1. Introduction

Restriction and an interdiction on use of toxic materials in electronics products since 2006 have promoted an intensification of development new ecologically friendly materials (glasses, glass ceramics, ceramics) with attractive properties. It has stimulated new lead (cadmium) free systems with good glass forming abilities investigations and new stoichiometric and eutectic points revealing and characterization. Alkaline-earth bismuth borate ternary systems were a good candidate for this purpose, because the binary \( \text{Bi}_2\text{O}_3-\text{B}_2\text{O}_3 \) system have propensity for glass formation and set of binary compounds and eutectics [1 - 3]. Furthermore, bismuth borate single crystals and glass ceramics have nonlinear optical (NLO) properties and other attractive properties [4 - 7]. Both these factors are reasons for further study of binary and ternary bismuth borate systems, and the glasses which they form.

The phase diagram of the \( \text{Bi}_2\text{O}_3-\text{B}_2\text{O}_3 \) system was first determined by Levin &Daniel in 1962 [2] and five crystalline compounds, \( \text{Bi}_{12}\text{B}_{12}\text{O}_{39}, \text{Bi}_4\text{B}_2\text{O}_{9}, \text{Bi}_5\text{B}_2\text{O}_{12}, \text{Bi}_3\text{O}_6 \) and \( \text{Bi}_2\text{B}_8\text{O}_{15} \) were identified. Later Pottier revealed a sixth compound, \( \text{BiBO}_3 \) (bismuth orthoborate) [8], which was missing in the original phase diagram [2]. There are no doubts about the existence of \( \text{BiBO}_3 \) now: Becker with co-workers have confirmed existence of bismuth orthoborate [5, 9, 10] and its transparent colourless single crystals of \( \text{BiBO}_3 \) have recently been grown from the melt and characterized by Becker & Froehlich [10]. Monophase samples of both crystalline \( \text{BiBO}_3 \) modifications were obtained by crystallisation below 550°C of bismuth borate glasses with 50-57 mol\% \( \text{B}_2\text{O}_3 \) [10]. However, these authors did not correct the phase diagram, and did not determine the melting point of \( \text{BiBO}_3 \) or the eutectic composition between \( \text{BiBO}_3 \) and \( \text{Bi}_3\text{B}_5\text{O}_{12} \). The compound \( \text{BiBO}_3 \) and this eutectic point are clearly given on the Zargarova & Kasumova’s version of the \( \text{B}_2\text{O}_3-\text{Bi}_2\text{O}_3 \) phase diagram, without indication of their melting points and the eutectic composition [11].
Kargin with co-authors [12] by DTA and X-ray analysis have studied conditions of metastable phases formation at system Bi2O3-B2O3 melts crystallization. They have confirmed existence of metastable BiBO3 compound and for the first time have specified on congruent character of its melting. Authors also establish formation of a metastable phase of 5Bi2O3•3B2O3 composition. Both compounds together with initial Bi2O3 and B2O3 are present on the metastable state diagram of the Bi2O3-B2O3 system constructed by them.

Presence of five compounds on the known Bi2O3-B2O3 phase diagram has naturally led to formation of five eutectics compositions containing (mol % B2O3): 19.14 (622°C), 44.4 (646 °C), 73.5 (698°C), 76.6 (695°C) and 81.04 (709°C). There is an area of phase separation traditional for borate systems, observed for compositions containing 81-100 mol % B2O3 [2]. Though according to [12], the area of stable phase separation is stretched to 58-95 mol % B2O3.

Interest to ternary alkali free bismuth borate systems MO3-yBi2O3-B2O3 (M=Zn,Sr,Ca,Ba) studies has amplified recently. Various research groups (Russian, Canadian, Armenian) worked in this area during 1990-2009 and revealed a number of ternary compounds, determined their structure, optical and nonlinear optical properties. Thus, three ternary zinc bismuth borate compounds have been revealed in the ZnO-Bi2O3-B2O3 system. At first Zargarova& Kasumova have revealed ZnBi2B10O30 and ZnBiBO4 compounds [11]. Later Barbier with co-authors by solid-state reaction have synthesized third melilite type ZnBi2B7O17 compound with large SHG (four time higher as KDP) [13].

