

## On the Glass Structure of the $\text{Bi}_2\text{O}_3\text{--SiO}_2\text{--GeO}_2$ System

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**Abstract**—Wide- and small-angle X-ray scattering is used to study the structure of the single-phase glass of the  $\text{Bi}_2\text{O}_3\text{--GeO}_2$  system and three-component  $\text{Bi}_2\text{O}_3\text{--GeO}_2\text{--SiO}_2$  system in three sections with the  $\text{GeO}_2/\text{SiO}_2$  molar ratios of 3, 1, and 1/3. The  $\text{Bi}_2\text{O}_3$  content is changed from 20 to 50 mol % in the first two sections; and from 10 to 50 mol %, in the third one. Based on the data of wide-angle X-ray scattering, it can be concluded that structural groupings containing  $\text{BiO}_3$  triangles and  $\text{SiO}_2$  and  $\text{GeO}_4$  tetrahedra connected with them are formed in the glass of the studied triple system due to the chemical reactions of  $\text{Bi}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{GeO}_2$ . When the  $\text{Bi}_2\text{O}_3$  content is increased the structural groupings are combined and local areas with three-dimensional structure are formed. As a result, each  $\text{BiO}_3$  triangle is connected with three tetrahedra, and each tetrahedron is connected with four triangles. It is established that the initial stages of the appearance of crystalline phases during the cooling of the melts are observed in the glass containing not less than 40 mol % of  $\text{Bi}_2\text{O}_3$ .

**Keywords:** structure, short-range order, middle-range order, wide-angle X-ray scattering, bismuth germinate glass

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### INTRODUCTION

The structure of the short- and medium-range orders in glass largely determines the physicochemical properties and their changes depending on the composition, temperature, heat-treatment regimes, etc. The formation of structural groupings in glass due to a chemical interaction has been reliably established based on the data of nuclear magnetic resonance (NMR), thermodynamic simulation, Raman scattering, and other methods.

The wide-angle X-ray scattering (WAXS) allows studying the structure of the short- and medium-range orders in amorphous compounds. It should be noted that the data about the structure obtained by the WAXS method are rather limited, even in the case of the simplest single-component vitreous oxides of silicon and boron [1–3]. In multicomponent systems, the interpretation of the WAXS data in the analysis of the structure beyond the first coordination spheres is extremely complicated. However, the WAXS method is still promising for the investigation of some specific structural features of both the short- and medium-range order, especially in glass containing oxides of heavy elements. It should be noted that the heavy elements have a higher scattering power and, at the same time, absorb X rays more; as a result, the intensity scat-

tered by a smaller sample volume is recorded. These two effects compensate each other, and, as a result, the diffraction patterns, both from glass with heavy elements and without them, show a scattering of comparable intensity. In the observed intensity of WAXS, the contribution of the scattering of heavy elements is predominant. As a result, the angular dependence of the intensity of WAXS and the correlational function obtained based on it contain information about both the structure of the environment of the modifier ions and their distribution in the glass volume. Therefore, two-component silicate and borate glass containing lead, barium, and cesium oxides were earlier studied by the WAXS method [4, 5]. In these works, the possibility of cluster formation in the glass of the given systems, at least the formation of couples of heavy ions, was mentioned.

Recently, using more complex equipment and high-intensity X rays, in particular synchrotron radiation, mainly two-component silicate and borate glass containing SrO and BaO have been studied [6, 7]. To study the glass structure, it is necessary to use other physicochemical techniques.

To date, glass of a number of  $\text{RO--B}_2\text{O}_3\text{--SiO}_2$  systems, where SrO [8], BaO [9], PbO, and CdO were taken as RO [10], have been studied by WAXS. A common regularity is observed in the glass of these systems: a shift of the maximum position on the angular

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dependences of the WAXS intensity towards large angles, i.e., decreasing interatomic distances when the ionic radius of the modifying cation is reduced. When the  $\text{B}_2\text{O}_3$  content in the glass was increased, a maximum at  $2\theta$  angles of  $16^\circ$  to  $17^\circ$  was noted, which indicates the appearance of a correlation in the positions of the heavy metal ions. This can be connected with the occurrence of repeated distances due to the formation of borate groups containing ions of heavy elements.

