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PROPERTIES AND STRUCTURAL CHARACTERISTICS OF GLASSES IN THE $SrO-BaO-Al_2O_3-B_2O_3-SiO_2$ SYSTEM FOR DIELECTRIC COMPOSITE MATERIALS

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Ceramic materials synthesized within alkali-free aluminosilicate systems are widely used as dielectrics in microelectronics, radio engineering, aviation, and rocket technologies. The addition of glass binders to these ceramic compositions significantly reduces the sintering temperature by promoting liquid phase formation at lower temperatures. This study investigates the effect of substituting SrO with BaO on the properties and structural characteristics of glasses in the $SrO-BaO-Al_2O_3-B_2O_3-SiO_2$ system. It is found that replacing up to 20 mol.% of SrO with BaO enhances the glass-forming ability and promotes the formation of monoclinic strontium anorthite during crystallization. Additionally, strontium anorthite forms a solid substitutional solution with celsian due to the close ionic radii of Sr^{2+} and Ba^{2+} ions. This similarity in ionic size and charge ensures that the basic structural units of the glass network remain unchanged. Moreover, increasing the BaO content to 20 mol.% reduces the coefficient of thermal expansion of the glass from $78 \cdot 10^{-7}$ $^0C^{-1}$ to $71 \cdot 10^{-7}$ $^0C^{-1}$, while slightly increasing the density from 3.20 g/cm^3 to 3.34 g/cm^3. The volumetric electrical resistance at 300^{0}C ranges between $10^{10.7}$ and $10^{11.6}$ ohm·cm, demonstrating the excellent insulating properties of these experimental glasses. The properties of the investigated glasses allow considering them as components of dielectric composite materials that can significantly intensify sintering processes.

Keywords: eutectic glass, strontium anorthite, thermal properties, dielectric, phase composition, structural features.

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Introduction

The swift advancement of microelectronics, radio engineering, and aerospace technologies, particularly in aviation and missile systems, demands innovative dielectric materials. These materials are essential for a range of applications, from substrates in hybrid integrated circuits to components of phased array radar systems and antenna fairings for radio-controlled missiles of various types. Traditionally, dielectric materials are synthesized from alkali-free aluminosilicate ceramics and glass-crystalline systems, which offer both benefits and drawbacks, depending on the specific functional requirements and the desired properties of the final products.

Powder manufacturing techniques are typically employed to produce dense ceramic materials, allowing the fabrication of complex-shaped items with precise chemical compositions. However, achieving high levels of sintering in such materials typically requires very high firing temperatures. To address this, glass binders can be incorporated into the ceramic composition, promoting the formation of a liquid phase at lower temperatures and, in turn, reducing the required sintering temperature.

Research has been conducted to develop densely compacted dielectric materials based on eucryptite ($Li_2O \cdot Al_2O_3 \cdot 2SiO_2$) [1], celsian ($BaO \cdot Al_2O_3 \cdot 2SiO_2$) [2], and strontium-anorthite ($SrO \cdot Al_2O_3 \cdot 2SiO_2$) [3] compositions, using lithium aluminum borosilicate glass as a binder. However, alkali oxides in these ceramic materials negatively affect their dielectric properties and fire resistance, limiting their potential

applications.

Study [4] has demonstrated the effectiveness of introducing eutectic glass from the pseudo-ternary system $BaO-Al_2O_3-SiO_2$ to enhance the sintering processes of ceramic materials with a celsian composition. These developed materials exhibit excellent dielectric properties and refractoriness, although their high sintering temperatures (1400–1450^{0}C) remain a significant drawback.

For improved high-temperature resistance, reduced dielectric losses, and enhanced thermomechanical properties, strontium anorthite ($SrO{\cdot}Al_2O_3{\cdot}2SiO_2$) presents a promising alternative. With a melting point of 1654^{0}C [5], strontium anorthite-based materials are well-suited for producing a wide range of densely sintered dielectric materials.

Previous studies [6] investigated the phase formation processes in glasses within the $SrO-Al_2O_3-SiO_2$ system, specifically of stoichiometric strontium-anorthite composition. It was noted that the formation of the hexagonal modification of strontium anorthite is undesirable, as it undergoes a phase transition to an orthorhombic structure, which is characterized by volumetric changes due to differences in the coefficient of thermal linear expansion.

Fu et al. [7] synthesized ceramic materials based on the $BaO-SrO-Al_2O_3-SiO_2$ system with a celsian composition. The study demonstrated that the equimolar substitution of BaO with SrO significantly enhances the transformation of hexagonal celsian into its monoclinic form, as well as accelerates the sintering process of ceramic materials.

This approach presents a promising pathway for synthesizing low-temperature ceramics based on both celsian and strontium-anorthite compositions. However, there are still relatively few studies on strontium-barium glasses that could serve as glass binders for ceramic and composite materials designed for dielectric applications.

Thus, this study aims to investigate the properties and structural characteristics of glasses within the $SrO-BaO-Al_2O_3-B_2O_3-SiO_2$ system, focusing on their potential use as components in dielectric composite materials.

Experimental

The synthesis of glasses in the $SrO-BaO-Al_2O_3-B_2O_3-SiO_2$ (SBABS) system was performed using a laboratory electric furnace equipped with silicon carbide heaters. The process was conducted in corundum crucibles at 1350^{0}C for 1 hour in an air atmosphere. The raw materials used for the batch included chemically pure grades of strontium and barium carbonates, along with marshalite and G-0 grade technical alumina (Ukraine). To enhance the fusibility of the glass, 10 wt.% of boron oxide (as chemically pure boric acid) was added to the total 100 wt.% batch composition. The readiness of the melt was confirmed using a filament test. Once the melt reached homogeneity and no crystalline inclusions were observed, it was deemed ready for further processing. For sample preparation, the molten glass was cast into metal molds and subsequently annealed in a muffle furnace at 500–520^{0}C, followed by slow cooling. The remaining glass mass was poured onto a metal plate for further production.

Glass properties were evaluated according to standard testing methods. The density (ρ) of the glass samples was determined via hydrostatic weighing in distilled water. Specific volume resistivity was measured on plane-parallel plates in a setup with graphite electrodes, within the temperature range of 100–400^{0}C, at a heating rate of 50^{0}C/min, using a teraohmmeter E6-13A. The relative elongation (Δl) of the glass samples as a function of temperature was measured on 5×5×50 mm specimens. From this data, the average coefficient of thermal expansion (CTE) in the 20–400^{0}C range was calculated at a heating rate of 10^{0}C/min.

The softening and crystallization temperatures of the SBABS glass were evaluated using Simultaneous Thermal Analysis (STA PT 1600, Linseis GmbH) over a temperature range of 20–1050^{0}C, with a heating rate of 10^{0}C/min. Glass powders, ground in an agate mortar and sieved through a No. 0063 mesh, were used for this analysis.

The crystalline phase composition of the crystallized SBABS glass was identified using a Philips APD-15 diffractometer with CoK_α radiation. Fourier-transform infrared (FTIR) spectra were recorded in the 1600–400 cm^{-1} range using the KBr pellet technique on a Thermo Nicolet Avatar 370 FTIR spectrometer.

Results and discussion

Previous studies have established [8] that the optimal glass-forming ability is typically found in compositions near eutectic points on phase diagrams. Based on earlier findings [9], a glass of eutectic composition (S-1) within the $SrO-Al_2O_3-SiO_2$ system was selected for this investigation. The crystallization of this glass leads to the formation of the strontium-anorthite phase, along with strontium metasilicate and strontium gelenite. To enhance the fusibility, 10 wt.% of boron oxide was added beyond the 100 wt.% of the primary components. Additionally, in the composition of glass S-1, SrO was systematically replaced by BaO in equimolar proportions, up to 20 mol.%, with increments of 5 mol.%. The chemical compositions of SBABS glass are shown in Table 1.

For all synthesized glasses, key properties were measured to evaluate their potential as glass binders for ceramic and composite materials used in dielectric applications. These properties include coefficient of thermal expansion, density, and volumetric electrical resistivity (Table 2).

Experimentally, we observed a decrease in CTE values from $78 \cdot 10^{-7}$ $^0C^{-1}$ to $71 \cdot 10^{-7}$ $^0C^{-1}$ as the barium oxide content increased to 20 mol.%. The glass density showed a slight increase, from 3.20 g/cm^3 in the base glass S-1 to 3.34 g/cm^3. Volumetric electrical resistivity at 300^{0}C ranged from $10^{10.7}$ to $10^{11.6}$ ohm·cm, indicating excellent electrical insulation properties in the experimental glasses.

Differential thermal analysis (DTA) was conducted to evaluate the softening and crystallization temperatures of the SBABS glasses. The DTA curves of the glass powders, shown in Fig. 1, were measured over a temperature range of 400–1050^{0}C. The glass transition temperature (T_g) was identified at the point where the DTA curve deviated from the baseline, indicating the onset of glass softening. T_g values for the experimental glasses ranged between 672^{0}C and 682^{0}C, increasing as the barium oxide content reached 20 mol.%. Additionally, the endothermic effect linked to glass softening showed a reduced intensity with increasing barium oxide, resulting in a more gradual softening process. The maximum temperature for glass softening also decreased from 724^{0}C to 718^{0}C. The presence of a second endothermic effect suggests a microheterogeneous structure in the experimental glasses. This indicates that the chemical composition can be represented by two compounds, each with distinct softening temperature intervals. Furthermore, the exothermic crystallization effect, which corresponds to the base S-1 glass composition (without BaO), diminished in intensity and shifted toward lower temperatures, from 984^{0}C to 904^{0}C. These trends in the DTA curves suggest that the introduction of barium oxide improves the glass-forming ability of the experimental compositions [10,11].

To further investigate the crystalline phases formed during the crystallization of SBABS glasses, the samples were heat-treated at temperatures corresponding to their softening and crystallization points, as determined by the DTA data (Fig. 1). The glass samples were held at these temperatures for two hours.

The X-ray diffraction (XRD) analysis results, shown in Fig. 2, reveal the crystalline phases in the crystallized glass of composition S-1. The primary crystalline phase identified is strontium metasilicate ($d \cdot 10^{10}$=3.55; 3.34; 2.90; 2.52; 2.05; 1.90 m), with the monoclinic form of strontium anorthite ($d \cdot 10^{10}$=3.72; 3.40; 3.24; 3.21; 2.90; 2.52 m) also present.

The addition of 5–20 mol.% barium oxide to the base S-1 glass composition led to the crystallization of the monoclinic form of strontium anorthite as the dominant phase. This phase forms a solid solution with celsian due to the similarity in the ionic radii of Sr^{2+} and Ba^{2+} [8]. This is evidenced by the gradual shift of the primary diffraction peaks ($d \cdot 10^{10}$=3.38;

Table 1

Chemical composition and melting temperature of SBABS glasses

Sample name	Contents of components, mol.%					Melting temperature, ^{0}C
	SiO_2	Al_2O_3	SrO	BaO	B_2O_3	
S-1	44.28	7.76	37.43	0	10.53	1350
S-2	44.28	7.76	32.43	5	10.53	1350
S-3	44.28	7.76	27.43	10	10.53	1350
S-4	44.28	7.76	23.43	15	10.53	1350
S-5	44.28	7.76	17.43	20	10.53	1350

Table 2

Properties of synthesized SBABS glasses

Sample name	CTE, $\alpha_{20-400^\circ C} \cdot 10^7$, $^0C^{-1}$	Density, g/cm^3	log $\rho_{300^\circ C}$, (ohm·cm)
S-1	78	3.20	11.6
S-2	76	3.22	11.5
S-3	74	3.25	11.4
S-4	73	3.30	11.1
S-5	71	3.34	10.7

3.22; 3.18; 2.93; 2.52 m) toward larger interplanar distances ($d \cdot 10^{10}$=3.43; 3.30; 3.24; 2.97; 2.54 m) as the BaO concentration increased to 20 mol.%.

As BaO replaces SrO in the glass composition, the amount of strontium metasilicate in the crystallization products decreases correspondingly. In compositions S-4 and S-5, diffraction peaks characteristic of strontium metasilicate either disappear or fall below the instrument's resolution.

Overall, the XRD patterns show a significant decrease in the intensity of the main diffraction peaks with increased barium oxide in the chemical composition of the base strontium glass S-1. This indicates a decrease in the crystallization ability of the experimental glasses.

The effect of barium oxide (BaO) on the structural changes of the S-1 glass sample was investigated using FTIR spectroscopy, with spectra recorded in the 400–1600 cm^{-1} range (Fig. 3). The FTIR spectra of the experimental SBABS glasses where up to 20 mol.% of SrO was replaced equimolarly by BaO, reveal several significant absorption bands. The broad region between 800 and 1300 cm^{-1} arises from the overlapping contributions of silicate and borate groups, with no distinct separation of their individual contributions. The absorption band centered at 1016 cm^{-1} can be attributed to asymmetric vibrations of Si–O–Si bonds in SiO_4 tetrahedra, as well as stretching vibrations of Si–O–B and Si–O–Al bonds, which connect the tetrahedral groups of SiO_4 and BO_4, as well as SiO_4 and AlO_4 [12].

This band highlights the interactions between silicate, aluminate, and borate structural units, underscoring the mixed nature of the glass matrix, where these groups collectively contribute to the vibrational modes. The region between 1300 and 1600 cm^{-1}, including the 1422 cm^{-1} band, is linked to B–O stretching vibrations in trigonal BO_3 units. Additionally, the band at 716 cm^{-1} is linked to both the bending vibrations of B–O–B bonds in BO_3

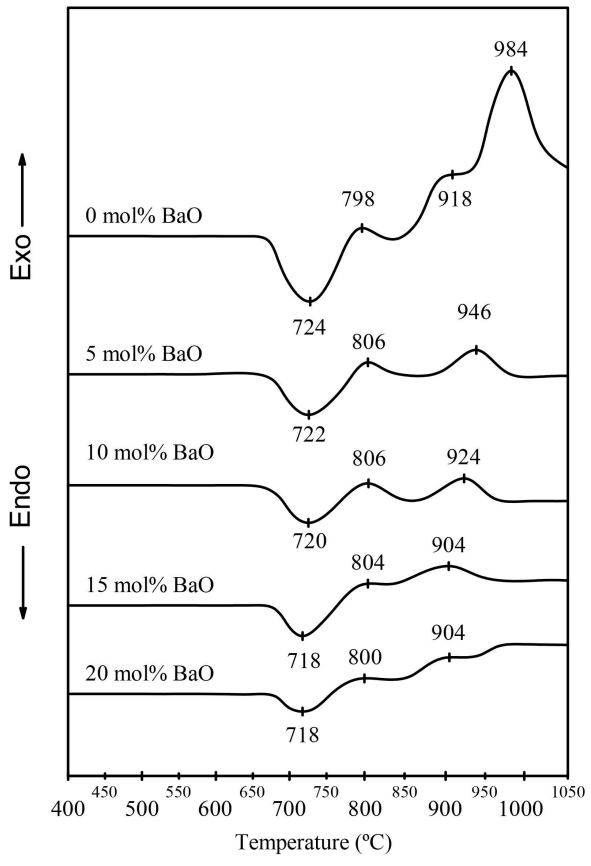

Fig. 1. DTA curves of SBABS glasses

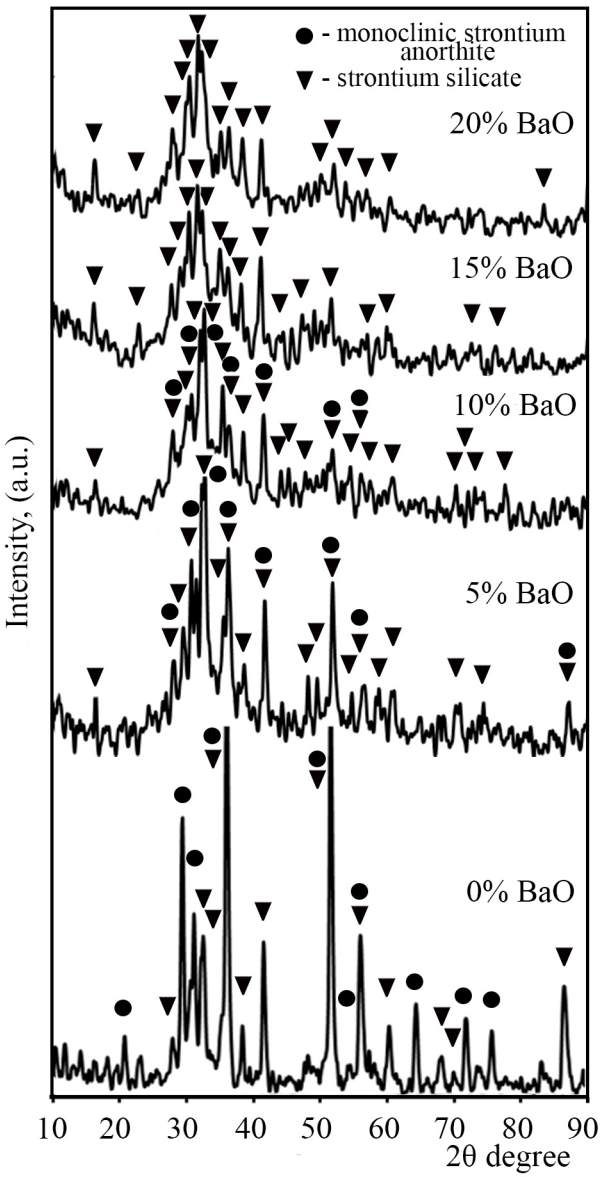

Fig. 2. XRD of crystallized SBABS glasses

triangles and the presence of Si–O–Si and Si–O–Al bridges, which result from the homogeneous distribution of SiO_4 and AlO_4 tetrahedra within the glass network [12]. The absorption band at 460 cm^{-1}, corresponding to the asymmetric deformation vibrations of Si–O–Si, signals the formation of silicate structures [13]. The spectra indicate that the replacement of SrO with BaO does not significantly alter the main structural units of the glass network, likely due to the similar ionic charge and size of Sr^{2+} and Ba^{2+}.

FTIR analysis of the crystallized experimental glasses, recorded within the 400–1500 cm^{-1} range (Fig. 4), reveals that as BaO content increases up to 20 mol.%, the absorption bands broaden and decrease in intensity. Despite these changes, the absorption bands' positions in the S series' crystallized glasses remain consistent. This suggests an increase in the vitreous phase content, likely due to the enhanced glass-forming ability of the experimental compositions. Furthermore, the Ba^{2+} cations do not significantly alter the fundamental structural units of the crystallized glasses, potentially indicating the formation of solid substitution solutions, given the similar ionic radii of Ba^{2+} and Sr^{2+} ions.

In the high-frequency region (800–1200 cm^{-1}), a distinct absorption band at 1074 cm^{-1} in crystallized glass S-1 (without BaO) is associated with asymmetric Si–O–Si stretching vibrations within tetrahedral units [13]. This finding indicates a high degree of polymerization in silicon-oxygen tetrahedra, characteristic of framework silicates, as observed in the strontium anorthite structure. Crystallization of the strontium anorthite phase is further supported by X-ray diffraction data (Fig. 3). The shift of the primary Si–O vibration band to lower frequencies reflects an increase in the (Si, Al)–O bond length, attributed to isomorphic substitution of Si^{4+} with Al^{3+} in the strontium anorthite structure. The broad absorption band from 800 to 1200 cm^{-1} is also typical of chain silicates, represented by strontium metasilicate, a phase confirmed by X-ray analysis of crystallized glass S-1. The redistribution of absorption band intensity is notable: in chain silicates, the asymmetric Si–O–Si vibration appears with greater intensity in the shorter-wavelength region of the spectrum, as observed here at 972 cm^{-1} [13]. In the spectral region between 1300 and 1500 cm^{-1}, an absorption peak at 1414 cm^{-1} is attributed to the B–O stretching vibrations in the trigonal BO_3 units within the glassy phase of the S-1 glass-crystalline material. Symmetric Si–O–Si stretching vibrations appear in the 500–800 cm^{-1} range, with a prominent band at 706 cm^{-1} and a secondary band at 750 cm^{-1}, which suggests a homogeneous distribution of Si^{4+} and Al^{3+} ions in (Si, Al)–O–(Al, Si) bridges [13]. The 400–500 cm^{-1} range features a strain absorption band typical to both framework and chain silicates, along with a band indicating the Me–O (Sr, Ba) bond stretching in the structure of glassy crystalline materials [14,15].

Conclusions

This research investigated the properties and structural features of glasses in the $(37.43-x)SrO-xBaO-Al_2O_3-B_2O_3-SiO_2$ system, with x ranging from 0 to 20 mol.%. It was established that substituting up to 20 mol.% of SrO with BaO positively influences the glass-forming ability of the experimental

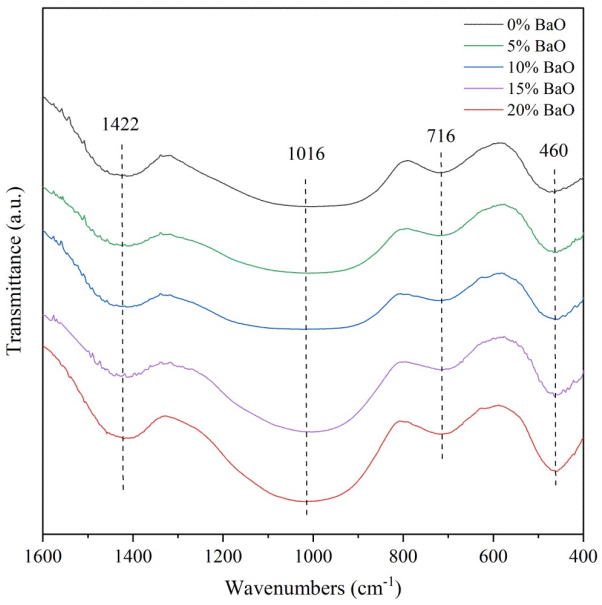

Fig. 3. FTIR spectra of SBABS glasses

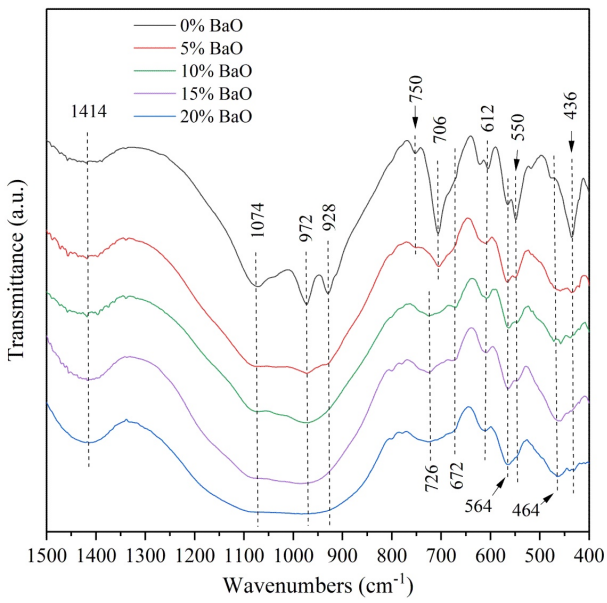

Fig. 4. FTIR spectra of crystallized SBABS glasses

glasses and promotes the formation of the monoclinic form of strontium anorthite during crystallization. Due to the similar ionic radii and charges of Sr^{2+} and Ba^{2+} cations, strontium anorthite forms a solid substitution solution with celsian, and the basic structural units of the glass network remain unchanged. As the amount of barium oxide increases to 20 mol.%, the coefficient of thermal expansion of the glass under study decreases from $78 \cdot 10^{-7}\ ^0C^{-1}$ to $71 \cdot 10^{-7}\ ^0C^{-1}$. The density of the glasses shows a slight increase compared to the base glass S-1, from 3.20 g/cm^3 to 3.34 g/cm^3. The volume electrical resistivity at 300^0C ranges from $10^{10.7}$ to $10^{11.6}$ ohm·cm, indicating high electrical insulating properties. These findings suggest that the experimental glasses are suitable components for composite materials intended for dielectric purposes.

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ВЛАСТИВОСТІ ТА СТРУКТУРНІ ОСОБЛИВОСТІ СТЕКОЛ В СИСТЕМІ $SrO-BaO-Al_2O_3-B_2O_3-SiO_2$ ДЛЯ КОМПОЗИЦІЙНИХ МАТЕРІАЛІВ ДІЕЛЕКТРИЧНОГО ПРИЗНАЧЕННЯ

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Як діелектрики для мікроелектроніки, радіотехніки, а також авіаційних і ракетних технологій широко використовують керамічні матеріали, синтезовані в безлужних алюмосилікатних системах. Введення до складу керамічних матеріалів склозв'язок сприятиме утворенню рідкої фази в системі при нижчих температурах і, як наслідок, зниженню температури спікання. Дане дослідження вивчає вплив заміни SrO на BaO на властивості та структурні особливості стекол в системі $SrO-BaO-Al_2O_3-B_2O_3-SiO_2$. Встановлено, що заміна SrO на BaO в кількості до 20 мол.% підвищує склоутворення і сприяє формуванню моноклінного стронцієвого анортиту в процесі їх кристалізації. Крім того, стронцієвий анортит утворює твердий розчин заміщення з цельзіаном внаслідок близьким іонним радіусам іонів Sr^{2+} і Ba^{2+}. Ця схожість в іонному розмірі та заряді забезпечує збереження основних структурних одиниць сітки скла. Більше того збільшення вмісту BaO до 20 мол.% знижує температурний коефіцієнт лінійного розширення (ТКЛР) скла з $78\cdot10^{-7}$ $^0C^{-1}$ до $71\cdot10^{-7}$ $^0C^{-1}$, одночасно трохи підвищуючи густину з 3,20 г/см^3 до 3,34 г/см^3. Значення об'ємного електричного опору при 300^0C коливається в межах $10^{10,7}$–$10^{11,6}$ Ом·см, демонструючи відмінні ізоляційні властивості дослідних стекол. Властивості дослі-джених стекол дозволяють розглядати їх як компоненти композиційних матеріалів діелектричного призначення, які можуть значно інтенсифікувати процеси спікання.

Ключові слова: евтектичне скло, стронцієвий анортит, термічні властивості, діелектрик, фазовий склад, структурні особливості.

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Ceramic materials synthesized within alkali-free aluminosilicate systems are widely used as dielectrics in microelectronics, radio engineering, aviation, and rocket technologies. The addition of glass binders to these ceramic compositions significantly reduces the sintering temperature by promoting liquid phase formation at lower temperatures. This study investigates the effect of substituting SrO with BaO on the properties and structural characteristics of glasses in the $SrO-BaO-Al_2O_3-B_2O_3-SiO_2$ system. It is found that replacing up to 20 mol.% of SrO with BaO enhances the glass-forming ability and promotes the formation of monoclinic strontium anorthite during crystallization. Additionally, strontium anorthite forms a solid substitutional solution with celsian due to the close ionic radii of Sr^{2+} and Ba^{2+} ions. This similarity in ionic size and charge ensures that the basic structural units of the glass network remain unchanged. Moreover, increasing the BaO content to 20 mol.% reduces the coefficient of thermal expansion of the glass from $78\cdot10^{-7}$ $^0C^{-1}$ to $71\cdot10^{-7}$ $^0C^{-1}$, while slightly increasing the density from 3.20 g/cm^3 to 3.34 g/cm^3. The volumetric electrical resistance at 300^0C ranges between $10^{10.7}$ and $10^{11.6}$ ohm·cm, demonstrating the excellent insulating properties of these experimental glasses. The properties of the investigated glasses allow considering them as components of dielectric composite materials that can significantly intensify sintering processes.

Keywords: eutectic glass; strontium anorthite; thermal properties; dielectric; phase composition; structural features.

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