Barbier & Cranswick at first two novel noncentrosymmetric MBi2O27 or MBi2O(BO2)2 (M=Ca, Sr) compounds have synthesized by solid-state reactions in air at temperatures in the 600–700°C range [14]. Their crystal structures have been determined and refined using powder neutron diffraction data. CaBi2B7O17 compound has SHG response two time higher as KDP [14]. However, authors didn’t pay attention for both compounds melting behavior.

Egorisheva with co-authors have studied phase relation in the CaO-Bi2O3-B2O3 system and constructs the 600 °C (subsolidus) section of its phase diagram [15]. A new ternary compound of composition CaBi2B10O16 was identified and the existence of CaBi2B7O17 ternary compound was confirmed. Both compounds had incongruent melting at 700 and 783 °C respectively and liquidus temperature about 900-930 °C.

Kargin with co-workers have studied phase relation in the SrO-Bi2O3-B2O3 system in subsolidus at 600 °C [16]. Two new ternary compound of SrBi2B16O46 and SrBiBO4 compositions were identified. Both compounds had incongruent melting at 760 and 820 °C without indication liquidus temperature. However, later Barbier et al. have discribe new novel centrosymmetric borate SrBi2OB3O9 (SrBi2B4O10) forming in the SrO–Bi2O3–B2O3 system [17], thereby having substituted under doubt existence of previously reported SrBi3B9O46 compound [16].

The uniqueness of the BaO-Bi2O3-B2O3 system is shown by the available sets of compounds and eutectics both in the binary Bi2O3-B2O3 and BaO–B2O3 systems. Seven compounds are known in the BaO-B2O3 system. Four congruent melting binary compounds Ba2B5O8, Ba2B10O17, BaB4O7, BaB3O7, with melting points (m.p.) 1383, 1105, 910, 889°C accordingly were found by Levin & McMurdie [18, 19]. Further, Green and Wahler have found out new congruent melted at 890°C Ba2B5O17 compound at the ternary BaO-B2O3-Al2O3 system investigation [20].
Hubner confirmed an existence of the congruent melted Ba$_2$B$_2$O$_7$ compound with m.p. 890 °C, and revealed two new compounds Ba$_4$B$_2$O$_7$, Ba$_2$B$_2$O$_5$ [21]. However, all scientists and researches have used the melting diagram of the BaO-B$_2$O$_3$ system created by Levin & McMurdie up to now, without the indication in it the specific areas of existence of new compounds and eutectic points among them [18].

Both these factors were the reason of the BaO-B$_2$O$_3$ system phase diagram correction made by Hovhannisyan R.M. [22]. Author has revealed fields of Ba$_2$B$_2$O$_7$ and Ba$_4$B$_2$O$_7$ compounds crystallisation and new eutectic points which are absent on the diagram constructed by Levin & McMurdie [18]. Six binary eutectic compositions containing 31.5, 37.5, 63.5, 68.5, 76.0, 83.4 mol % B$_2$O$_3$ with melting points 1025, 915, 905, 895, 869 and 878°C accordingly were on the diagram after correction.

Area of two immiscible liquids established by Levin & McMurdie [35] in the BaO-B$_2$O$_3$ system in an interval of 1.5 to 30wt. % BaO content, it has been confirmed in the subsequent by other authors. However, the temperature of the liquation couple, which are 1150, 1180, 1256 °C according to [23] and 1539°C according to [24] is discussed till now.

There are no full version of the phase diagram of the BaO-Bi$_2$O$_3$ system till now [1]. It is very complex system, which is very critical to atmosphere and pressure at experiment carrying out [25 - 28]. Two low melted eutectic areas (740-790°C) clear observed on phase diagram studied in air or oxygen in high bismuth content region around 5-7 mol% BaO and 25-30 mol %BaO [26 - 28].

All research groups payd special attention to BaO-Bi$_2$O$_3$-B$_2$O$_3$ system studies and new ternary compounds revealing and characterisation. Barbier et al. have studied seven compositions in the ternary BaO-B$_2$O$_3$-Bi$_2$O$_3$ system by solid state synthesis at temperatures below 650°C and BaBiBO$_4$ or BaBi(BO$_3$)$_2$O, a novel borate compound, has been made and characterised [29]. Above 650°C it decays with bismuth borate glass formation. A powder sample of BaBiBO$_4$ had a second harmonic signal with a NLO efficiency equal to five times that of KDP.