In the study of glass of the  $\text{Bi}_2\text{O}_3\text{--B}_2\text{O}_3\text{--SiO}_2$  system by the WAXS method [11], a fundamental difference was found in the effect of  $\text{Bi}_2\text{O}_3$  on the above-mentioned heavy elements on the form of the angular dependences of the WAXS intensity, and, consequently, on the glass structure. Glass of the  $\text{Bi}_2\text{O}_3\text{--GeO}_2\text{--SiO}_2$  system was studied earlier in [12–15]. The interest in the glass and crystalline compounds of the  $\text{Bi}_2\text{O}_3\text{--GeO}_2\text{--SiO}_2$  system is primarily connected with the prospect of their use as scintillators in the registration of high-energy radiation. In [12], the location of the glass-forming area was specified in the use of different methods of cooling a melt: when casting a melt onto a platinum foil and cooling a crucible in cold water. The densities and refraction indexes were determined for the glass in the  $\text{Bi}_2\text{O}_3\text{--GeO}_2$  system. In the three-component system, an extended area of opalescent glass was found, and one of them ( $30\text{Bi}_2\text{O}_3 \cdot 50\text{GeO}_2 \cdot 20\text{SiO}_2$ ) was studied by scanning electron microscopy. In the authors' opinion, this structure was caused by the phase separation processes. According to [12], transparent glass was obtained only at a  $\text{Bi}_2\text{O}_3$  content of 40 mol % at the cooling of the crucible in cold water. When the  $\text{Bi}_2\text{O}_3$  content was  $\geq 50$  mol %, the glass was fully crystallized; and at the  $\text{Bi}_2\text{O}_3$  content of  $\leq 30$  mol %, as a rule, the glass was opalescent and partly crystallized.

In the study of glass with eulytine  $2\text{Bi}_2\text{O}_3 \cdot 3[(\text{GeO}_2)_x \cdot (\text{SiO}_2)_{1-x}]$  and sillenite  $6\text{Bi}_2\text{O}_3 \cdot [(\text{GeO}_2)_x \cdot (\text{SiO}_2)_{1-x}]$  compositions by the vibrational spectroscopy method [13], it was noted that in a low-frequency area the Raman spectra is independent of the  $\text{GeO}_2/\text{SiO}_2$  ratio, and in a high-frequency area the intensities of the scattering peaks are correlated with the concentrations of  $\text{GeO}_4$  and  $\text{SiO}_4$ . Note, that in [13] the X-ray diffraction (XRD) patterns of glass of the  $40\text{Bi}_2\text{O}_3 \cdot 30\text{SiO}_2 \cdot 30\text{GeO}_2$  composition are given for the initial state and during crystallization at temperatures ranging from  $500$  to  $800^\circ\text{C}$ . At low-temperature heat treatments, two crystalline phases are distinguished in the sample, and they have the following component ratio: 2 : 3 ( $2\text{Bi}_2\text{O}_3 \cdot 3[(\text{GeO}_2)_x \cdot (\text{SiO}_2)_{1-x}]$ ) and 1 : 1 ( $\text{Bi}_2\text{O}_3 \cdot [(\text{GeO}_2)_x \cdot (\text{SiO}_2)_{1-x}]$ ), where  $x$  changes from 0 to 1. When the temperature is increased, the share of the 1 : 1 phase decreases, and only the 2 : 3 phase remains after the heat treatment at  $800^\circ\text{C}$ . Crystallization processes on glass of the

$\text{Bi}_2\text{O}_3\text{--GeO}_2$  binary system were studied in [14, 15]. In heat-treated glass of the  $\text{Bi}_2\text{O}_3\text{--GeO}_2$  system, the following crystalline phases were found:  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  in glass with the component ratio of 1 : 3,  $\text{Bi}_2\text{GeO}_5$  and  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  in glass with the component ratio of 2 : 3 and 1 : 1, and  $\text{Bi}_{12}\text{GeO}_{20}$  in glass with the component ratio of 6 : 1.

In this work, glass of the two-component  $\text{Bi}_2\text{O}_3\text{--GeO}_2$  and three-component  $\text{Bi}_2\text{O}_3\text{--GeO}_2\text{--SiO}_2$  systems are studied. The glass compositions are located on the concentration triangle in the sections with the ratio of molar concentrations of  $\text{SiO}_2/\text{GeO}_2$  glass-forming oxides of 3/1, 1/1, and 1/3 at the  $\text{Bi}_2\text{O}_3$  content ranging from 10 to 50 mol % with a step of 5 to 10 mol %. At the  $\text{Bi}_2\text{O}_3$  content ranging from 60 to 80 mol %, glass was not obtained due to the crystallization of the melts at quenching. In the present work, when interpreting and discussing the results, we used the data collected earlier in [11]. This study is a continuation of the earlier works [8–11] devoted to the study of the glass structure of two- and three-component systems containing oxides of heavy elements.

## EXPERIMENTAL

Glass was melted in a platinum crucible at temperatures of  $900$  to  $1400^\circ\text{C}$  depending on the composition. Silicon, germanium, and bismuth oxides with a purity of 99.9% were used as the starting materials. The duration and temperature of the sample synthesis were chosen according to the necessity of reaching a complete mixing of the components and avoiding the evaporation of highly volatile bismuth oxide. Table 1 lists the glass compositions by the synthesis in molar percent. It should be noted that when the bismuth oxide content was increased, the color of the glass changed from red-brown to red, and for the crystallized samples it changed to yellow-green. It is well known that yellow and orange colors are characteristic for different crystalline modifications of  $\text{Bi}_2\text{O}_3$ , and  $\text{Bi}_2\text{O}_5$  crystals have a red color with a brown tint. Thus, the variation of the color of the synthesized glass indicated the presence of bismuth in different oxidation states; however, their qualitative ratio cannot be determined based only on the observed color shades.

