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PHASE, GLASS FORMATION AND THE PROPERTIES OF BaO–Bi_2O_3–B_2O_3 GLASSES

N. M. Bobkova,[1] E. E. Trusova,[1, 2] and G. B. Zakharevich[1]

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Information on phase and glass formation in bismuth-borate systems as a basis for obtaining lead-free low-melting glasses with wide ranging physical and optical properties is generalized. Information on the phase composition and structure in Bi_2O_3–B_2O_3 and BaO–Bi_2O_3–Bi_2O_3 systems is presented. Data on glass formation and properties in the system BaO–Bi_2O_3–B_2O_3 system are presented, including data obtained by the present authors.

Key words: low-melting glass, phase formation, glass formation, structure, coordination number.

The rapid development of opto-electronics is making it necessary to search for new optical systems among which bismuth borates occupy a special place, ensuring that glasses based on them are low-melting, comparable to many lead glasses, and giving glass with a considerably higher refractive index together with a much lower heavy-metal oxide content.

A number of low-melting compounds and eutectics form in the system Bi_2O_3–B_2O_3 in stable equilibrium [1 – 3]. The compositions and melting temperatures of compounds and eutectics in this system are presented in Table 1.

In addition, it has been established that the metastable compounds $Bi_2O_3 \cdot B_2O_3$ and $5Bi_2O_3 \cdot 3B_2O_3$ are formed [4], though the compound $Bi_2O_3 \cdot B_2O_3$ is presented in [5] as stable with melting temperature 685°C.

The formation of a eutectic with the composition $48.5Bi_2O_3 \cdot 51.5B_2O_3$ and melting temperature 665°C is reported in [6]. In addition, a more accurate value is given for the decomposition temperature of the compounds with molar ratios $Bi_2O_3 : B_2O_3 = 12 : 1$ – 628°C [7].

As follows from the data in Table 1 all compounds and eutectics in the system Bi_2O_3–B_2O_3 are characterized by quite low melting temperatures.

For comparison the compositions and melting temperatures of compounds and eutectics in the system PbO–B_2O_3 are presented in Table 2.

Even though the melting temperatures of the compounds and eutectics in both systems are comparable to one another, in many cases the system Bi_2O_3–B_2O_3 is preferable, because it permits obtaining very low-melting glasses with considerably lower Bi_2O_3 content compared with PbO (see composition of eutectics).

The structure of bismuth borates has been studied quite fully by vibrational spectroscopy (RS and IRS) and x-ray structural analysis [3, 9]. The structure of the compound α-$Bi_2O_3 \cdot 4B_2O_3$ is of the frame type. A series of chains and rings is observed. The coordination polyhedral [BO_3] and [BO_4], joining at common vertices, form an infinite chain parallel to the X axis. The trigonal pyramids [BO_3], combined into a six-member ring, form an infinite chain parallel to the Z axis. The [BiO_6] octahedra joined along edges also form an infinite chain parallel to the X axis [9].

The first vibrational spectra of bismuth borate crystals $12Bi_2O_3 \cdot B_2O_3$, $2Bi_2O_3 \cdot B_2O_3$, $Bi_2O_3 \cdot B_2O_3$, and $Bi_2O_3 \cdot 4B_2O_3$ in the range 30 – 1600 cm^{-1} were obtained, analyzed and presented in [3]. Analysis of the RS spectra of bismuth borates has established that they are determined by the vibrations of bismuth-oxygen and boron-oxygen structural units. The characteristic spectral regions where bands due to vibrations along Bi–O and B–O bonds occur have been identified.

The IR spectrum of the oxide γ-Bi_2O_3, characterized by a distinct wide absorption band in the region 430 – 540 cm^{-1}, which is also present for the compound $12Bi_2O_3 \cdot B_2O_3$, is also presented in [3].

The $12Bi_2O_3 \cdot B_2O_3$ crystal belong to the cubic system. The boron atoms are located in isolated [BO_3] groups, joining coordination BiO_x polyhedral. The form of the vibrational spectra is determined by the vibrations of the Bi–O framework.

[1] Belorussian State Technological University, Minsk, Belarus.
[2] E-mail: trusovakaterina@mail.ru.