Practically in parallel, Egorysheva with co-workers have been investigated phase equilibrium in the Bi$_2$O$_3$-BaB$_2$O$_4$-B$_2$O$_3$ system by X-ray analysis and DTA [30, 31]. Studies were spent by the samples solid state synthesis in closed Pt crucibles in muffle furnaces at the temperature range 500-750 °C, that corresponds to sub-solidus area. The synthesis duration (with intermediate cakes regrinding) were 6-16 days. They confirmed presence of BaBiBO$_4$ and have revealed three new compounds: BaBiB$_{11}$O$_{19}$, BaBi$_2$B$_4$O$_{10}$, Ba$_3$BiB$_2$O$_9$. BaBiB$_{11}$O$_{19}$, BaBi$_2$B$_4$O$_{10}$ have congruent melting at 830 and 730 °C respectively and BaBiBO$_4$ melt incongruently at 780°C. Ba$_3$BiB$_2$O$_9$ undergoes a phase transition at 850°C and exist up to 885°C, were decompose in the solid state [31].

Recently single crystals of BaBi$_2$B$_4$O$_{10}$ composition were grown by cooling of a melt with the stoichiometric composition with cooling rate 0.5 K/h [32]. They have once again confirmed existence of BaBi$_2$B$_4$O$_{10}$ stoichiometric compound earlier obtained by solid state synthesis.
In 1972 Elwell with co-workers investigated the BaO–B₂O₃–Bi₂O₃ system by hot stage microscopy and a new ternary eutectic composition, 23.4BaO•62.4Bi₂O₃•14.2B₂O₃ (wt%), with a low liquidus temperature of 600°C, was revealed for ferrite spinel growth [33].

Using different melts cooling rates Hovhannisyan, M. with co-authors at first have determined large glass-forming field in the BaO-Bi₂O₃-B₂O₃ system, which includes all eutectics in the binary Bi₂O₃-B₂O₃, BaO-B₂O₃, and BaO-Bi₂O₃ systems and covers majority of the concentration triangles, reaching up to 90 mol% Bi₂O₃ [34, 35].

The methodology based on glass samples investigation was more effective at BaO-Bi₂O₃-B₂O₃ system phase diagram construction, than a traditional technique based on solid state sintered samples studies. Because DTA curves of glasses, to the contrary DTA curves of solid state sintered samples, indicates their all characteristics temperatures, includes exothermal effects of glass crystallizations and endothermic effects of formed crystalline phases melting. It has allowed us to reveal two new BaBi₂B₂O₇ and BaBi₁₀B₆O₂₅ congruent melted at 725 and 690°C respectively compounds in the BaO-Bi₂O₃-B₂O₃ system [34 - 36].

However, our further studies of glasses and glass ceramics in this system have shown necessity of glass forming diagram correction and phase diagram construction in the ternary BaO-Bi₂O₃-B₂O₃ system and present these data to scientific community. Another aim of this work is both known and novel stoichiometric ternary barium bismuth borates compounds characterisation in glassy, glass ceramic and ceramic states for further practical application.

2. Experimental

About three hundred samples of various binary and ternary compositions have been synthesized and tested in BaO- Bi₂O₃-B₂O₃ system. Compositions were prepared from “chemically pure” grade BaCO₃, H₃BO₃ and Bi₂O₃ at 2.5-5.0 mol % intervals. The most part of samples has been obtained as glasses by various cooling rates depending on melts glass forming abilities: as bulk glass plates with thickness 6,5 ±7mm by casting on metallic plate (up to 10³ K/s), as monolithic glass plates with thickness up to 3mm by casting between two steel plates (~10² K/s), and glass tapes samples with thickness 30–400 μm through super cooling method (10³–10⁴ K/s). Glass formation was determined visually or by x-ray analysis. The glass melting was performed at 800–1200°C for 15–20 min with a 20–50 g batch in a 20–50 ml uncovered quartz glass or corundum crucible, using an air atmosphere and a “Superterm 17/08” electric furnace. Compositions in the BaO-B₂O₃ system were melted in a 25 or 50 ml uncovered Pt crucibles at 1400–1500°C for 30 min with a 20–50 g batch. The chemical composition of some glasses was determined by traditional chemical analysis, and the results indicate a good compatibility between the calculated and analytical amounts of B₂O₃, BaO and Bi₂O₃. SiO₂ contamination from quartz glass crucibles did not exceed 2 wt%, and alumina contamination did not exceed 0.5–1 wt%, according to the chemical analysis data.

