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INFLUENCE OF R_2O_3 (R=Al, La, Y) ON THE STRUCTURE AND PROPERTIES OF STRONTIUM BOROSILICATE GLASSES

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The influence of R_2O_3 (R=Al, La, Y) on the structure, thermal, and some physical properties of strontium borosilicate glasses have been investigated by differential thermal analysis, X-ray diffraction, and Fourier-transform infrared spectroscopy. Fourier-transform infrared spectroscopy results showed that the network of the investigated glasses consists mainly of BO_3, BO_4, and SiO_4 structural units. The influence of R_2O_3 on the properties of strontium borosilicate glasses depends on the structural role of R^{3+} ions. The experimental results suggest that Al^{3+} ions act as intermediate in the investigated composition range, while La^{3+} and Y^{3+} ions act as modifiers and depolymerize the glass network. The obtained results showed that the glass transition temperature (610–660^{0}C), dilatometric softening temperature (640–675^{0}C), and molar volume (25.03–29.22 cm^3/mol) values of the investigated glasses were increased with equimolar substitution of SrO by R_2O_3. The thermal expansion coefficient (6.8–9.5 ppm/K) of the investigated glasses was found to decrease with increasing the R_2O_3 content. The obtained results showed that the density (3.03–3.68 g/cm^3) values of the investigated glasses were increased with increasing the Y_2O_3 and La_2O_3 content and decreased with increasing the Al_2O_3 content. The tendency to crystallize is higher in glasses containing La_2O_3 compared to glasses containing Y_2O_3 or Al_2O_3. The results obtained in this study indicate that the investigated glasses can be potential candidates for advanced aerospace and electronic applications as heat-resistant electrical insulating glass- and glass-ceramic-to-metal seals and coatings.

Keywords: borosilicate glass, crystallization, thermal expansion, glass transition, glass structure.

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Introduction

Glasses and glass-ceramics based on alkaline-earth borosilicate systems have recently gained importance from both scientific and technological points of view. They constitute a subject of widespread interest owing to various promising technological applications in instrumentation and rocketry as heat-resistant electrical insulating coatings [1], in the energy sector as high-temperature sealants in solid oxide fuel cells [2], in the production of heat-resistant and radio-transparent materials for the aerospace and military industries [3,4], and as a potential material for radioactive waste immobilization [5].

In recent decades, strontium borosilicate glasses have received considerable attention due to their wide range of possibilities for adapting physicochemical properties to specific technological applications. Strontium borosilicate system is a relevant source for the synthesis of new materials that present value and, at the same time, specific properties such as mechanical strength, thermal stability, chemical resistance, biocompatibility, impermeability to gases and water, and protection against ionizing radiation [6]. The properties of these glasses can be changed in a wide range by selecting appropriate modifiers or intermediate oxides that modify the structure of boron and affect the degree of the local order or disorder of the glass network [7]. The change in the local structure and properties of the glass highly depends upon the nature and amount of modifiers or

intermediate oxides in the glass composition. It is well known that the structure, thermal and dielectric properties of the borosilicate glasses are improved by adding trivalent metal oxides such as Al_2O_3, Y_2O_3, and La_2O_3 [2,6–11]. Aluminum and yttrium oxides have a dual nature and can act simultaneously as both a network former and a modifier, positively affecting the glass-forming ability, structure, and properties of the glass [2]. The role of lanthanum oxide is mainly to reinforce the thermal and mechanical properties of glass and glass-ceramic materials. Lanthanum oxide is widely known for regulating the viscosity (fluidity) of glasses, which helps the sealant maintain the required fluidity after softening and the required mechanical stiffness after ceramization [9]. While there are some studies [8–11] that provide an overview of the likely nature of Al^{3+}, Y^{3+}, and La^{3+} ions, the structural roles of these ions in alkaline earth borosilicate glasses are not well understood. Understanding the composition-structure-property relationships is an important first step in developing new glasses and glass-ceramics for advanced aerospace, military, and electronic applications.

Therefore, the aim of this study was to investigate the effect of R_2O_3 (R=Al, La, Y) on the structural changes and properties of strontium borosilicate glasses using differential thermal analysis, X-ray diffraction, and Fourier-transform infrared spectroscopy (FTIR).

Materials and methods

The details of the batch composition of the investigated glasses with their label are given in Table 1. Reagent grade chemicals of $SrCO_3$, H_3BO_3, SiO_2, Al_2O_3, La_2O_3, and Y_2O_3 were used as starting raw materials. The glass batches were prepared by mixing an appropriate mole fraction of the desired oxide ingredients in an agate mortar with a pestle to ensure complete homogeneity. The homogeneous glass batches were melted in the alumina crucibles with the volume of 50 mL in an electric furnace with silicon carbide heaters at the temperature of 1400°C in an air atmosphere for 1 h. The homogeneous melts were quickly cast onto a preheated stainless-steel mold to obtain glasses which were then transferred into a muffle furnace preset to 600°C.

Table 1

Chemical composition (mol.%) of the investigated glasses

Sample name	SrO	B_2O_3	SiO_2	Al_2O_3	La_2O_3	Y_2O_3
Sr50	50	30	20	0	0	0
Sr45Al5	45	30	20	5	0	0
Sr45La5	45	30	20	0	5	0
Sr45Y5	45	30	20	0	0	5
Sr40A10	40	30	20	10	0	0
Sr40La10	40	30	20	0	10	0
Sr40Y10	40	30	20	0	0	10
Sr40	40	30	30	0	0	0
Sr35Al5	35	30	30	5	0	0
Sr35La5	35	30	30	0	5	0
Sr35Y5	35	30	30	0	0	5
Sr30Al10	30	30	30	10	0	0
Sr30La10	30	30	30	0	10	0
Sr30Y10	30	30	30	0	0	10

The glass transition temperature (T_g) and crystallization temperature (T_c) were determined using a derivatograph Q-1500D at a heating rate of 10°C/min from room temperature to 1000°C in an air atmosphere. The reference substance was alumina powder of high purity, and the temperature error was ±5°C.

Crystalline phases precipitated during heat treatment were identified by X-ray diffractometer DRON-3M using Co-K_α radiation in the $10^0<2\Theta<90^0$ range.

The FTIR spectra of the glasses were recorded in the 1600–400 cm^{-1} region using the KBr pellet technique (Thermo Nicolet Avatar 370 FTIR Spectrometer).

The thermal expansion coefficient (TEC) from 20 to 400°C and dilatometric softening temperature (T_d) of the glass samples were determined using a dilatometer (Dilatometer1300 L, Italy) at a heating rate of 3°C/min. The density of the glasses was determined at room temperature by the Archimedes principle using distilled water as the immersion liquid and a digital balance of sensitivity of 10^{-4} g. The weight of each glass sample was measured three times, and an average was taken to minimize the sources of error. The volume resistivity of the investigated glasses was measured on flat-parallel plates in a cell with graphite electrodes in the temperature range of 100–400°C at a heating rate of 5°C/min using the teraohmmeter E6-13A.

Results and discussion

Differential thermal analysis

Differential thermal analysis (DTA) was used to determine the thermal behavior of the investigated glasses. DTA curves of the glass powders in the temperature range of 500–1000°C are shown in Fig. 1, and the thermal analysis values of the curves are given in Table 2. In this study, the onset of the endothermic peak on the DTA curves was taken as glass transition temperature (T_g). It was observed that the glass transition temperature increases with increasing the R_2O_3 (R= Al, La, Y) content.

The observed increase in the T_g values in the investigated glasses can be explained on the basis of

Table 2

The values of the characteristic temperatures (T_g, T_d, and T_c), thermal expansion coefficient (TEC), density (d), molar volume (V_m), volume resistivity (lgρ) of the investigated glasses

Sample name	T_g, (^{0}C)	T_d, (^{0}C)	T_{c1}, (^{0}C)	T_{c2}, (^{0}C)	TEC, (ppm/^{0}C)	d, (g/cm^3)	V_m, (cm^3/mol)	lgρ at 150^{0}C (Ohm·cm)
Sr50	610	640	710	900	9.5	3.36	25.21	12.80
Sr45Al5	615	640	705	910	8.9	3.29	25.72	13.03
Sr45La5	630	650	730	935	8.8	3.48	27.53	12.25
Sr45Y5	640	660	735	–	8.8	3.42	26.56	12.44
Sr40Al10	620	650	710	–	8.4	3.24	26.09	13.23
Sr40La10	645	660	740	900	8.5	3.68	29.06	11.85
Sr40Y10	655	670	755	900	8.6	3.54	27.38	12.13
Sr40	620	640	720	880	8.8	3.21	25.03	12.61
Sr35Al5	625	645	730	910	7.6	3.11	25.81	12.85
Sr35La5	630	650	730	880	8.4	3.37	27.14	12.34
Sr35Y5	650	670	745	–	8.2	3.28	26.36	12.41
Sr30Al10	630	660	735	–	6.8	3.03	26.47	13.12
Sr30La10	650	670	750	880	8.0	3.51	29.22	12.18
Sr30Y10	660	675	760	930	7.8	3.40	27.23	12.26

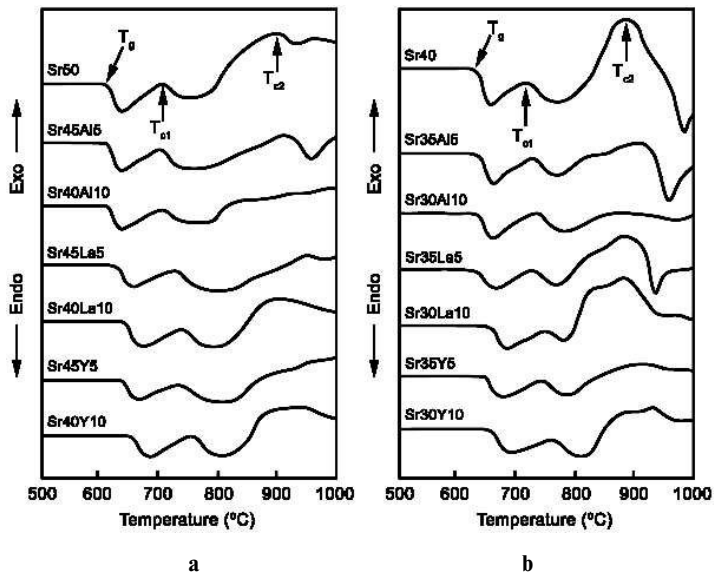

Fig. 1. DTA curves of the glass powders containing SiO_2: a – 20 mol.% and b – 30 mol.%

Ray's analysis of the composition-property relationships in inorganic oxide glasses [12]. According to Ray, the glass transition temperature is a sensitive structural parameter to even small substitutions of the glass network forming ions with high field strength network modifiers due to their high coordination number. The role played by the cation in the glass network may be classified as network former, intermediate, and modifier by general criteria based upon bond strength and ionic field strength. Based on Dietzel's ionic field strength theory, McMillan [13] reported that metal ions act as network formers when ionic field strength ($I=Z/r^2$, where Z is the cation charge and r is the ion radius) is greater than 5 Å^{-2}. In contrast, when the ionic field strength is less than 5 Å^{-2}, the metal ions act as network modifiers. The ionic field strengths of Al^{3+}, La^{3+} and Y^{3+} are 11.53 Å^{-2}, 2.90 Å^{-2} and 3.78 Å^{-2}, respectively [14]. Therefore, the La^{3+} and Y^{3+} ions act as modifiers destroying the glass network, but Al^{3+} ions act as network formers or as an intermediate in the glass structure. When a cation enters the glass structure as a network modifying ion, a coordination number similar to that of the pure oxide structure should be expected [15]. Therefore, according to Ray, greater values of T_g

would be expected with the addition of La^{3+} and Y^{3+} than with Al^{3+} entering the glass structure as network-forming ions, i.e., fourfold coordination. These conclusions are consistent with the results of this study. According to the DTA data, the equimolar substitution of SrO by La_2O_3 or Y_2O_3 into the composition of strontium borosilicate glass greatly increases the glass transition temperature. In the case of glasses containing Al_2O_3, increasing Al_2O_3 content increases the stability of the glasses against crystallization, while the glass transition temperature values change by only 10°C. Similar dependences of the thermal characteristics with the addition of Al_2O_3 were found in other glass compositions with increased SiO_2 content [6,8]. The substitution of SrO by R_2O_3 (R=Al, La, Y) in the composition of strontium borosilicate glass leads to an increase in the crystallization temperature and a change in the shape of the high-temperature exothermic peak. The above results show that the additives affect the glass structure and the crystallization process of the strontium borosilicate glasses.

X-ray diffraction analysis

In order to identify the crystalline phase corresponding to each exothermic peak on DTA curves, the glass powder was heat-treated at around the crystallization temperature (T_c) in the air for 5 hours. The crystallization temperatures, determined by DTA, were 720 and 880°C for Sr40, 910°C for Sr35Al5, 880°C for Sr30La10, and 930°C for Sr30Y10. Figure 2 shows the corresponding X-ray diffraction patterns.

In the case of the glass samples Sr40 and Sr35Al5, strontium metaborate (SrB_2O_4) and slawsonite ($SrAl_2Si_2O_8$) precipitated as the main crystalline phases. Corrosion of the alumina crucible by molten glass leads to the leaching of a part of Al_2O_3 from the crucible material into the glass melt, which contributes to the formation of the slawsonite phase in the base glass (Sr40), the glass batch which did not contain Al_2O_3. The addition of La_2O_3 enhanced the crystallization tendency and reduced the thermal stability of the base glass. In the case of the Sr30La10 glass sample with the addition of 10 mol.% La_2O_3, the new crystalline phase formed in the sample obtained by a heat treatment at 880°C for 5 h is lanthanum borate ($LaBO_3$). In the case of the Sr30Y10 glass sample with 10 mol.% Y_2O_3, the crystalline phase formed in the sample obtained by a heat treatment at 930°C for 5 h is yttrium borate (YBO_3). The abovementioned results imply that La_2O_3 and Y_2O_3 are nucleating agents that promote the formation of the RBO_3 (R=La; Y) crystalline phase, while Al_2O_3 mainly inhibits the formation of the $SrAl_2Si_2O_8$ crystalline phase in the base glass.

FTIR analysis

Fourier-transform infrared spectroscopy is a powerful tool to study the structural changes in the glass. The influence of R_2O_3 on the structural properties of $40SrO-30B_2O_3-30SiO_2$ glass was investigated by detecting their FTIR spectra (Fig. 3) in the range 1600–400 cm^{-1}.

The silicate and borate groups were found to play a dominant role in the FTIR spectra of the

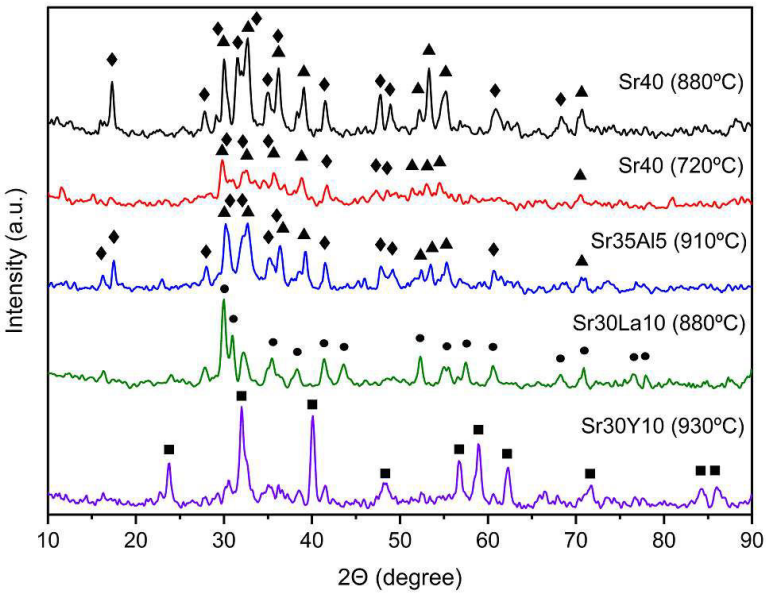

Fig. 2. X-ray diffraction patterns of glass powders heat-treated at the crystallization temperature:
▲ – SrB_2O_4; ◆ – $SrAl_2Si_2O_8$; ● – $LaBO_3$; ■ – YBO_3

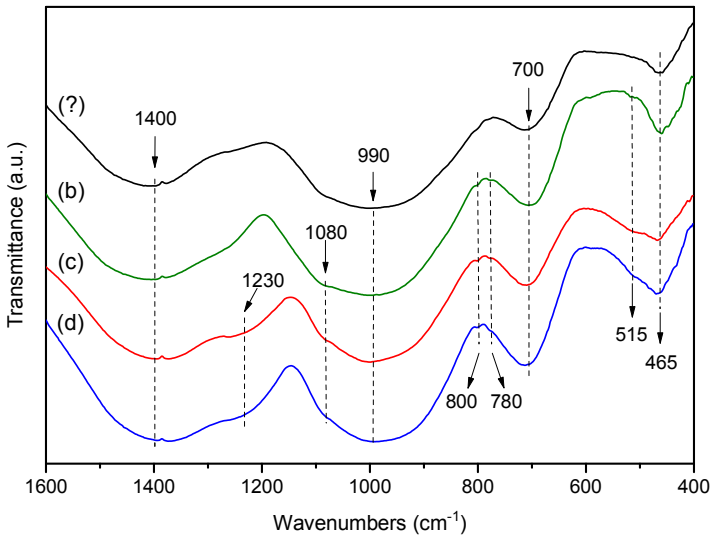

Fig. 3. FTIR spectra of glass samples: a – Sr40; b – Sr30Al10; c – Sr30Y10; and d – Sr30La10

investigated glasses. The absorption bands centered at 1230 cm^{-1} and 1410 cm^{-1} are due to the vibration of the boroxol rings and the stretching vibrations of B–O–B in [BO_3] triangles, respectively [9–11]. It is the wider, the greater the content of the modifier oxide. According to the FTIR analysis results, the substitution of SrO by La_2O_3 or Y_2O_3 into the composition of $40SrO–30B_2O_3–30SiO_2$ glass leads to the transformation of [BO_4] tetrahedral units into [BO_3] trigonal units with the formation of non-bridging oxygens, causing the absorption band to shift to lower frequencies [11]. The band in the range 850–1150 cm^{-1} is attributed to the stretching vibration of B–O–B in [BO_4] tetrahedrons [9–11]. The absorption band centered at 1080 cm^{-1} can be assigned to the antisymmetric stretching vibration of Si–O–Si in [SiO_4] tetrahedrons [9,10]. Since the stretching vibration band of [SiO_4] tetrahedra at about 1080 cm^{-1} overlaps with the stretching vibration band of [BO_4], therefore, it could not be detected in the FTIR spectrum of the glass sample Sr40. The absorption peaks located at 780 cm^{-1} and 800 cm^{-1} may be related to the symmetric stretching vibration of Si–O–Si and Si–O–R linkages (R=Al, La, Y), respectively [10,15]. The strong absorption band centered around 700 cm^{-1} is attributed to the bending vibration of B–O–B in [BO_3] triangles [9–11]. The peaks at 465 cm^{-1} and 515 cm^{-1} are mostly associated with bending vibrations of Si–O–Si and Si–O–R linkages, respectively [15].

Physical properties of the investigated glasses

The physical properties of oxide glasses are closely related to their structure, which is determined by their composition. The physical properties of the glasses were investigated by measuring the volume resistivity, thermal expansion coefficient, dilatometric softening temperature, density, and calculating the molar volume values to shed light on the structural behavior of the investigated glasses. The obtained values are given in Table 2. At the temperature of 150^0C, the volume resistivity of the investigated glasses is in the range of $10^{11}–10^{13}$ Ohm·cm, which indicates their high electrical insulation properties. It can be seen from the dilatometry results that the glasses containing Y_2O_3 have higher T_d values, as do the glasses containing La_2O_3. The thermal expansion coefficient of investigated glasses was found to decrease with the substitution of SrO by R_2O_3. The base glass showed a higher TEC value than all other glasses in the current investigation. The higher TEC in the base glass compared to other glasses can be associated with the larger ionic radius (1.26 Å) and lower field strength (1.26 $Å^{-2}$) of the Sr^{2+} ions than that of substituting R^{3+} ions. The obtained results showed that the density (3.03–3.68 g/cm^3) values of the investigated glasses were increased with increasing the Y_2O_3 and La_2O_3 content and decreased with increasing the Al_2O_3 content. The changes in the density are due to the different molar mass of the substitution oxides. The molar volume of investigated glasses was found to increase with the substitution of SrO by R_2O_3. The increase in the molar volume of the glass samples may be due to the formation of non-bridging oxygen and the expansion of the structure of the network of strontium borosilicate glass. The obtained values of the characteristic temperatures (T_g, T_d, and T_c), thermal expansion coefficient, density, and molar volume suggest that

Al^{3+} ions act as intermediate in the investigated composition range, while La^{3+} and Y^{3+} ions act as network modifiers. FTIR spectra agree with this assumption which is consistent with expectations based on the literature criteria.

Conclusions

Strontium borosilicate glasses were obtained by equimolar substitution of SrO for Al_2O_3, Y_2O_3, and La_2O_3. The influence of these substitutions on the structural, thermal, and physical properties of the investigated glass was determined. The main building units forming the glass network are BO_3 (peak at 700, 1280, 1400 cm^{-1}), BO_4 (peak at 990 cm^{-1}), and SiO_4 (peak at 465, 1080 cm^{-1}). The influence of R_2O_3 on the properties of strontium borosilicate glasses depends on the structural role of R^{3+} ions. The experimental results suggest that Al^{3+} ions act as intermediate in the investigated composition range, while La^{3+} and Y^{3+} ions act as network modifiers and increase the number of non-bridging oxygen in the glass network. The substitution of SrO by La_2O_3 or Y_2O_3 served to an increase in the values of characteristic temperatures (T_g, T_d, and T_c), density and molar volume, as well as a decrease in the values of TEC and volume resistivity. In contrast, the substitution of SrO by Al_2O_3 led to a slight increase in the values of characteristic temperatures, volume resistivity and molar volume, as well as a decrease in the values of TEC and density. The tendency to crystallize is higher in glasses containing La_2O_3 compared to glasses containing Y_2O_3 or Al_2O_3. The obtained results in this study indicate that these glasses can be potential candidates for advanced aerospace and electronic applications as heat-resistant electrical insulating glass- and glass-ceramic-to-metal seals and coatings.

Acknowledgments

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ВПЛИВ R_2O_3 (R=Al, La, Y) НА СТРУКТУРУ ТА ВЛАСТИВОСТІ СТРОНЦІЙ-БОРОСИЛІКАТНИХ СТЕКОЛ

Ю.С. Гордєєв, О.В. Зайчук

Вплив R_2O_3 (R=Al, La, Y) на структуру, теплові та деякі фізичні властивості стронцій-боросилікатних стекол досліджено методами диференціального термічного аналізу, рентгенофазового аналізу та інфрачервоної Фур'є-спектроскопії. Методом інфрачервоної Фур'є-спектроскопії встановлено, що сітка дослідних стекол сформована переважно структурними одиницями BO_3, BO_4 та SiO_4. Визначено, що вплив R_2O_3 на властивості стронцій-боросилікатних стекол залежить від структурної ролі R^{3+} іонів. Встановлено, що Al^{3+} іони мають значення проміжних в дослідному діапазоні складів, тоді як La^{3+} та Y^{3+} іони діють як модифікатори, що деполімерізують сітку скла. Експериментально встановлено, що значення температури склування (610–660°C), дилатометричної температури розм'якшення (640–675°C) та молярного об'єму (25,03–29,22 см^3/моль) дослідних стекол збільшуються при заміні SrO на R_2O_3. Встановлено, що теплове розширення ($(6.8–9.5)\cdot10^{-6}$ K^{-1}) дослідних стекол зменшується зі збільшенням вмісту R_2O_3. Визначено, що щільність (3,03–3,68 г/см^3) дослідних стекол зростає зі збільшенням вмісту Y_2O_3 та La_2O_3, та зменшується зі збільшенням вмісту Al_2O_3. Методом диференціального термічного аналізу встановлено, що схильність до кристалізації вища у скла, що містить La_2O_3, порівняно зі склом, що містить Y_2O_3 або Al_2O_3. Результати, отримані в цьому дослідженні, свідчать про те, що дослідні стекла можуть бути потенційними кандидатами для перспективних аерокосмічних технологій та електронних приладів в якості термостійкого електроізоляційного скло- та склокераміка-метал покриття або герметика.

Ключові слова: боросилікатне скло, кристалізація, температурне розширення, склування, структура скла.

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The influence of R_2O_3 (R=Al, La, Y) on the structure, thermal, and some physical properties of strontium borosilicate glasses have been investigated by differential thermal analysis, X-ray diffraction, and Fourier-transform infrared spectroscopy. Fourier-transform infrared spectroscopy results showed that the network of the investigated glasses consists mainly of BO_3, BO_4, and SiO_4 structural units. The influence of R_2O_3 on the properties of strontium borosilicate glasses depends on the structural role of R^{3+} ions. The experimental results suggest that Al^{3+} ions act as intermediate in the investigated composition range, while La^{3+} and Y^{3+} ions act as modifiers and depolymerize the glass network. The obtained results showed that the glass transition temperature (610–660°C), dilatometric softening temperature (640–675°C), and molar volume (25.03–29.22 cm^3/mol) values of the investigated glasses were increased with equimolar substitution of SrO by R_2O_3. The thermal expansion coefficient (6.8–9.5 ppm/K) of the investigated glasses was found to decrease with increasing the R_2O_3 content. The obtained results showed that the density (3.03–3.68 g/cm^3) values of the investigated glasses were increased with increasing the Y_2O_3 and La_2O_3 content and decreased with increasing the Al_2O_3 content. The tendency to crystallize is higher in glasses containing La_2O_3 compared to glasses containing Y_2O_3 or Al_2O_3. The results obtained in this study indicate that the investigated glasses can be potential candidates for advanced aerospace and electronic applications as heat-resistant electrical insulating glass- and glass-ceramic-to-metal seals and coatings.

Keywords: borosilicate glass; crystallization; thermal expansion; glass transition; glass structure.

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