TABLE 1. Compositions of Compounds and Eutectics in the System Bi_2O_3–B_2O_3

Compounds			Eutectics		
Compositions, molar ratio $Bi_2O_3 : B_2O_3$	Melting temperature, °C	Refractive index	Molar content, %		Melting temperature, °C
			Bi_2O_3	B_2O_3	
12 : 1	632 inc.	–	80.5	19.5	622
2 : 1	675	> 1.8	55.0	45.0	646
3 : 5	722	1.88	27.5	72.5	698
1 : 3	708	< 1.9	24.0	76.0	696
1 : 4	715	1.748	–	–	–

TABLE 2. Compositions of Compounds and Eutectics in the System PbO–B_2O_3

Compounds			Eutectics		
Compositions, molar ratio PbO : B_2O_3	Melting temperature, °C	Refractive index	Molar content, %		Melting temperature, °C
			PbO	B_2O_3	
4 : 1	565	2.175	82.4	17.6	560
2 : 1	497 inc.	2.0258	–	–	–
5 : 4	548 inc.	1.92	–	–	–
1 : 2	742	1.74	–	–	–

The boron atoms in the compound $2Bi_2O_3 \cdot B_2O_3$, just as in the compound $12Bi_2O_3 \cdot B_2O_3$, are in trigonal coordination with respect to oxygen.

Increasing the boron content in the compound $2Bi_2O_3 \cdot B_2O_3$ results in an appreciable increase of the intensities of the bands corresponding to boron-oxygen vibrations of the $[BO_3]$ anions.

The pentaborate anion $[B_5O_{11}]^{7-}$ in the compound $3Bi_2O_3 \cdot 5B_2O_3$ is comprised of two six-member rings lying in perpendicular planes, one ring being comprised of two $[BO_3]^{3-}$ triangles and one $[BO_4]^{5-}$ tetrahedron and the other of one $[BO_3]^{3-}$ triangle and two $[BO_4]^{5-}$ tetrahedra.

The presence of the groups $[BO_3]^{3-}$ and $[BO_4]^{5-}$, belonging to neighboring fragments $[B_3O_9]_{\infty\infty}$ in which none of the $[BO_3]$ groups are directly joined with one another, is observed in the vibrational spectrum of $Bi_2O_3 \cdot 3B_2O_3$.

The frame structure of $Bi_2O_3 \cdot 4B_2O_3$ contains 4-, 6-, 8-, 12- and 24-member rings formed successively by joined $[BO_3]^{5-}$, $[BiO_6]^{9-}$ and $[BO_4]^{5-}$ groups [3].

The structure of the compound $3Bi_2O_3 \cdot 5B_2O_3$ contains the compact fragment $[B_5O_{11}]^{7-}$, which includes three trigonal pyramids $[BO_3]$ and two tetrahedra $[BO_4]$ while the structure of the compound α-$Bi_2O_3 \cdot 4B_2O_3$ is a quite complex frame structure in which several types of infinite chains can be singled out.

A tendency for the coordination numbers of the bismuth atoms to change from 7 to 6 with decreasing ratio $Bi_2O_3 : B_2O_3$ can be seen in the structures of bismuth borate crystals. Bismuth borates with molar content less than 50% B_2O_3 are characterized by single trigonal pyramids coupling coordination polyhedra $[BO_x]$. There are no $[BO_4]$ tetrahedra in the structure of these crystals.

Bismuth borate crystals have a wide transmission range (300 – 3500 nm), which makes them the most important materials for use in the UV region of the spectrum. It has been determined that a number of compositions of the bismuth–borate system exhibit a tendency to form glass with molar content 20 – 75% [8, 10]. The glasses are distinguished by high density ranging from 4660 to 7860 kg/m^3, CLTE in the range $(71 – 123) \times 10^{-7}$ K^{-1} and low glass formation temperature from 426 to 294°C with increasing Bi_2O_3 content and possess optical properties [11]. The glass-forming framework of the glasses consists of $[BO_3]$, $[BO_4]$ and $[BiO_6]$ chains [10].

According to [12], it has been established that when Bi_2O_3–B_2O_3 glasses with 20 – 60 mol.% Bi_2O_3 crystallize phases with the compositions $12Bi_2O_3 \cdot B_2O_3$, $4Bi_2O_3 \cdot B_2O_3$ and $Bi_2O_3 \cdot 2B_2O_3$ precipitate, but subsequent studies have not confirmed the formation of compounds with the composition $4Bi_2O_3 \cdot B_2O_3$.

In recent years special attention has been devoted to obtaining low-melting lead-free glasses based on three-component bismuth-borate systems, such as ZnO–Bi_2O_3–B_2O_3 and BaO–Bi_2O_3–B_2O_3, which give higher chemical stability, though a number of studies of such glasses were also performed previously.

An extensive region of glass formation in the following oxide content ranges (molar fractions, %) has been established in the zinc-containing system: 20 – 65 ZnO; 0 – 60 Bi_2O_3 and 30 – 80 Bi_2O_3 [13]. Some data on the optical and physical properties of ZnO–Bi_2O_3–B_2O_3 are presented in [14]. Glasses with the following compositions (molar fractions, %) were studied: 15 – 70 Bi_2O_3; 15 – 40 ZnO; and 15 – 70 B_2O_3.

As the Bi_2O_3 content increased from 45 to 70% the glass density changed in the range 5910 – 6320 kg/cm^3 and the glass formation temperature t_g = 501 – 492°C. On the basis of the IR spectroscopy data for these glasses the absorption bands at 420 – 450 and 480 cm^{-1} were attributed to Bi–O bonds.

The properties of some zinc–bismuth–borate glasses with added SiO_2, Al_2O_3 and K_2 are presented in [15]. It was determined that as the ratios of ZnO, Bi_2O_3 and B_2O_3 change the temperatures at which the glasses melt completely change from 610 to 655°C, the softening temperatures fall into the range 450 – 550°C and the CLTE into the range $(72 – 86) \times 10^{-7}$ K^{-1}. However, there are virtually no data on phase formation in the zinc–bismuth–borate system.

Interest in the system BaO–Bi_2O_3–B_2O_3 has increased sharply in recent years in connection with the need to find

TABLE 3. Compositions of Triple Compounds in the System $BaO–Bi_2O_3–B_2O_3$

Compositions of compounds		Melting temperature, °C
Formula	Oxide ratio	
$BaBiBO_4$	$2BaO \cdot Bi_2O_3 \cdot B_2O_3$	780 inc.
$Ba_3BiB_3O_9$	$6BaO \cdot Bi_2O_3 \cdot 3B_2O_3$	Decomposes in solid form at 885°C
$BaBi_2B_4O_{10}$	$BaO \cdot Bi_2O_3 \cdot 2B_2O_3$	730
$BaBiB_{11}O_{19}$	$2BaO \cdot Bi_2O_3 \cdot 11B_2O_3$	807

TABLE 4. Glass Formation Boundaries in the System $BaO–Bi_2O_3–B_2O_3$ According to Different Authors

Oxide	Oxide molar content, %			
	according to [13]	according to [20]	according to [12]	according to [21]
BaO	0 – 40	0 – 40	0 – 60	0 – 40
Bi_2O_3	0 – 70	0 – 70	0 – 60	0 – 75
B_2O_3	25 – 80	25 – 80	20 – 80	25 – 75

new optical materials as well as to develop based on it optical glasses with high refractive index, low dispersion coefficient and a wide optical transmission range in the visible and IR regions. Complex studies on phase formation and glass formation in this system have been done.

The formation of the following triple compounds was discovered in the subsolidus region of the system $BaO–Bi_2O_3–B_2O_3$: $BaO \cdot Bi_2O_3 \cdot 2B_2O_3$ and $2BaO \cdot Bi_2O_3 \cdot 11B_2O_3$, obtained by solid-phase reactions in the temperature range 500 – 750°C and with a long synthesis time ranging from 6 to 16 days [16]. The isothermal section of the system $B_2O_3–BaO \cdot Bi_2O_3–B_2O_3$ was constructed using the XPA data for samples annealed at 500°C. A eutectic point corresponding to the composition (molar content, %) 15% $BaO \cdot Bi_2O_3 \cdot 2B_2O_3$ and 85% Bi_2O_3 with melting temperature 616 ± 5°C was found in the section Bi_2O_3–$BaO \cdot Bi_2O_3 \cdot 2B_2O_3$. The compounds $BaO \cdot Bi_2O_3 \cdot 2B_2O_3$ and $2BaO \cdot Bi_2O_3 \cdot 11B_2O_3$ melt congruently at temperatures 780 and 807°C, respectively.

A more complete isothermal section of the system $BaO–Bi_2O_3–B_2O_3$ at 600°C is presented in [17]. The compositions and melting temperatures of the triple compounds in this system are presented in Table 3.

Subsequent studies of phase formation in this system established that two additional compounds probably form in this system — $BaO \cdot 5Bi_2O_3 \cdot 3B_2O_3$ [18] and $BaO \cdot Bi_2O_3 \cdot B_2O_3$ [6, 19] with melting temperatures 690 ± 5 and 725 ± 5°C.

Even though phase formation in the system $BaO–Bi_2O_3–B_2O_3$ has been studied quite completely only in recent years the formation and properties of glasses in this system were studied much earlier. A feature of the system $BaO–Bi_2O_3–B_2O_3$ from the standpoint of glass formation is the presence of a quite extensive region of glass formation in a wide range of Bi_2O_3 and B_2O_3 contents. Apparently, the earliest data on the establishment of the region of glass formation in the system $BaO–Bi_2O_3–B_2O_3$ are presented by Imaoka [13]. Subsequent determination of the glass formation region in this system differs only partially from Imaoka's data (Table 4).

Glasses in the system $BaO–Bi_2O_3–B_2O_3$ were synthesized in order to study the optical constants of glasses in a number of triple systems with heavy metals and the glass formation region was determined more accurately [20].

The glasses were made at temperatures 600 – 1400°C in platinum crucibles in a Silit furnace.

A region of liquid immiscibility was found in the high-borate part of the system. The crystallizability of the glasses was studied; it was noted that glasses with comparatively low Bi_2O_3 content are comparatively stable against crystallization. The optical constants and the CLTE were measured for transparent glasses. The glasses have high refractive indices and in most cases possess strong relative frequency dispersion. On the Abbe diagram they fall in the regions of heavy and superheavy barite flints. The refractive indices of the glasses are in the range 1.7599 – 2.0899. A characteristic of these glasses is the relatively high (85 – 95%) visible- and near-IR-range transmission [20].

Glass formation and the phase composition of the products of crystallization were examined in [12]. It was determined from the results obtained for the composition of the products of crystallization that the barium borates $3BaO \cdot B_2O_3$, $BaO \cdot B_2O_4$ and bismuth borates $12Bi_2O_3 \cdot B_2O_3$, $4Bi_2O_3 \cdot B_2O_3$, and $Bi_2O_3 \cdot 2B_2O_3$ precipitate. However, as noted previously, subsequent studies did not confirm the formation of the compound $4Bi_2O_3 \cdot B_2O$. The CLTE of the experimental glasses lies in the range $(85 – 140) \times 10^{-7}\ K^{-1}$.

It is noted in [21] on the basis of studies of glass formation in the system $BaO–Bi_2O_3–B_2O_3$ that the region of existence of strongly stable glasses corresponds to compositions with lower barium oxide content that indicated in [13, 20]. It was established for the glasses $xBi_2O_3 \cdot (95 – x)B_2O_3 \cdot 5BaO$ with x = 20, 35, 50 and 70% (molar fraction) that as the bismuth oxide content increases the density of the glasses increases from 4438 to 8005 kg/m^3, the glass formation temperature t_g decreases from 650 to 400°C. An essential feature of the IR spectra of the glasses is that irrespective of the composition the wide absorption band in the region 800 – 900 cm^{-1} indicates the presence of $[BO_4]$ tetrahedra in them. The bismuth-oxygen polyhedra make the main contribution to the IR spectrum at wavenumbers below 500 cm^{-1}. New optical materials with nonlinear optical properties have been obtained on the basis of the complex bismuth borates $6BaO \cdot Bi_2O_3 \cdot 3B_2O_3$, $2BaO \cdot Bi_2O_3 \cdot 11B_2O_3$, and $2BaO \cdot Bi_2O_3 \cdot B_2O_3$ [22].

In [23] a number of glasses based on the system $BaO–Bi_2O_3–B_2O_3$ were obtained and studied; they were synthesized at 1200°C in quartz crucibles. These glasses contained (wt.%) from 50 to 65 Bi_2O_3, 20 – 40 B_2O_3 and 5 – 15 BaO (with additives Al_2O_3, ZnO and Sb_2O_3 totaling 10%); t_g of the glasses varied in the range 485 – 481°C and the softening temperature from 490 to 512°C.

The present authors have performed a series of studies in the system $BaO–Bi_2O_3–B_2O_3$. In order to synthesize lead-free low-melting glasses and obtain on their basis light-transforming coatings the glasses were synthesized on the basis of the barium–bismuth–borate system in the composition range (wt.%) 15 – 30 Bi_2O_3, 25 – 40 BaO, and 30 – 45 B_2O_3 with additives SiO_2 and Al_2O_3. The glasses were synthesized in corundum crucibles in a gas-flame furnace at 1000°C. All experimental glasses were characterized by high stability of the glassy state and did not crystallize during heat treatment. The yield temperature in the ceramic boat was 550 – 650°C, CLTE (65 – 86) × 10^{-7} K^{-1}, and refractive index 1.6 – 1.7

These glasses are recommended for obtaining coatings on sheet or electrotechnical glass substrates. These coatings acquire light-conversion properties when any luminophor, e.g., yttrium-aluminum garnet, is introduced into them.

In summary, the heightened interest in the system $BaO–Bi_2O_3–B_2O_3$ is based on the quite high glass-forming capability of compositions based on it and the wide range of variation of the physical and optical characteristics of the glasses. In addition, highly fusible glasses can be obtained without introducing lead oxide.

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