Samples of compositions laying outside of a glass formation field or having high melting temperature, have been obtained by solid-phase synthesis. Mixes (15-20 g) were carefully
frayed in an agate mortar, pressed as tablets, located on platinum plates and passed the thermal treatment in “Naber” firm electric muffles. After regrinding powders were tested by DTA and X-ray methods. The synthesized samples of binary barium borate system compositions containing 60 mol% and more of BaO and also compositions containing over 90 mol% B$_2$O$_3$ had very low chemical resistance and were hydrolyzed on air at room temperature. In this connection the synthesized samples were kept in a dryer at 200°C.

DTA and X-ray diffraction data of glass and crystallized glass samples have been used for phase diagram construction in the ternary BaO- Bi$_2$O$_3$-B$_2$O$_3$ system. The DTA analysis (pure Al$_2$O$_3$ crucible, powder samples weight ~600 mg, heating rates 10 K/min) on Q-1500 type derivatograph were carried out. Glass transition -T$_g$ crystallization peaks -T$_{cr}$, melting -T$_m$ and liquidus -T$_l$ temperatures have been determined from DTA curves. Reproducibility of temperatures effects on DTA curves from melting to melting was ±10 K. The accuracy of temperature measurement is ±5 K.

Thermal expansion coefficient (TEC) and glass transition temperature (T$_g$) measurements were made on a DKV-4A type vertical quartz dilatometer with a heating rate of 3 K/min. Glass samples in the size of 4×4×50 millimeters have been prepared for TEC measurement. The dilatometer was graduated by the quartz glass and sapphire standards. The TEC measurement accuracy is ±(3÷4)•10$^{-7}$ K$^{-1}$, T$_g$ ±5 °C.

X-ray patterns were obtained on a DRON-3 type diffractometer (powder method, CuK$\alpha$–radiation, Ni-filter). Samples for glass crystallization were prepared with glass powder pressed in the form of tablets. Crystallization process was done in the electrical muffles of “Naber” firm by a single-stage heat treatment. This was done within 6-12 hours around a temperature at which the maximum exothermal effects on glasses by DTA were observed.

Crystalline phases of binary and ternary compounds formed both at glasses crystallization and at solid-phase synthesis have been identified by using JCPDS-ICDD PDF-2 release 2008 database [43].

Computerized methodic of ferroelectric hysteresis test and measurement of ferroelectric properties such as coercive field and remanent polarization at wide temperature (up to 250°C and frequency (10-5000Hz) ranges was used. Methodic based on the well known Sawyer – Tower’s [44] modified scheme, which is allowing to compensate phase shifts concerned with dielectric losses and conductivity. The desired frequency signal from waveform generator is amplifying by high voltage amplifier and applying to sample. The signals, from the measuring circuit output, proportional to applied field and spontaneous polarization are passing throw high impedance conditioning amplifiers, converting by ADC and operating and analyzing in PC. The technique allows to perform tests of synthesized glass ceramics obtained by means of controlling crystallization of thin (above 30 micrometer thick) monolithic tape (film) specimens by applying up to 300kV/cm field to our thin samples (~50 micrometer thick) and obtain hysteresis loops for wide diversity of hard FE materials.
3. Results

3.1. Glass forming and phase diagrams of the $\text{BaO-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ system

The traditional method of phase diagram construction based on solid-phase sintered samples investigation takes long time and is not effective. The glass samples investigation technique is progressive, because the DTA curves have registered all processes taking place in glass samples, including the processes of glass crystallizations, quantity of crystal phases and temperature intervals of their formation and melting. However, inadequate amount of glass samples restrict their use during phase diagram construction. The super-cooling method promotes the mentioned problem solving and open new possibilities for phase diagrams constructions.

Hovhannisyan R.M. with co-workes successfully developed this direction last time and have constructed phase diagrams in binary and ternary alkiline-earth bismuth borate, barium boron titanate, barium aluminum boron titanate, barium gallium borate, yttrium aluminum borate, yttrium gallium borate, lanthanum gallium borate, zinc tellurium molibdate and other systems [34 - 42].

3.1.1. Glass forming diagram of the $\text{BaO-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ system

Figure 1 shows the experimental data on glass formation in the $\text{BaO-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ system obtained by different authors from 1958 to 2007 [45 - 49]. For defining the glass forming ability of the pointed system, the authors of the mentioned works used different amounts of melt, glass melting crucibles, temperature–time melting regimes, and technological methods of melt cooling. Imaoka & Yamazaki studied glass formation by melts cooling on air Glasses were melted at temperatures below 1200 °C in gold-palladium or platinum-rhodium crucibles (Fig.1.1) [45]. Janakirama-Rao glass formation studied by melts cooling on air. Glasses melted in platinum crucibles at 600- 1400 °C with 0.5-1.0 h melts exposition and its cooling in air (Fig. 1.2) [46]. Izumitani [47] experiments spent in 10g crucibles at 1100-1350 °C with melts cooling on air (Fig. 1.3). Milyukov with co-authors glass formation studied by melts casting in steel mold. Glasses melted in platinum crucibles at 600-1400 °C with melts stirring by Pt stirrer for 1h (Fig. 1.4) [48]. Kawanaka & Matusita glass formation studied by silica rod stirred melts pouring into preheated to 250-300°C carbon mold (Fig. 1.5) [49].

Authors used different weights of glass forming melts, melting crucibles, temperature-time of melting regimes and technological methods of melts cooling. Obtained data are difficultly comparable and remote from two basic criteria promoting glass formation: liquidus temperature and speeds of melts cooling,
Figure 1. Glass forming regions in the BaO-Bi$_2$O$_3$-B$_2$O$_3$ system according to the data of the authors: 1- [45], 2- [46], 3- [47], 4- [48], 5- [49].

Figure 2 shows corrected glass formation diagram in the BaO-Bi$_2$O$_3$-B$_2$O$_3$ system based on phase diagrams of the BaO–B$_2$O$_3$, BaO–Bi$_2$O$_3$, and B$_2$O$_3$–Bi$_2$O$_3$ binary systems and controllable melt cooling rates. Using the term “diagram,” but not the glass formation region, we take into account the interrelation between the phase diagram and the glass forming ability of the system.

Figure 2. Glass forming diagram in the BaO-Bi$_2$O$_3$-B$_2$O$_3$ system depending of melts cooling rates: 1-up to 10 K/s; 2–10$^2$K/s; 3-(10$^3$-10$^4$) K/s; 4-stable phase separation region.

Area of glass compositions with low crystallization ability and stable glass formation in the studied ternary BaO-Bi$_2$O$_3$ - B$_2$O$_3$ system have been determined at melts cooling rate ~ 10 K/s.
(Fig.2-1). It included binary Bi$_2$B$_2$O$_7$, BiBO$_3$, Bi$_3$Bo$_5$O$_{12}$, Ba$_2$B$_{10}$O$_{17}$, BaB$_5$O$_{13}$ compounds in the BaO-B$_2$O$_3$ and BaO-B$_2$O$_3$ systems and five ternary BaBi$_{11}$O$_{19}$ (D), BaBi$_2$B$_4$O$_{10}$ (C), BaBi$_2$Bo$_7$ (E), BaBi$_{16}$Bo$_{25}$ (F), and BaBiBo$_4$ (B) compounds. However, we didn’t confirm presence of Ba$_3$BiB$_3$O$_9$ (A) compound in area of stable glasses at melts cooling rate ~ 10 K/s, which was reported earlier [34, 35].

Increasing of melts cooling speed up to ~10$^2$ K/s has led to glass formation area expansion (Fig.2-2). This cooling rate is enough for monolithic glass plates with thickness up to 3mm fabrication by melts casting between two steel plates (Fig.2-2). The glass plates of compositions correspondings to Ba$_3$BiB$_3$O$_9$ (A) and supposed BaBi$_8$Bo$_{16}$ (G) compounds have been obtained by this way.

Super cooling technique constructed by our group allowed to expand the borders of glass formation in studied system under high melts cooling rates equal to (10$^3$-10$^4$) K/s (Fig.2-3). Determined glassforming area include compositions content: 80 – 95 mol% Bi$_2$O$_3$ in the binary B$_2$O$_3$–Bi$_2$O$_3$ system; 43-70 mol% BaO in the binary BaO–B$_2$O$_3$ system, including BaB$_2$O$_4$ composition. Area of glass formation from both these areas moves to 55-95 mol% content compositions in the binary BaO–Bi$_2$O$_3$ system (Fig.2-3).

Traditional for borate systems a stable phase separation region was also observed for high B$_2$O$_3$ content compositions contents more than 84 -87 mol%B$_2$O$_3$ (Fig.2-4).

3.1.2. Phase diagram of the BaO-Bi$_2$O$_3$-B$_2$O$_3$ system

Our investigation of the ternary BaO-B$_2$O$_3$-Bi$_2$O$_3$ system have purposefully been directed on construction of the phase diagram through first of all glass forming diagram construction and revealing both new compounds and eutectic compositions. Constructed by us glass forming diagram (Fig.2) practically occupies the most part of the BaO-B$_2$O$_3$-Bi$_2$O$_3$ concentration triangles. It has allowed to use synthesized glasses as initial compositions at phase diagram construction. It was basic difference of our methodology from technologies used by other authors. Phase equilibriums reached at isothermal sections construction do not allow to have a full picture of processes in cases of the solid state synthesized samples investigations. Whereas at glass samples studies we determine not only characteristic points of glasses($T_g$ and $T_x$) by DTA, but also quantity of crystal phases, temperatures of their crystallization and then temperatures of their melting. It has allowed us to reveal new stoichiometric compositions which have been lost by other research groups at isothermal sections construction by traditional methods. In some cases we also in parallel used samples obtained by solid state synthesis for comparison with their glassy analogues or in those cases, when their obtaining in the glassy form was impossible.
Experimental data concerning phase diagrams of binary systems $\text{Bi}_2\text{O}_3$-$\text{B}_2\text{O}_3$, $\text{BaO}$-$\text{B}_2\text{O}_3$, $\text{BaO}$-$\text{Bi}_2\text{O}_3$, and pseudo-binary sections in the $\text{BaO}$-$\text{B}_2\text{O}_3$-$\text{Bi}_2\text{O}_3$ system have allowed us to estimate fields of primary crystallization of co-existing phases and divided all concentration triangle into elementary triangles, i.e. to make triangulation.

The triangulation scheme in the $\text{BaO}$-$\text{B}_2\text{O}_3$-$\text{Bi}_2\text{O}_3$ system is presented on Fig. 3. By means of a triangulation all concentration triangle is divided into following elementary triangles: $\text{BiBO}_3$-$\text{F}$-$\text{C}$, $\text{BiBO}_3$-$\text{F}$-$\text{Bi}_2\text{O}_3$, $\text{BiBO}_3$-$\text{C}$-$\text{Bi}_3\text{B}_5\text{O}_{12}$, $\text{F}$-$\text{E}$-$\text{C}$, $\text{C}$-$\text{BaB}_2\text{O}_4$-$\text{E}$, $\text{C}$-$\text{Bi}_3\text{B}_5\text{O}_{12}$-$\text{D}$, $\text{Bi}_3\text{B}_5\text{O}_{12}$-$\text{F}$-$\text{Bi}_2\text{O}_3$, $\text{E}$-$\text{Bi}_2\text{O}_3$-$\text{F}$, $\text{C}$-$\text{BaB}_2\text{O}_4$-$\text{Ba}_2\text{B}_{10}\text{O}_{17}$, $\text{Ba}_2\text{B}_{10}\text{O}_{17}$-$\text{D}$-$\text{Bi}_2\text{O}_3$, $\text{Bi}_3\text{B}_5\text{O}_{12}$-$\text{D}$-$\text{Bi}_3\text{B}_5\text{O}_{15}$, $\text{D}$-$\text{Bi}_3\text{B}_5\text{O}_{15}$-$\text{B}_2\text{O}_3$.

### 3.1.2.1. Phase diagram of the binary $\text{Bi}_2\text{O}_3$-$\text{B}_2\text{O}_3$ system

First of all we have attempt to finished phase diagram construction in area of compositions around of $\text{BiBO}_3$ compound. Compositions containing 45–65 mol% $\text{B}_2\text{O}_3$ in the $\text{Bi}_2\text{O}_3$-$\text{B}_2\text{O}_3$ system were tested to determine the melting point of $\text{BiBO}_3$ and to determine the eutectic composition between $\text{BiBO}_3$ and $\text{Bi}_3\text{B}_5\text{O}_{12}$. The compositions used to correct the $\text{B}_2\text{O}_3$-$\text{Bi}_2\text{O}_3$ phase diagram were prepared by solid state synthesis at 520°C, with steps of 0.5–1.0 mol% $\text{B}_2\text{O}_3$ over the interval 45–55 mol% $\text{B}_2\text{O}_3$. As a result, the eutectic composition, 48.5$\text{Bi}_2\text{O}_3$•51.5$\text{B}_2\text{O}_3$ (mol%), between $\text{BiBO}_3$ and $\text{Bi}_3\text{B}_5\text{O}_{12}$, was determined, and its melting point was measured by DTA as 665±5°C (Fig. 4). It was also found that $\text{BiBO}_3$ melts congruently at 685±5°C.
3.1.2.2. Phase diagram of the pseudo-binary BiBO$_3$–BaB$_2$O$_4$ system

BaBi$_2$B$_4$O$_{10}$ is a congruently melting compound, with a melting point of 730°C, and it occupies the central area of the BiBO$_3$–BaB$_2$O$_4$ pseudo-binary system (Fig. 5). This system forms two simple pseudo-binary eutectics, $E_1$ at 15 mol% BaB$_2$O$_4$, with a melting point of 620°C, and $E_2$ at 60 mol% BaB$_2$O$_4$, with a melting point of 718°C.

3.1.2.3. Phase diagram of the pseudo-binary Bi$_4$B$_2$O$_9$–BaBi$_2$B$_2$O$_7$ system

The introduction of 12 mol% BaBi$_2$B$_2$O$_7$ in the pseudo-binary system Bi$_4$B$_2$O$_9$–BaBi$_2$B$_2$O$_7$ reduced the melting point of initial Bi$_4$B$_2$O$_9$, and resulted in the formation of a simple pseudo-binary eutectic, $E_3$, with melting point 605°C (Fig. 6). A maximum of the liquidus with melting point of 690°C is seen at 33.33 mol% BaBi$_2$B$_2$O$_7$, which indicates the formation of the new congruently melting ternary compound BaBi$_{10}$B$_6$O$_{25}$ (11.11BaO•55.55Bi$_2$O$_3$•33.33B$_2$O$_3$). Further increase of the BaBi$_2$B$_2$O$_7$ content (49 mol%) leads to a second pseudo-binary eutectic, $E_4$, with melting point 660°C. Increasing of the liquidus temperature is observed in the post eutectic region of composition, with a maximum at 725°C. It corresponds to the formation of the new congruently melting ternary compound BaBi$_2$B$_2$O$_7$ (Fig. 6).
Two new crystalline ternary compounds, BaBi$_2$B$_2$O$_7$ and BaBi$_{10}$B$_6$O$_{25}$, were revealed by crystallisation at the same glass composition. Both compounds, BaBi$_2$B$_2$O$_7$ and BaBi$_{10}$B$_6$O$_{25}$, melt congruently at 725±5°C and 690±5°C, respectively. The X-ray characteristics of BaBi$_2$B$_2$O$_7$ and BaBi$_{10}$B$_6$O$_{25}$ were determined and are given in Tables 1 and 2.

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Table 1. X-ray characteristics of the new ternary compound BaBi$_2$B$_2$O$_7$, synthesized at the same glass composition crystallization (640°C, 20 h).
Single crystals of BaBi$_{10}$B$_6$O$_{25}$ were obtained by cooling of a melt with the stoichiometric composition. Glass powder of composition 11.11BaO·55.55Bi$_2$O$_3$·33.33B$_2$O$_3$ (mol%) was heated in a quartz glass ampoule up to 750°C at a rate 10 K/min. After 2 h exposition at high temperature, the melt was cooled at a rate 0.5 K/h. Single crystals with sizes up to 1.66×0.38×0.19 mm$^3$ were grown.

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Table 2. X-ray characteristics of the new ternary BaBi$_{10}$B$_6$O$_{25}$ single crystals.

The x-ray powder diffraction patterns of BaBi$_2$B$_6$O$_{17}$ and BaBi$_{10}$B$_6$O$_{25}$ could be indexed on an orthorhombic cell with lattice parameters as follows:

- for BaBi$_2$B$_6$O$_{17}$, $a=11.818$ Å, $b=8.753$ Å, $c=7.146$ Å, cell volume $V=739.203$ Å$^3$, $Z=4$;
- for BaBi$_{10}$B$_6$O$_{25}$, $a=6.434$ Å, $b=11.763$ Å, $c=29.998$ Å, cell volume $V=2270.34$ Å$^3$, $Z=8$.

3.1.2.4. Phase diagram of the pseudo-binary BiBO$_3$–BaBi$_{10}$B$_6$O$_{25}$ system

BiBO$_3$–BaBi$_{10}$B$_6$O$_{25}$ is a very important system (Fig.7). Initial BiBO$_3$ has a melting point of 685°C. The second maximum in the liquidus curve (Fig.7) of 690°C is connected with the for-
formation of the new ternary compound $\text{BaBi}_{10}\text{B}_6\text{O}_{25}$. There is a simple pseudo-binary eutectic $E_5$ between these two compounds at 54 mol% $\text{BaBi}_{10}\text{B}_6\text{O}_{25}$, with a melting point of 595°C.

Figure 7. Phase diagram of the pseudo-binary system $\text{BiBO}_3$–$\text{BaBi}_{10}\text{B}_6\text{O}_{25}$.

3.1.2.5. Phase diagram of the pseudo-binary $\text{BaBi}_{10}\text{B}_6\text{O}_{25}$–$\text{BaBi}_2\text{B}_4\text{O}_{10}$ system

The $\text{BaBi}_{10}\text{B}_6\text{O}_{25}$–$\text{BaBi}_2\text{B}_4\text{O}_{10}$ system confirms the presence of the new congruently melting ternary compound $\text{BaBi}_2\text{B}_6\text{O}_{25}$, with a melting point of 690°C (Fig. 8). $\text{BaBi}_2\text{B}_4\text{O}_{10}$ melts congruently at 730°C. There is a simple pseudo-binary eutectic $E_6$ between these two compounds at 28 mol % $\text{BaBi}_2\text{B}_4\text{O}_{10}$, with a melting point of 660°C.

Figure 8. Phase diagrams of the pseudo-binary system $\text{BaBi}_{10}\text{B}_6\text{O}_{25}$–$\text{BaBi}_2\text{B}_4\text{O}_{10}$.

3.1.2.6. Phase diagram of the pseudo-binary $\text{BaBi}_2\text{B}_4\text{O}_{10}$–$50\text{BaO}•50\text{Bi}_2\text{O}_3$ section

This pseudo-binary section consists of two ternary compounds $\text{BaBi}_2\text{B}_6\text{O}_{10}$, $\text{BaBi}_2\text{B}_2\text{O}_7$ and two eutectics $E_7$, $E_8$ dividing fields primary crystallisations these compounds. Initial composition is $\text{BaBi}_2\text{B}_6\text{O}_{10}$ (Fig. 9). The introduction of 20 mol% $50\%\text{BaO}•50\%\text{Bi}_2\text{O}_3$ in the pseudo-binary
system BaBi$_2$B$_4$O$_{10}$ – 50BaO•50Bi$_2$O$_3$ reduced the melting point of initial BaBi$_2$B$_4$O$_{10}$ and resulted in the formation of a simple pseudo-binary eutectic, $E_7$, with melting point 680°C (Fig.9). A maximum of the liquidus with melting point of 725°C is seen at 33.33 mol% of 50% BaO•50% Bi$_2$O$_3$, which indicates the formation of the new congruently melting ternary compound BaBi$_2$B$_4$O$_7$. Further increase of the 50% BaO•50% Bi$_2$O$_3$ content (52.5 mol%) leads to a second pseudo-binary eutectic, $E_8$, with melting point 700°C. Increasing of the liquidus temperature is observed in the post eutectic region of composition (more than 52.5 mol% of 50% BaO•50% Bi$_2$O$_3$). Unidentified phase is in the post eutectic ($E_8$) region of composition (Fig.9).

3.1.2.7. Phase diagram of the pseudo-binary BaB$_2$O$_4$-Bi$_2$O$_3$ section

BaB$_2$O$_4$ - Bi$_2$O$_3$ section consist of two pseudo-binary BaB$_2$O$_4$- BaBi$_2$B$_4$O$_7$, BaBi$_2$B$_2$O$_7$- