceramics as well as aluminosilicate-based ceramic and glass-ceramic materials [2]. However, quartz ceramics exhibit

significant limitations, notably low mechanical strength and a working temperature of around 1000°C [3]. Aluminosilicate systems offer an alternative for producing radio-transparent materials with improved sintering and thermomechanical performance. Nevertheless, many existing aluminosilicate glass-ceramic and ceramic materials still fall short of the comprehensive functional property requirements demanded by the aerospace and missile industries. Glass-ceramic [4] and ceramic [5] materials based on cordierite ( $2\text{MgO}-2\text{Al}_2\text{O}_3-5\text{SiO}_2$ ) exhibit high thermomechanical stability. However, cordierite's relatively low melting point (1465°C) limits its practical application to operating temperatures no higher than 1100°C.

Celzian-based materials ( $\text{BaO}-\text{Al}_2\text{O}_3-2\text{SiO}_2$ )

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*Heat-resistant radio-transparent ceramics in the  $\text{SrO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  system modified with  $\text{BaO}$*

demonstrate superior thermal resistance owing to their high melting point (1740°C). Still, their widespread adoption is hindered by inherent drawback – specifically, comparatively low mechanical strength and higher specific gravity relative to other aluminosilicate radio-transparent materials [6].

Strontium anorthite ( $\text{SrO}-\text{Al}_2\text{O}_3-2\text{SiO}_2$ )-based ceramics emerge as promising candidates for high-temperature applications, offering excellent thermal stability (up to and beyond 1400°C), consistent dielectric properties at high temperatures and frequencies, improved mechanical strength, and lower density compared to celcian-based counterparts. For example, the calculated density of celcian, crystallizing in monoclinic symmetry, is 3.30 g/cm<sup>3</sup>, whereas that of monoclinic strontium anorthite is 3.08 g/cm<sup>3</sup> [7].

Conventional glass-crystalline synthesis of strontium-anorthite ceramics involves high energy costs, requiring glass melting temperatures of 1650–1700°C and crystallization times up to 20 hours. Additionally, the process limits the complexity of product geometries and the precision of composition control. To achieve greater reproducibility and consistency in functional properties, ceramic technology is preferable. However, ceramic methods often struggle to produce water-resistant materials, which are essential for erosion resistance [7,8].

The addition of a fluxing component like  $\text{SrO}-3\text{B}_2\text{O}_3$  facilitates liquid-phase sintering and recrystallization, promoting a dense microstructure [9]. However, the high  $\text{B}_2\text{O}_3$  content significantly reduces the material's thermal resistance. Similarly, introducing borosilicate glass or spodumene-based glasses in the  $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$  system [10,11] activates sintering. While full densification occurs at 1350°C with 10 wt.% borosilicate glass, excessive glass leads to quartz or cristobalite formation, which is detrimental to thermal stability. Optimal spodumene glass content (20–30 wt.%) also reduces thermal resistance and increases dielectric losses due to  $\beta$ -spodumene formation.

Studies on  $\text{SrO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  (SAS) glasses show that hexagonal strontium-anorthite typically forms first and persists as a metastable phase at lower temperatures. It undergoes a volume-changing phase transition (3%) to the orthorhombic form, compromising thermomechanical performance. In contrast, the monoclinic modification offers superior properties, including a high melting point (1650°C), a low coefficient of thermal expansion (CTE) of  $35 \cdot 10^{-7} \text{ }^\circ\text{C}^{-1}$ , and enhanced strength [12].

Studies [13] have demonstrated that solid-state sintering of  $(\text{Ba},\text{Sr})\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  ceramics can promote the transformation of hexagonal celcian into

its monoclinic form through the controlled addition of SrO. This approach also has the potential to lower sintering temperatures. Moreover, SrO additions enhance the crystallization of celcian-based glass ceramics, broadening the gap between crystallization and softening temperatures and improving densification. Celcian and strontium-anorthite form continuous solid solutions of the  $(\text{Ba}, \text{Sr})\text{Al}_2\text{Si}_2\text{O}_8$  type across the full compositional range of the  $\text{BaAl}_2\text{Si}_2\text{O}_8-\text{SrAl}_2\text{Si}_2\text{O}_8$  binary system. This allows for the fine-tuning of the microstructure and thermal, physical, and mechanical properties of both ceramic types.

Thus, the aim of this work is to study the physical, mechanical, thermal properties and structural features of strontium-anorthite ceramics modified with barium oxide, as well as the technological parameters of its production.

#### **Materials and methods**

The strontium-anorthite ceramics modified with barium oxide were synthesized using glass from the  $(37.4-x)\text{SrO}-x\text{BaO}-7.8\text{Al}_2\text{O}_3-10.5\text{B}_2\text{O}_3-44.3\text{SiO}_2$  (SBABS) system (with  $x$  ranging from 0 to 20 mol.% BaO), enriched kaolin grade zref-1 (Ukraine), strontium carbonate (reagent-grade, China), technical alumina (H-0 grade, Ukraine), and silicon(IV) oxide (grade A, Ukraine).

For the preparation of the glass, technically pure raw materials were employed, comprising strontium carbonate ( $\text{SrCO}_3 \geq 99.9 \text{ wt.}\%$ ), barium carbonate ( $\text{BaCO}_3 \geq 99.9 \text{ wt.}\%$ ), technical alumina (grade G-0, purity  $\geq 98 \text{ wt.}\%$   $\text{Al}_2\text{O}_3$ ), silicon(IV) oxide (grade A, purity  $\geq 99.5 \text{ wt.}\%$   $\text{SiO}_2$ ), and boric acid (purity  $\geq 99.8 \text{ wt.}\%$   $\text{H}_3\text{BO}_3$ ).

#### **Glass melting**

The SBABS glass was melted at 1350°C for 1 hour in corundum crucibles within an electric furnace equipped with silicon carbide heaters. A low melting temperature was achieved through the addition of  $\text{B}_2\text{O}_3$ , which did not affect the crystalline phase composition after subsequent thermal treatment.

#### **Methodology for ceramic sample preparation**

Ceramic slips were prepared via joint wet milling of raw materials in a porcelain ball mill until the slurry fully passed through a 63  $\mu\text{m}$  sieve. Slips with 21–22% moisture content were cast into gypsum molds, producing cylindrical (10 mm in diameter and 10 mm in height), square ( $5 \times 5 \times 50 \text{ mm}^3$ ), and elongated cylindrical bars (8 mm in diameter and 80 mm in height), as well as disks (50 mm in diameter and 5 mm in thickness). The blanks were dried to a residual moisture content of no more than 1.0%. Samples for pyrometers were made in the form of a truncated triangular pyramid with a height of 30 mm, a side of the lower base of 8 mm, and the upper base

of 2 mm. The dried samples were fired in an electric furnace in air. The maximum firing temperature was 1200–1375°C with an isothermal hold for 1 hour. Firing was carried out in an electric furnace with silicon carbide heaters. The heating rate was 3°C/min. The duration of heating and holding the ceramic samples at the maximum temperature was 7.0–8.0 hours. Cooling of the ceramic samples was carried out slowly along with the furnace.

#### *Research methods*

The properties of strontium-anorthite ceramic were determined according to standard methods. Water absorption ( $W$ ), open porosity ( $P$ ), and apparent density ( $\rho$ ) of the ceramic samples were measured using the saturation method followed by weighing in air and water. Compressive strength ( $\sigma_c$ ) was measured using a hydraulic press on cylindrical samples ( $d=h=10$  mm).

For measuring the relative elongation of ceramic samples ( $\Delta l$ ) depending on the temperature, ceramic samples of  $5 \times 5 \times 50$  mm<sup>3</sup> were used. The obtained data were used to calculate the average value of the CTE in the range of 20–400°C at a heating rate of 10°C/min.

The qualitative crystal phase composition of the strontium-anorthite ceramic was determined using a Philips APD-15 diffractometer in  $\text{CoK}\alpha$  radiation.

Electron microscopic studies of the strontium-anorthite ceramic fracture surfaces were conducted on a scanning electron microscope (SEM) using the MIRA3 TESKAN.

FTIR spectra in the range of 1300–400 cm<sup>-1</sup> were recorded with a Shimadzu IRSpirit-X spectrometer equipped with an ATR accessory (QATR-S, Specac).

Thermal stability ( $\theta$ ) was determined by the maximum temperature difference, in K, that the samples could withstand before showing signs of damage. An electric muffle furnace was used for the test. The holding time of the ceramic samples in the furnace at the specified temperature was 20 minutes. The heated samples were rapidly cooled in water at 20°C.

The refractoriness number ( $R$ ) was determined using pyroscopic cones fabricated from ceramic powders. The cones, placed vertically on refractory stands inside a furnace, were heated progressively until softening and tilting occurred. The refractoriness was identified by the temperature at which the pyroscope tip touched the surface of the stand on which it was placed.

The relative dielectric permittivity ( $\epsilon$ ) and the tangent of the angle of dielectric losses ( $\tan\delta$ ) were measured on a measuring device consisting of a

G4-83 generator, a C4-11 spectrum analyzer, and a biconical resonator. The samples were positioned along the axis of the resonator and connected in a unidirectional scheme. Measurements were taken at a frequency of  $10^{10}$  Hz at a temperature of 20°C. The dielectric parameters  $\epsilon$  and  $\tan\delta$  of the ceramic samples were determined by analyzing their relationships with the resonant frequency and quality factor of the biconical resonator, which were obtained through the finite element method.

#### *Results and discussion*

##### *Selection of glass compositions for strontium-anorthite ceramics*

The central objective of this study was to develop dense strontium-anorthite ceramics at reduced sintering temperatures by partially introducing the components of the  $\text{SrO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  (SAS) system through low-melting glasses.

To further reduce the firing temperature and enhance the mechanical strength of the ceramics, previous findings on celzian-type ceramics were considered [13]. These works highlighted the beneficial role of SrO, particularly in promoting favorable crystalline phases. Building on this, our earlier study investigated the partial substitution of SrO with BaO (0–20 mol.%, in 5 mol.% increments) in the eutectic glass composition S-1 of the pseudoternary SAS system. The eutectic point S-1 is characterized by the simultaneous crystallization of three phases: strontium anorthite ( $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ), strontium helenite ( $2\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ), and strontium metasilicate ( $\text{SrO} \cdot \text{SiO}_2$ ), with a reported melting point of 1355°C [14].

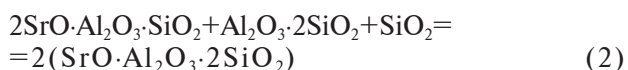
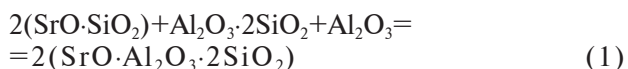
The resultant SBABS ( $\text{SrO}-\text{BaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ ) glasses were designated S-1 through S-5, corresponding to BaO contents of 0, 5, 10, 15, and 20 mol.%, respectively. Experimental results demonstrated that partial substitution of strontium oxide with barium oxide enhanced the formation of glass and promoted the crystallization of the of strontium anorthite. Because  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  have similar ionic radii, strontium anorthite is capable of forming a solid solution with celzian. These glasses were subsequently incorporated into the ceramic formulations at a fixed content of 50 wt.%.

##### *Properties of strontium-anorthite ceramics modified with BaO*

The binding of glass constituents ( $\text{SrO} \cdot \text{SiO}_2$  and  $2\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ) into the strontium anorthite phase followed «the principle of reaction structure formation», wherein the absent components were introduced through crystalline additives. The thermodynamic instability of glass imparts high thermal activity, enhancing reactivity with crystalline phases during

sintering.

The chemical reactions that demonstrate the interaction between glass components and crystalline additives are listed below:



The crystalline fillers ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ ) were added in stoichiometric amounts to ensure complete binding of the  $\text{SrO} \cdot \text{SiO}_2$  and  $2\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  phases into strontium anorthite. Firing was conducted at 1200–1375°C, with a 1-hour hold at peak temperature.

It was anticipated that the SBABS glasses (S-1 ... S-5) would act as effective mineralizers in the ceramic mixtures. Their role was to help to the forming of the strontium anorthite or solid solutions between strontium anorthite and celzian, and to enhance the sintering process.

The measured properties of the ceramics are illustrated in Table 1. Ceramic samples were labeled according to the glass type (S-1 through S-5) used in

their composition.

Glasses S-2 through S-5, created by the equimolecular substitution of SrO by BaO in the base composition (S-1), significantly enhanced the sintering behavior of the ceramics. Densely sintered ceramics with zero W and P were obtained at low sintering temperatures (1250–1300°C). The apparent density of these ceramics ranged from 2.40 to 2.53 g/cm<sup>3</sup>, increasing with BaO content across compositions S-2 to S-5. A distinct trend was observed in the relationship between firing temperature and apparent density for S-3 to S-5: apparent density peaked at 1250°C (2.46–2.53 g/cm<sup>3</sup>), coinciding with maximum compressive strength (168–197 MPa). However, increasing the firing temperature to 1300°C resulted in a decrease in density (down to 2.43–2.47 g/cm<sup>3</sup>), accompanied by a noticeable decline in compressive strength (144–159 MPa). This suggests the existence of an optimal sintering window, beyond which excessive grain growth or other microstructural changes may negatively impact mechanical properties.

The CTE of strontium-anorthite ceramics in the range of 20–400°C shows a linear relationship with firing temperature. As the firing temperature increases from 1200°C to 1300°C, the CTE gradually rises from  $(36.5\text{--}38.1) \cdot 10^{-7} \text{ } ^\circ\text{C}^{-1}$  to

Table 1

The measured physical, mechanical, and thermal properties of the experimental ceramics fired at temperatures between 1200 and 1375°C

Composition number	Firing temperature, °C	Properties of ceramic materials				
		W, %	P, %	$\rho$ , g/cm <sup>3</sup>	$\sigma_{\text{st}}$ , MPa	CTE <sub>20–400</sub> , $\times 10^{-7} \text{ } ^\circ\text{C}^{-1}$
S-1	1300	9.5	20.1	2.13	81.1	38.1
	1350	3	6.4	2.32	88.7	38.9
	1375	0	0	2.38	150.0	39.2
S-2	1200	9.2	19.1	2.17	82.5	38.0
	1250	2.5	5.3	2.34	94.8	38.5
	1300	0	0	2.40	154.5	38.9
S-3	1200	7.7	17.1	2.23	126.8	37.3
	1250	0	0	2.46	167.6	37.8
	1300	0	0	2.43	144.2	38.3
S-4	1200	2.6	6.1	2.35	135.3	36.8
	1250	0	0	2.52	194.3	37.5
	1300	0	0	2.47	158.9	38.0
S-5	1200	2.2	5	2.36	136.3	36.5
	1250	0	0	2.53	197.0	37.0
	1300	0	0	2.46	156.0	37.4



$(37.4-39.2) \cdot 10^{-7} \text{ }^{\circ}\text{C}^{-1}$ . Replacing SrO with up to 20 mol.% barium oxide in the chemical compositions of the studied glasses (compositions S-2 to S-5) results in a reduction of the CTE from  $(38.1-39.2) \cdot 10^{-7} \text{ }^{\circ}\text{C}^{-1}$  to  $(36.5-37.4) \cdot 10^{-7} \text{ }^{\circ}\text{C}^{-1}$ .

A key requirement for ultra-high-frequency (UHF) radio-transparent ceramics is low dielectric loss ( $\varepsilon < 10$ ,  $\tan \delta = 10^{-2}$  to  $10^{-5}$ ) in the frequency range of 3–30 GHz [1]. Since dielectric properties of ceramics typically remain stable across this range, measurements were conducted at a representative operating frequency of 10 GHz ( $10^{10}$  Hz), where such materials are commonly used. Dielectric parameters ( $\varepsilon$  and  $\tan \delta$ ) were measured on strontium-anorthite ceramic samples exhibiting zero water absorption (W) and open porosity (P), besides the highest compressive strength values. Thermal stability and refractoriness were also assessed for these samples, as summarized in Table 2.

The results show that strontium-anorthite ceramics possess a low relative dielectric constant, ranging from 4.9 to 6.0. Increasing the BaO content in the SBABS glass phase composition further decreases  $\varepsilon$ . Additionally, BaO-modified ceramics exhibit low dielectric losses ( $\tan \delta = 0.001-0.002$ ). The presence of BaO also enhances thermal performance: thermal stability increases from 750 $^{\circ}\text{C}$  to 800 $^{\circ}\text{C}$ , and refractoriness improves from 1440 $^{\circ}\text{C}$  to 1460 $^{\circ}\text{C}$  (Table 2).

Overall, compositions S-4 and S-5 demonstrate the best combination of properties. These compositions achieve zero water absorption at a comparatively moderate firing temperature of 1250 $^{\circ}\text{C}$ . The partial substitution of  $\text{Sr}^{2+}$  (smaller ionic radius) with  $\text{Ba}^{2+}$  (larger ionic radius) in the glass phase (composition S-1) creates internal compressive stresses, thereby enhancing the ceramic's strength ( $\sigma_{\text{st}} = 194-197$  MPa). The resulting ceramics exhibit a CTE of  $(37.0-37.5) \cdot 10^{-7} \text{ }^{\circ}\text{C}^{-1}$ , ensuring thermal stability at temperatures up to 800 $^{\circ}\text{C}$ . Additionally, their low dielectric losses ( $\varepsilon = 4.9-5.0$ ;  $\tan \delta = 0.001$ ) make them excellent candidates for use in UHF electromagnetic

applications.

#### *Phase structure and microstructural characteristics of strontium anorthite-based ceramic*

XRD analysis was performed to investigate the degree of bonding between the SBABS glass components (specifically strontium metasilicate and strontium gellenite) and the other ceramic constituents within the strontium anorthite. Figures 1 and 2 show the corresponding XRD patterns.

The XRD analysis indicated complete incorporation of the ceramic components into the crystalline phase of strontium anorthite upon firing within the temperature range of 1250–1375 $^{\circ}\text{C}$ . This conclusion is supported by the absence of diffraction peaks corresponding to other phases in the recorded patterns. The resulting strontium anorthite exhibits a stable monoclinic structure, which appears to form solid substitution solutions with celsian as the BaO content in the glass matrix increases up to 20 mol.%. As a result, the ceramic exhibits stable physical, mechanical, thermal, and dielectric characteristics.

In ceramics of composition S-1, prepared with a glass binder free of BaO, increasing the firing temperature from 1300 $^{\circ}\text{C}$  to 1375 $^{\circ}\text{C}$  enhanced the intensity of primary diffraction peaks at  $d \cdot 10^{10} = 6.40$ , 3.72, 3.40, 3.24, 3.22, 2.95, and 2.53 m associated with strontium anorthite. A similar trend was observed in the S-2 ceramic composition, produced using a glass binder containing 5 mol.% BaO, particularly upon raising the firing temperature to 1300 $^{\circ}\text{C}$ .

This enhancement results from the formation of larger and more structurally perfect monoclinic strontium anorthite crystals, a conclusion further supported by SEM examination of ceramics fracture surfaces (Fig. 3).

The S-1 ceramic samples that were fired at 1300 $^{\circ}\text{C}$  had a relatively loose microstructure, which was characterized by incompletely developed glassy and crystalline (strontium anorthite) phases. Strontium anorthite crystals are mostly spherical, with sizes ranging from 0.5 to 1.0  $\mu\text{m}$ , interconnected by thin vitreous layers forming a branched network of

Table 2

**Dielectric and thermal properties of experimental strontium-anorthite-based ceramics**

Composition number	Firing temperature, $^{\circ}\text{C}$	Dielectric properties		Thermal properties	
		$\varepsilon$	$\tan \delta$	$\theta$ , $^{\circ}\text{C}$	$R$ , $^{\circ}\text{C}$
S-1	1375	6.0	0.002	750	1440
S-2	1300	5.9	0.002	750	1450
S-3	1250	5.1	0.002	800	1450
S-4	1250	5.0	0.001	800	1460
S-5	1250	4.9	0.001	800	1460

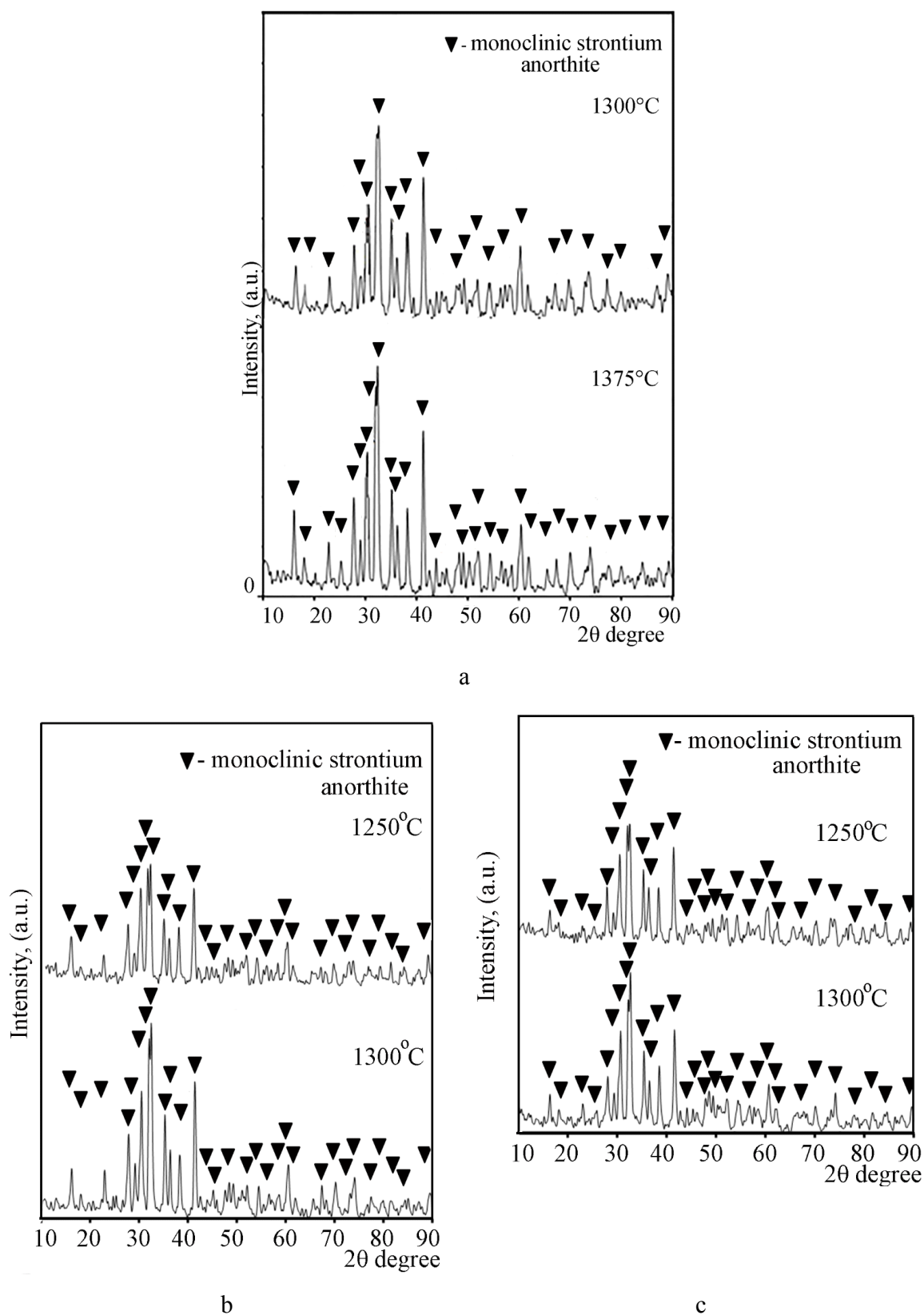


Fig. 1. XRD patterns of S-1 (a), S-2 (b) and S-3 (c) ceramics fired at different temperatures

micropores. Upon increasing the sintering temperature was to 1375°C, the microstructure evolved significantly, resulting in flat, prismatic, predominantly tetragonal-shaped strontium anorthite crystals (Fig. 3).

Crystal size increased to approximately 2–3  $\mu\text{m}$ , with occasional larger irregular crystals measuring 4–5  $\mu\text{m}$ .

The resulting microstructure becomes denser and more homogeneous, with minimal porosity, as the crystals are closely packed and bonded via thin glassy layers. In the S-2 ceramics, fired between 1250°C and 1300°C, a well-developed glassy phase is observed, effectively binding irregularly shaped flat prismatic strontium anorthite crystals. With increasing firing temperature, crystal sizes notably expand, reaching approximately 3–4  $\mu\text{m}$  (Fig. 3).

Introducing BaO into the glass phase at concentrations of 10–20 mol.% result in lowered intensity of the monoclinic strontium anorthite diffraction peaks in S-3 to S-5 ceramics. However, increasing the firing temperature from 1250°C to 1300°C results in an enhancement of these peaks, indicating the growth of strontium anorthite crystals up to 2–3  $\mu\text{m}$ . Larger crystalline aggregates (5–6  $\mu\text{m}$ ) are also formed (Fig. 4).

Although crystal enlargement negatively impacted the density and mechanical strength (Table 1), samples fired at 1250°C contained smaller, finely distributed crystals (0.5–1.0  $\mu\text{m}$ ), creating a microstructure with enhanced mechanical properties due to the presence of a well-developed glassy phase (Fig. 5 and associated data in Table 1).

The spectra obtained by FTIR analyses of the experimental ceramics in the 400–1300  $\text{cm}^{-1}$  range (Fig. 5) revealed a gradual decrease in the intensity of absorption bands with the introduction of BaO and its increasing concentration up to 20 mol.%. This reduction in absorption intensity is attributed to structural imperfections within the crystalline formations of strontium anorthite. Despite these changes, the incorporation of  $\text{Ba}^{2+}$  cations does not significantly alter the fundamental structural units of strontium anorthite. This suggests the formation of solid substitution solutions, facilitated by the similar ionic radii of  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  [14].

The absorption bands observed in the upper-frequency range (800–1200  $\text{cm}^{-1}$ ) of the FTIR spectra for the S-series strontium anorthite ceramics are associated with asymmetric stretching vibrations of Si–O–Si bonds within tetrahedral units [14,15]. These bands reflect a high degree of polymerization of silicon–oxygen tetrahedra, characteristic of the framework silicate structure to which strontium anorthite belongs. The formation of the strontium anorthite phase is additionally confirmed by X-ray diffraction data (Figs. 1 and 2).

A shift in the main Si–O stretching vibration band toward lower frequencies ( $\sim 935 \text{ cm}^{-1}$ ) is observed, which is indicative of an increase in the average (Si,Al)–O bond length. This shift results from the isomorphic substitution of  $\text{Si}^{4+}$  with  $\text{Al}^{3+}$  in the tetrahedral sites of the strontium anorthite lattice. The bands in the 500–800  $\text{cm}^{-1}$  region correspond to symmetric stretching vibrations of the Si–O–Si bonds

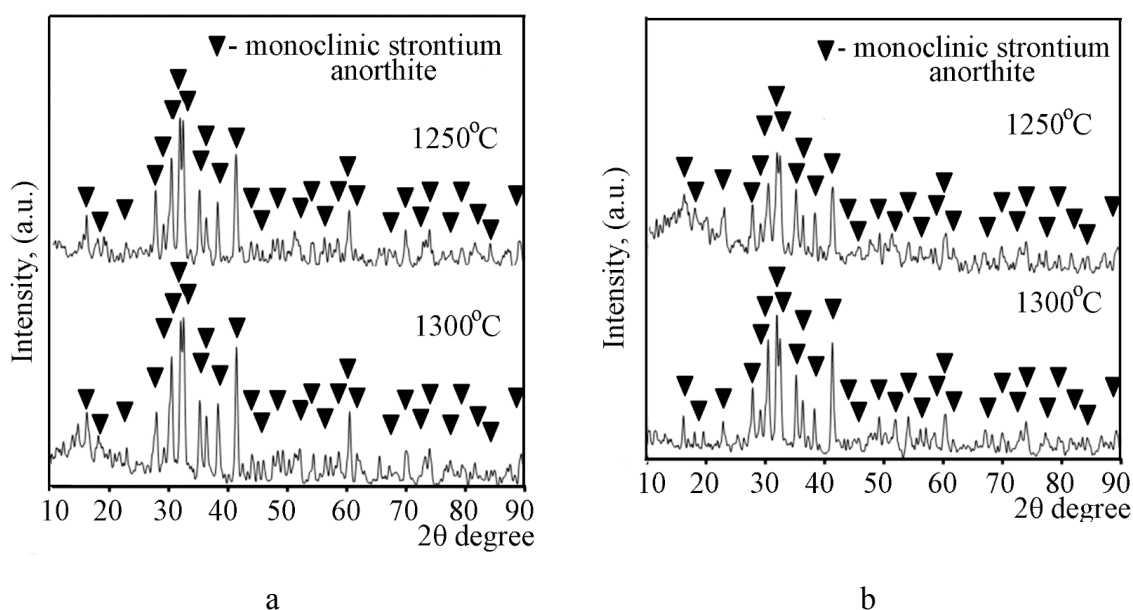


Fig. 2. XRD patterns of S-4 (a) and S-5 (b) ceramics fired at different temperatures

[15]. Notably, in the  $650\text{--}800\text{ cm}^{-1}$  range, BaO-modified ceramics show distinct spectral differences. Specifically, the doublet observed in the  $650\text{--}700\text{ cm}^{-1}$  range for the S-1 ceramic transforms into a single absorption band centered at  $668\text{ cm}^{-1}$  in the BaO-modified samples (S-2 to S-5), as shown in Fig. 5. This observation may indicate that the incorporation of BaO promotes structural disorder, leading to a random distribution of  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  cations within the tetrahedral positions of the strontium anorthite lattice. Additional spectral differences are found in the  $400\text{--}500\text{ cm}^{-1}$  region, corresponding to bending (deformation) vibrations of Si–O bonds in silicate frameworks [15]. In the unmodified ceramic, two distinct absorption bands at  $458\text{ cm}^{-1}$  and  $478\text{ cm}^{-1}$  are evident, but in the BaO-modified ceramics, these merge into a single broad band centered at  $458\text{ cm}^{-1}$  [13]. This spectral range also includes contributions from Me–O stretching vibrations (where

Me=Sr or Ba) in the silicate matrix [13,15].

### Conclusions

In this study, heat-resistant radio-transparent ceramics were developed within the  $\text{SrO}\text{--}\text{BaO}\text{--}\text{Al}_2\text{O}_3\text{--}\text{B}_2\text{O}_3\text{--}\text{SiO}_2$  system by partially substituting the raw components with a specially designed low-melting-point glass of the following composition  $(37.4\text{--}x)\text{SrO}\text{--}x\text{BaO}\text{--}7.8\text{Al}_2\text{O}_3\text{--}10.5\text{B}_2\text{O}_3\text{--}44.3\text{SiO}_2$  ( $x=0\text{--}20\text{ mol.}\%$ ). Substituting portions of the ceramic components with this SBABS glass significantly accelerated mineral formation and sintering processes. As a result, dense ceramic materials with desirable properties were synthesized at a comparatively low temperature of  $1250^\circ\text{C}$ . The obtained ceramics demonstrate a combination of properties suitable for use in radio guidance systems and protective enclosures for onboard missile electronics. The final crystalline phase is primarily monoclinic strontium anorthite. Increasing the BaO

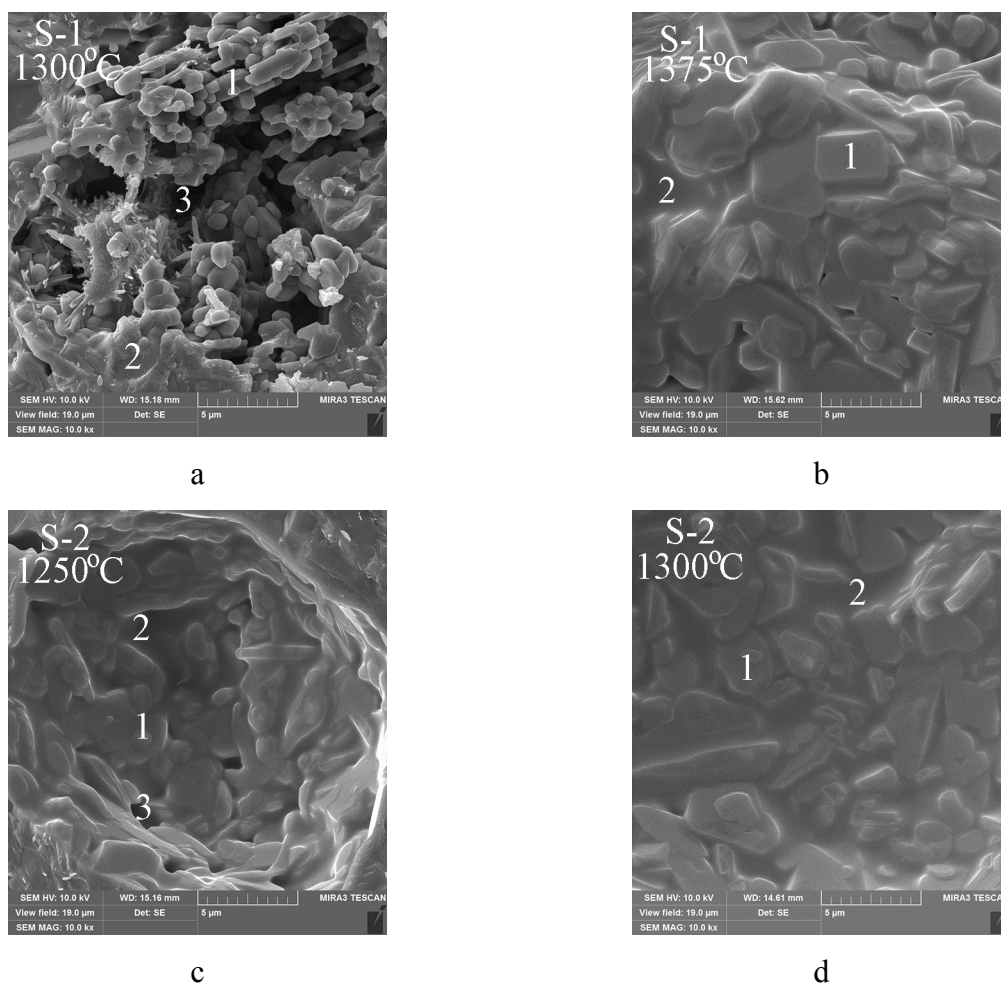


Fig. 3. SEM images of S-1 and S-2 ceramics fired at different temperatures: a – S-1 ( $1300^\circ\text{C}$ ); b – S-1 ( $1375^\circ\text{C}$ ); c – S-2 ( $1250^\circ\text{C}$ ); d – S-2 ( $1300^\circ\text{C}$ ). 1 – monoclinic strontium anorthite; 2 – glass phase; 3 – pore



content in the SBABS glass matrix up to 20 mol.% leads to the formation of solid substitution solutions between strontium anorthite and celsian. Owing to the similar ionic radii and charges between  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ , the fundamental structural framework of strontium anorthite remains largely intact. Strontium anorthite crystals predominantly measure 0.5–1.0  $\mu\text{m}$  in size. The formation of a fine-crystalline framework embedded in a well-developed glassy matrix contributes to the high density and mechanical strength of the material. The developed ceramics exhibit excellent thermal performance (thermal stability up to 800°C and refractoriness of 1460°C) and low dielectric losses at  $10^{10}$  Hz ( $\epsilon=4.9\text{--}5.0$ ;  $\tan\delta=0.001$ ).

The suggested approach has demonstrated high effectiveness in modifying the microstructure and phase composition of ceramics within the  $\text{SrO}\text{--}\text{BaO}\text{--}\text{Al}_2\text{O}_3\text{--}\text{B}_2\text{O}_3\text{--}\text{SiO}_2$  system and may be

extended to the development of other aluminosilicate-based ceramics for diverse functional applications.

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#### Conflict of interest

The authors declare that they have no conflict of interest.

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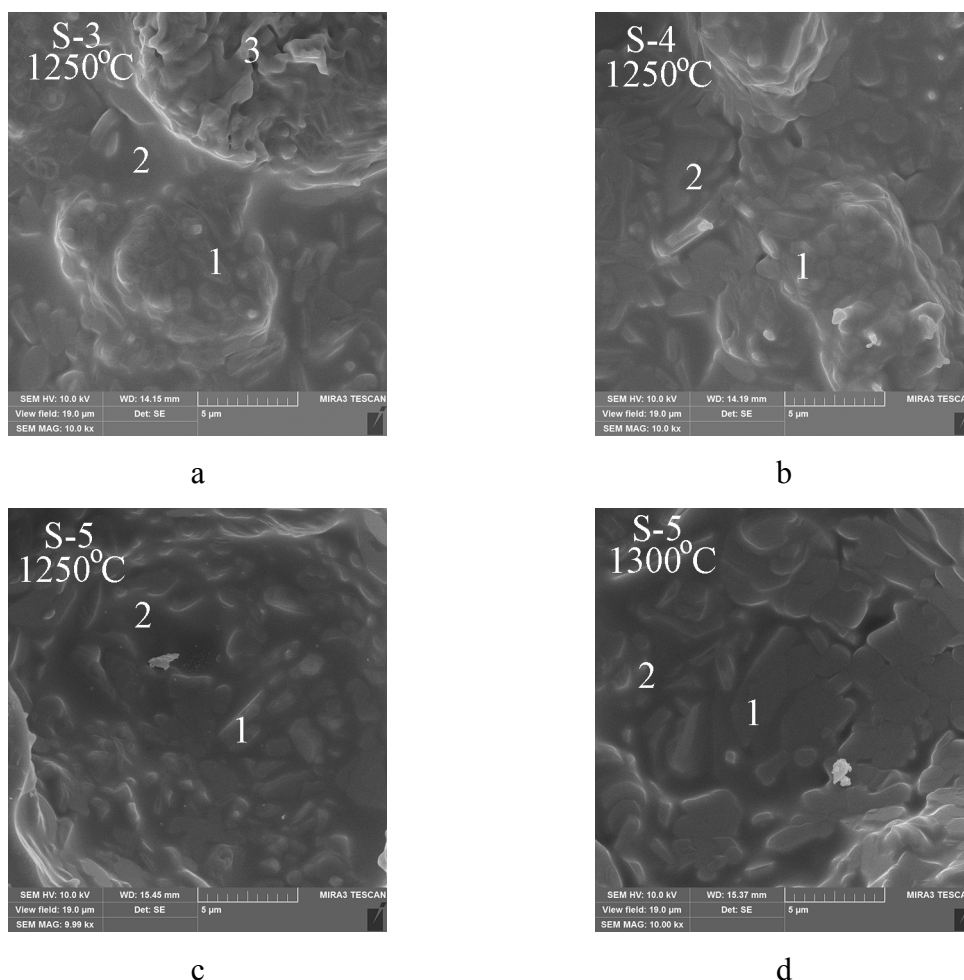


Fig. 4. SEM images of S-3 to S-5 ceramics fired at different temperatures: a – S-3 (1250°C); b – S-4 (1250°C); c – S-5 (1250°C); d – S-5 (1300°C). 1 – monoclinic strontium anorthite; 2 – glass phase; 3 – pore

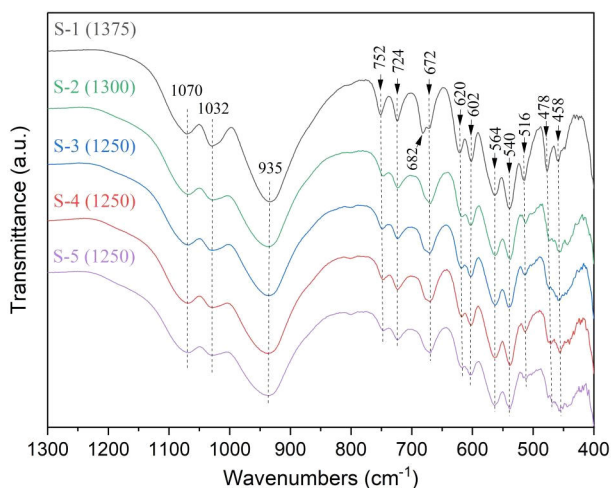


Fig. 5. FTIR spectra of experimental strontium anorthite ceramics

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## ТЕРМОСТІЙКА РАДІОПРОЗОРА КЕРАМІКА В СИСТЕМІ $\text{SrO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ , МОДИФІКОВАНА $\text{BaO}$

Зайчук О.В., Амеліна О.А., Гордєєв Ю.С., Філоненко Д.В., Калішенко Ю.Р., Хоменко О.С.

Для одержання стронцій-анортитової кераміки, модифікованої барій оксидом, використовували скло складу  $(37,4-x)\text{SrO}-x\text{BaO}-7,8\text{Al}_2\text{O}_3-10,5\text{B}_2\text{O}_3-44,3\text{SiO}_2$  (де  $x=0-20$  мол.%). Зв'язування компонентів дослідного скла в фазу стронцієвого анортиту реалізовували згідно з принципом реакційного формування структури шляхом додавання відсутніх компонентів (кристалічних наповнювачів). При цьому отриманий водонепроникний матеріал при низькій температурі  $1250^\circ\text{C}$ . Єдиною кристалічною фазою розробленої кераміки є моноклінна форма стронцієвого анортиту, який формує однорідну структурну матрицю матеріалу. Стронцієвий анортит утворює твердий розчин заміщення з цельзіаном внаслідок близькості іонних радіусів і подібності зарядів катіонів  $\text{Sr}^{2+}$  і  $\text{Ba}^{2+}$ , практично не змінюючи основні структурні одиниці стронцієвого анортиту. Розроблена стронцій-анортитова кераміка володіє високими термічними показниками (термічна стійкість  $800^\circ\text{C}$ , число вогнетривкості  $1460^\circ\text{C}$ ). За рівнем відносної діелектричної проникності (4,9–5,0) і діелектричних втрат (0,001) на частоті  $10^{10}$  Гц розроблена кераміка відповідає вимогам до надвисокочастотних радіопрозорих матеріалів для авіаційної і ракетної техніки, яка працює в умовах швидкісного високотемпературного нагрівання.

**Ключові слова:** радіопрозора кераміка, спікання, мікроструктура, стронцієвий анортит, термічні властивості.

# HEAT-RESISTANT RADIO-TRANSPARENT CERAMICS IN THE $\text{SrO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ SYSTEM MODIFIED WITH BaO

O.V. Zaichuk \*, A.A. Amelina, Y.S. Hordieiev, D.V. Filonenko, Y.R. Kalishenko, O.S. Khomenko

Ukrainian State University of Science and Technologies, Dnipro, Ukraine

\* e-mail: zaychuk\_av@ukr.net

Strontium anorthite ceramics modified with barium oxide were synthesized using glasses of composition  $(37.4-x)\text{SrO}-x\text{BaO}-7.8\text{Al}_2\text{O}_3-10.5\text{B}_2\text{O}_3-44.3\text{SiO}_2$ , where  $x$  ranged from 0 to 20 mol.%. The crystallization of the strontium anorthite phase was achieved through reaction-based structure formation, incorporating crystalline fillers to supply any deficient components. The ceramics demonstrated zero water absorption at a low firing temperature of 1250°C. The primary crystalline phase identified was monoclinic strontium anorthite, forming a uniform structural matrix. Strontium anorthite formed a solid solution with barium owing to the similar ionic radii and charges of  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ , preserving the integrity of the basic structural units. The ceramics demonstrated excellent thermal characteristics, including thermal stability up to 800°C and refractoriness of 1460°C. Dielectric characterization at  $10^{10}$  Hz showed a relative permittivity of 4.9–5.0 and low dielectric losses ( $\tan\delta=0.001$ ), which allows the developed ceramics to be used in the aerospace and rocket industries.

**Keywords:** radio-transparent ceramics; firing; microstructure; strontium anorthite; thermal characteristics.

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