After the casting, the glass was annealed in a muffle furnace. Then, the glass samples were studied as powders; further fine annealing was not required because the sensitivity of the WAXS method is insufficient to reliably control the changes in the interatomic distances during annealing.

This work aims to study the short- and medium-range order in glass of the  $\text{Bi}_2\text{O}_3\text{--SiO}_2\text{--GeO}_2$  system, especially interatomic distances, structural groups, and their mutual distribution.

Angular dependences of the scattering intensity at  $2\theta$  angles ranging from  $4^\circ\text{--}6^\circ$  to  $55^\circ\text{--}70^\circ$  were obtained

**Table 1.** Compositions of glass in the Bi<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–GeO<sub>2</sub> system by synthesis (mol %), positions of the first and the second maxima of WAXS curves, the width of the first maxima, and interatomic distances calculated by the position of the first diffraction maximum

Bi <sub>2</sub> O <sub>3</sub>	GeO <sub>2</sub>	SiO <sub>2</sub>	First maximum position, 2θ ± 0.1°	Second maximum position, 2θ ± 0.1°	First maximum width 2θ ± 0.1°	Interatomic distance for the first maximum, Å
10	90		26.7	—	12.5	4.11
20	80		27.8	51.6	9.0	3.95
30	70		28.1	51.0	7.2	3.91
50	50		28.5	50.5	5.5	3.96
20	40	40	28.0	50.6	7.4	3.93
30	35	35	28.0	50.6	6.7	3.93
35	32.5	32.5	28.1	51.6	6.3	3.91
40	30	30	28.1	50.4	5.9	3.91
45	27.5	27.5	28.2	50.4	5.8	3.89
50	25	25	28.3	51.3	5.2	3.88
10	67.5	22.5	27.5	51.5	10.4	4.00
20	60	20	27.7	51.5	8.1	3.97
30	52.5	17.5	27.9	51.6	7.2	3.94
35	48.8	16.2	28.3	52.0	6.3	3.88
40	45	15	28.3	51.1	6.2	3.88
45	41.3	13.7	28.4	51.1	5.8	3.87
50	37.5	12.5	28.4	51.6	5.3	3.87
30	17.5	52.5	28.0	50.4	6.7	3.93
35	16.3	48.7	28.1	51.0	6.3	3.91
40	15	45	28.1	50.0	5.9	3.91
45	13.8	41.2	28.4	50.0	5.5	3.87
50	12.5	37.5	28.4	52.0	4.7	3.87
20–40		80–60	27.9*	48.0*	7.0*	3.95*

\* Data of work [11].

in the study by the WAXS method using a Rigaku X-ray diffractometer with CuK<sub>α</sub> radiation. The correlational functions were not calculated in the study of a number of other systems containing heavy elements [8–11]. A reliable angular dependence in a wide range of scattering vectors cannot be obtained using a common diffractometer. Nevertheless, some conclusions on the structure can be made based on the positions of the diffraction maxima in the WAXS angular dependences.

The presence of pronounced diffraction maxima in the angular dependence of the WAXS intensity gives reason us to connect the appearance of these maximums with the existence of repeated interatomic distances. The interatomic distances were calculated using the approximate formula [16]

$$d = \frac{1.23\lambda}{2 \sin \theta}, \quad (1)$$

where λ = 1.54 Å is the wavelength of CuK<sub>α</sub> radiation. Equation (1) is, in fact, the Bragg–Wolfe equation.

Interatomic distances act as an interplanar distance. The coefficient in the numerator is associated with an arbitrary orientation of the pairs of atoms relative to the direction of the primary beam. The value of this coefficient can be specified for each experimental setting by the positions of the maximums on the angular dependences of the WAXS intensity of the samples if the interatomic distances are known. For example, in vitreous B<sub>2</sub>O<sub>3</sub> such distances are the interatomic distances of O–O in BO<sub>3</sub> or boroxol rings. The O–O interatomic distance in the structure of vitreous Bi<sub>2</sub>O<sub>3</sub> is accurately determined, and its value is 2.37 Å [2]. It follows from Eq. (1) that the maximum on the angular dependence of WAXS should be at θ = 23.6° (2θ = 47.2°). As a result of the test, the correct use of Eq. (1) in determining the interatomic distances was confirmed for boric anhydride.

In the case of the glass studied in this work, BiO<sub>3</sub> triangle and SiO<sub>4</sub> and GeO<sub>4</sub> tetrahedra can be considered the main structural groups. In crystalline structures, for example, eulytine Bi<sub>4</sub>Si<sub>3</sub>O<sub>12</sub> or its analog

$\text{Bi}_4\text{Ge}_3\text{O}_{12}$ , the three Bi–O distances in the  $\text{BiO}_3$  triangle are 2.155 Å (Mincrust database, nos. 1417 and 1418, respectively). The coordination number of bismuth by oxygen is 6. The other three Bi–O distances are 2.616 Å. Assuming the similarity of the structure of the short-range order of the liquid and crystalline state, the appearance of a smoothed maximum on the angular dependences of the WAXS intensity by bismuth-containing glass can be expected; this maximum corresponds to the average interatomic distance of about 2.38 Å.

It should be noted that although the obtained values of interatomic distances are approximate and may slightly differ from those calculated by the maxima on the correlational functions, we can assume that their changes depending on the composition are close to the correct values.

In the research on the short- and medium-range orders, controlling the single-phase and homogeneity of glass is important. It can be performed using the small-angle X-ray scattering (SAXS) method. The intensity of the SAXS of a single-phase homogeneous liquid is caused only by the heat fluctuations of density, and it is independent of the scattering angle [17]. This makes it possible to reliably record the appearance of the additional scattering associated with the development of an inhomogeneity as a result of phase separation.

A thickness of a few microns of samples of bismuth-containing glass for studying SAXS is optimal. The samples having such a thickness cannot be obtained by conventional methods of grinding and polishing. When powders are used, intense scattering by the surface of the powder grains appears in the small-angle range. The intensity of this scattering  $I(\varphi)$  decreases proportionally to  $\varphi^{-3}$  (Porod's law), where  $\varphi$  is the scattering angle. Considering Porod's law, the surface scattering can be excluded, and the intensity of scattering by the bulk structure of the grains can be obtained in the use of powder samples.

## RESULTS

The powder samples of synthesized glass were studied by the SAXS method only to control the homogeneity and the single phase. According to the SAXS data, nanosized areas exist in glass containing 10 mol %  $\text{Bi}_2\text{O}_3$ . According to the XRD analysis, there are no crystalline phases in the sample. The appearance of these areas can be connected with the processes of the separation of the liquid phase occurring during the cooling of the sample.

The SAXS intensity by the glass samples containing 20–40 mol % of  $\text{Bi}_2\text{O}_3$  is almost independent of the scattering angle; i.e., the structure of these types of glass is homogeneous, and the observed intensity is caused only by the heat fluctuations of the density. According to the SAXS data, the synthesized glass

containing 20–40 mol % of  $\text{Bi}_2\text{O}_3$  is single-phase and homogeneous. In glass containing at least 50 mol %  $\text{Bi}_2\text{O}_3$ , the initial stages of the crystallization that occurred during quenching are detected by the XRD method. Our work does not confirm the data of [12] on the crystallization and liquation of samples of the studied glass at the  $\text{Bi}_2\text{O}_3$  content of 30 mol %.

Figure 1 presents angular dependences of WAXS in the angle range  $2\theta = 4^\circ\text{--}55^\circ$  by vitreous  $\text{SiO}_2$  and  $\text{GeO}_2$  (dependences 1 and 2, respectively) and glass containing  $10\text{Bi}_2\text{O}_3 \cdot 90\text{GeO}_2$  and  $35\text{Bi}_2\text{O}_3 \cdot 32.5\text{GeO}_2 \cdot 32.5\text{SiO}_2$  (dependences 3 and 4, respectively). On the angular WAXS dependence by vitreous  $\text{SiO}_2$ , the first diffraction maximum at the scattering angle  $\sim 21.3^\circ$  corresponds to the more probable (most common) interatomic distance of 5.15 Å between atoms of the first and the second coordination spheres. The fine structure of the angular dependence in the range of angles  $30^\circ\text{--}40^\circ$ , which was previously observed in [1], was not observed in this work due to the resolution of the equipment in the technique used.

On the WAXS curve by vitreous  $\text{GeO}_2$ , the first diffraction maximum is located at  $22.6^\circ$ , and it is shifted relative to the maximum in the scattering curve by vitreous  $\text{SiO}_2$  by approximately  $1.3^\circ$  and corresponds to an interatomic distance of 4.84 Å. To analyze the data obtained on studying three-component systems containing bismuth oxide, it is more important that in single-component glass, the first diffraction maxima are located at  $2\theta$  angles equal to  $21^\circ\text{--}23^\circ$ .

In this work, two-component glass of the  $\text{SiO}_2\text{--GeO}_2$  system was not synthesized. Further, in [18], it was established that the angular dependence of the WAXS intensity by the three-component glass of the  $\text{Na}_2\text{O--B}_2\text{O}_3\text{--SiO}_2$  system can be presented, in the first approximation, as the sum of the WAXS intensities by the glass of the  $\text{Na}_2\text{O--B}_2\text{O}_3$  and  $\text{Na}_2\text{O--SiO}_2$  systems if the composition of the three-component glass is equal to the sum of the compositions of the two-component glass. This result was called the additivity principle in [18]. Assuming the correctness of the mentioned additivity principle, it can be suggested that the first diffraction maximum in the angular dependences of the WAXS intensity by the glass of the  $\text{SiO}_2\text{--GeO}_2$  system will be located within the range of  $21.3^\circ$  to  $22.6^\circ$ , and the intensity of the second maximum will be dependent on the component ratio.

It is seen from Fig. 1 (curve 3) that in the case of two-component bismuth-germanate glass containing 10 mol %  $\text{Bi}_2\text{O}_3$ , the form of the angular dependence of the WAXS intensity significantly changes. The first and the second maxima are observed at the  $2\theta$  angle of  $27^\circ$  and  $50^\circ$ , respectively. As the  $\text{Bi}_2\text{O}_3$  content increases (curve 4), the first maximum shifts to the  $2\theta$  angle of  $28^\circ$  and its width decreases noticeably. The table lists the positions and widths of the maxima of the WAXS curves for all the studied types of glass.

Let us consider the most characteristic glass series of the studied two- and three-component systems. Figure 2 demonstrates the angular dependences of the WAXS intensity by the two-component glass of the  $\text{Bi}_2\text{O}_3\text{--SiO}_2$  system with the bismuth oxide content of 20, 30, and 40 mol %. Two maxima are observed on each of the WAXS curves. In general, the angular dependences are very close to each other, although the second maximum shifts slightly towards the wide-angle area (table) as the  $\text{Bi}_2\text{O}_3$  content is increased, which indicates a decrease in the corresponding interatomic distance.

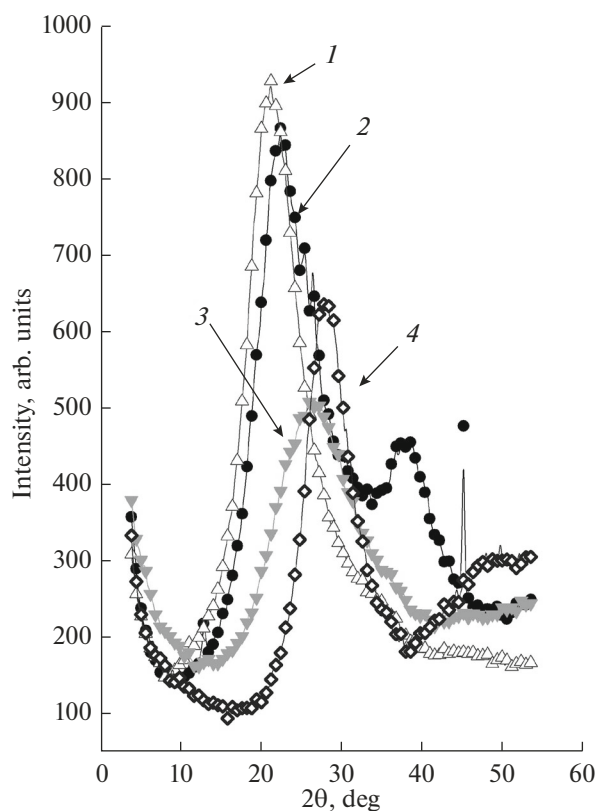
The angular scattering dependences by glass of the  $\text{Bi}_2\text{O}_3\text{--GeO}_2$  two-component system with the  $\text{Bi}_2\text{O}_3$  content of 10, 20, 30, and 50 mol % are given in Fig. 3. Two maxima are also observed on the WAXS curves by these types of glass. Unlike the glass of the  $\text{Bi}_2\text{O}_3\text{--SiO}_2$  system, in the bismuth-germanate system, as the  $\text{Bi}_2\text{O}_3$  content increases, the first maximum shifts significantly towards large angles, its width decreases significantly (table), and its height increases. An increase in the  $\text{Bi}_2\text{O}_3$  content also leads to a growth of the intensity of the second maximum.

Figure 4 demonstrates the angular dependences of WAXS by the three-component glass containing 20, 30, 40, and 50 mol %  $\text{Bi}_2\text{O}_3$  at the  $\text{GeO}_2/\text{SiO}_2$  molar ratio of 1 : 1 (dependences 1–4, respectively). The observed angular dependences are almost similar, and the positions of the maxima are independent of the  $\text{Bi}_2\text{O}_3$  content.

Weak diffraction reflections of crystalline phases appear on the angular dependences of the WAXS intensity by some glass containing ~50 mol %  $\text{Bi}_2\text{O}_3$ . The volumes of these phases are negligible and have no effect on the form of the angular scattering dependences by the vitreous phase; however, they are sufficient for the phase analysis.

In the glass of the  $\text{Bi}_2\text{O}_3\text{--GeO}_2$  system containing 40 mol %  $\text{Bi}_2\text{O}_3$ , the  $\text{Bi}_2\text{GeO}_5$  crystalline phase is indicated, while this phase is not observed at the  $\text{Bi}_2\text{O}_3$  content of 50 mol %. The  $\text{Bi}_2\text{GeO}_5$  phase is also observed in three-component glass with the  $\text{GeO}_2/\text{SiO}_2$  molar ratio of 3 : 1 at 50 mol %  $\text{Bi}_2\text{O}_3$ . In the glass of this section,  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  eulytine is released at the  $\text{Bi}_2\text{O}_3$  content of 40 mol %.

In the two-component glass of the  $\text{Bi}_2\text{O}_3\text{--SiO}_2$  system containing 50 mol %  $\text{Bi}_2\text{O}_3$ , eulytine  $\text{Bi}_4\text{Si}_3\text{O}_{12}$  and  $\text{Bi}_{12}\text{SiO}_{20}$  are formed. The sample containing 80 mol %  $\text{SiO}_2$  was fully crystallized, and  $\text{Bi}_{12}\text{SiO}_{20}$  was the main phase. In glass with the  $\text{GeO}_2/\text{SiO}_2$  molar ratio of 1 : 3 and with the  $\text{Bi}_2\text{O}_3$  content of 50 mol %, sillenite  $\text{Bi}_{12}\text{SiO}_{20}$  is released.

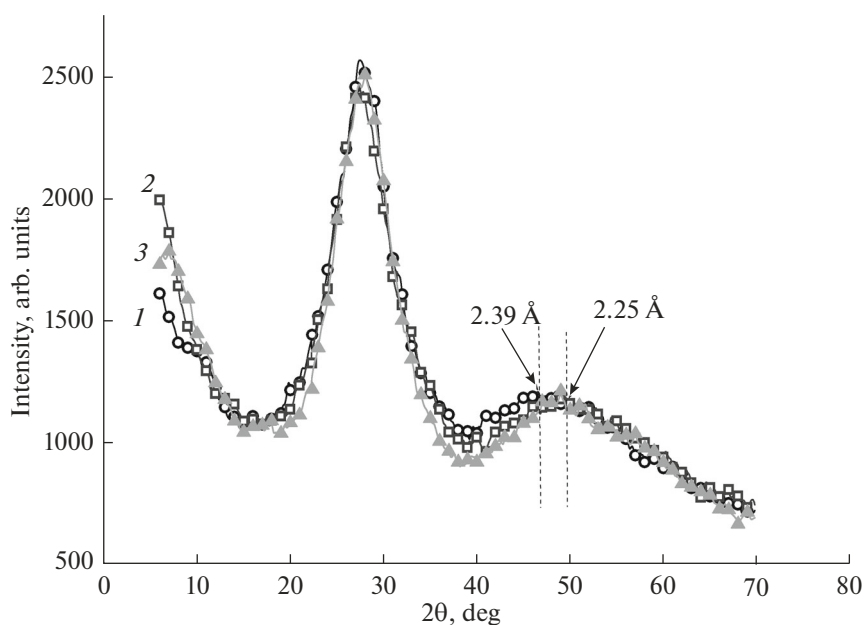


**Fig. 1.** Angular dependences of WAXS intensity by vitreous  $\text{SiO}_2$  (1),  $\text{GeO}_2$  (2), and glass containing  $10\text{Bi}_2\text{O}_3 \cdot 90\text{GeO}_2$  (3) and  $35\text{Bi}_2\text{O}_3 \cdot 32.5\text{GeO}_2 \cdot 32.5\text{SiO}_2$  (4).

## DISCUSSION

As is seen from Fig. 1 (dependence 3), in bismuth-germanate glass, a significant change in the appearance of the angular dependences of the WAXS intensities is observed at the  $\text{Bi}_2\text{O}_3$  content of 10 mol % in comparison with vitreous germanium oxide; i.e., the character of medium-range interaction changes. The complete disappearance of the main diffraction maximum of vitreous  $\text{GeO}_2$  at angles of  $21^\circ\text{--}22^\circ$  can be partly connected with the contribution of the scattering by the bismuth atoms to the measured WAXS intensity. However, the main reason is apparently connected with the chemical interactions leading to the formation of bismuth-germanate structural groups with the molar ratio of the components coinciding with the stoichiometry of the compounds formed in the studied system.

It can be assumed that the structural groups correspond to the structure of the crystalline phases, whose appearance is observed in the studied glass containing 40 and 50 mol % of  $\text{Bi}_2\text{O}_3$ . An intense reflection (310) is observed in the XRD powder patterns of the cubic modifications of bismuth silicates and germinates ( $\text{Bi}_4(\text{GeO}_4)_3$ ,  $\text{Bi}_4(\text{SiO}_4)_3$ , and  $\text{Bi}_{12}\text{SiO}_{20}$ ) at the  $2\theta$  angles of  $26.766^\circ$  (84-505),  $27.376^\circ$  (35-1007), and



**Fig. 2.** Angular dependences of WAXS intensity by glass of  $\text{Bi}_2\text{O}_3\text{--SiO}_2$  system at  $\text{Bi}_2\text{O}_3$  content of 20, 30, and 40 mol % (1, 2, and 3, respectively).

$27.892^\circ$  ( $37\text{--}0485$ ), respectively. This area of the angles coincides with the area where the main WAXS maximum is observed in the corresponding glass. In glass with a high germanium content, the first diffraction maximum is located at  $2\theta$  angles equal to  $26.7^\circ\text{--}27.5^\circ$ . In glass with a high content of  $\text{Bi}_2\text{O}_3$  or  $\text{SiO}_2$ , the diffraction maximum is located within the  $2\theta$  angle range of  $28^\circ\text{--}28.4^\circ$ .

The proximity of the positions ( $2\theta$  angles) of these diffraction reflections on the powder XRD patterns of the crystalline compounds with the position of the first diffraction maximum on the angular WAXS dependences by glass can also be considered as an indicator of the existence of a similarity in the structures of the considered crystals and glass.

The structure of eulytine  $\text{Bi}_4(\text{SiO}_4)_3$  consists of oxygen tetrahedra around silicon atoms in their centers and oxygen triangles over the plane of which bismuth atoms are located (the structure of  $\text{Bi}_4(\text{GeO}_4)_3$  is similar). Such a configuration is frequently called an *umbrella* [19].

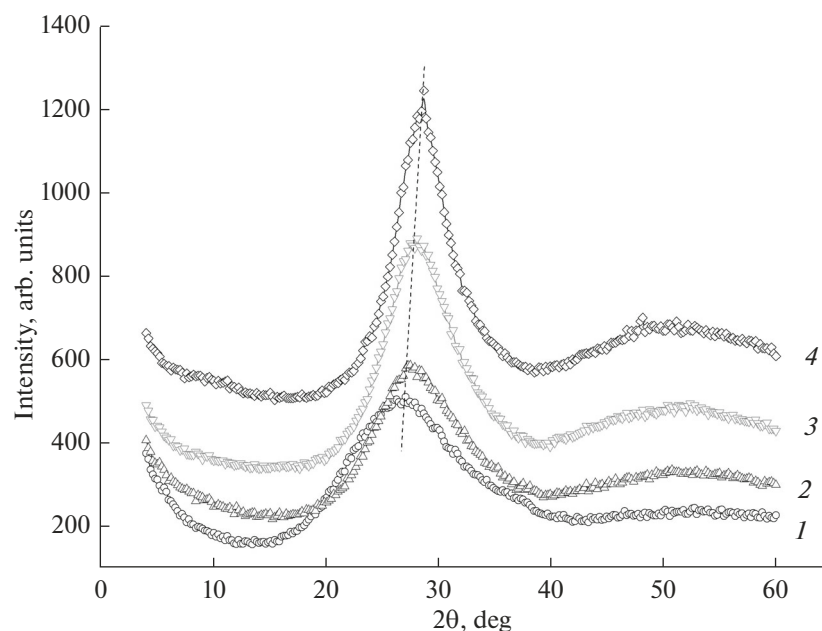
In crystal structures, the Bi–O distance in the  $\text{BiO}_3$  triangle is  $2.15 \text{ \AA}$ . Considering that the Si–O bond length in the  $\text{SiO}_4$  tetrahedron is  $1.62 \text{ \AA}$  [1], and the length of the Ge–O bond in the germanate tetrahedron is slightly larger, the average interatomic distance between the centers of Bi atoms and central atoms of  $\text{SiO}_4$  or  $\text{GeO}_4$  tetrahedra linked to the  $\text{BiO}_3$  triangle could be  $3.8\text{--}4.0 \text{ \AA}$ . According to EQ. (1), the first diffraction reflection on the angular dependences of the WAXS intensity at  $2\theta = 27\text{--}28.4^\circ$  corresponds to interatomic distances of  $3.9$  to  $4.1 \text{ \AA}$ . Therefore, it can

be assumed that the  $\text{BiO}_3$  triangles (umbrellas) connected with three  $\text{SiO}_4$  or  $\text{GeO}_4$  tetrahedra are the main structural groups in the studied glass.

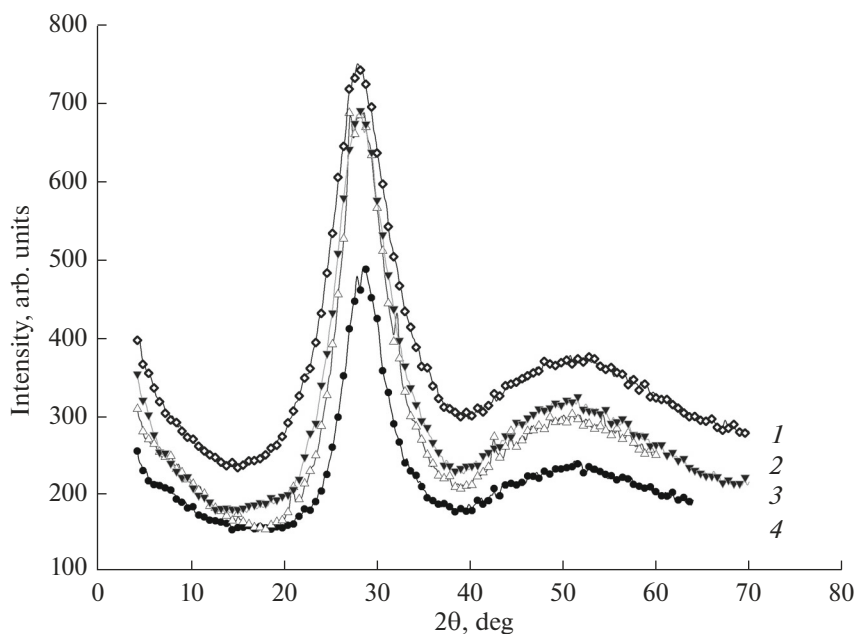
As is seen from the results given in Figs. 3 and 4 and in the table, on the WAXS curves by glass, the position of the first diffraction maximum changes insignificantly. At the same time, the width of this reflection changes noticeably, especially for glass with a high  $\text{GeO}_2/\text{SiO}_2$  molar ratio. At a high  $\text{Bi}_2\text{O}_3$  content, the half-width of the first diffraction reflection becomes equal to  $5.5^\circ$  or even smaller. In the case of nanocrystallites, such a width of the diffraction reflection by the Debye–Scherrer equation is expected at the linear size of the crystallites of about  $16 \text{ \AA}$ .

As was mentioned above, the structural groups can be rather large and contain several  $\text{BiO}_3$  triangles (umbrellas) and, correspondingly, several  $\text{SiO}_4$  or  $\text{GeO}_4$  tetrahedra. This could be used to explain the constancy and reproducibility of the interatomic distances and, accordingly, the positions of the main diffraction maximum on the WAXS curves.

The narrowing of the diffraction maximum indicates a decrease in the distribution by the length of interatomic distances relative to the most probable interatomic distance. This effect may be connected with the association of structural groups, which is accompanied by a local ordering of the structure. Consequently, we can assume the appearance of the medium-range order in the structure of the glass studied. In a certain sense, this process can be considered as a stage of the formation of nanocrystals of the critical and supercritical sizes, so that at the content of 40



**Fig. 3.** Angular dependences of WAXS intensity by glass of  $\text{Bi}_2\text{O}_3\text{--GeO}_2$  system and  $\text{Bi}_2\text{O}_3$  content of 10, 20, 30, and 50 mol % (1, 2, 3, and 4, respectively).



**Fig. 4.** Angular dependences of WAXS intensity by glass containing 20 (1), 30 (2), 40 (3), and 50 (4) mol %  $\text{Bi}_2\text{O}_3$  at  $\text{GeO}_2/\text{SiO}_2$  molar ratio of 1.

and 50 mol %  $\text{Bi}_2\text{O}_3$ , the precipitation of the crystalline phases is observed during the cooling of the melts.

### CONCLUSIONS

The glass formation in the  $\text{Bi}_2\text{O}_3\text{--GeO}_2\text{--SiO}_2$  system is observed at the  $\text{Bi}_2\text{O}_3$  content  $\leq 50$  mol %. In

glass containing 10 mol %  $\text{Bi}_2\text{O}_3$ , signs of the separation of the liquid phase were found, and single-phase glass was obtained at the  $\text{Bi}_2\text{O}_3$  content of 20 to 40 mol %. The angular dependences of the WAXS intensity by the glass of all the studied compositions in the considered system are largely similar. In the  $2\theta$  range from  $4^\circ$  to  $60\text{--}70^\circ$ , two diffraction maxima are observed on the WAXS curves.



The observed changes in the character of the angular dependences of WAXS by the glass of the studied system when the composition changes can be explained by the existence of large structural groups, which leads to the formation of the reproducible average interatomic distance. The positions of the diffraction maxima change with the composition within narrow limits. The width of the observed maxima decreases significantly at an increase in the  $\text{Bi}_2\text{O}_3$  content. The structural groups in the studied glass are probably  $\text{BiO}_3$  triangles (umbrellas) connected with three  $\text{SiO}_4$  or  $\text{GeO}_4$  tetrahedra.

When the  $\text{Bi}_2\text{O}_3$  content is increased, the association of structural groups, accompanied by the ordering in local areas, occurs, which leads to a significant narrowing of the width of the diffraction reflections. It can be considered as evidence of the existence of a medium-range order in the structure of the studied glass.

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#### CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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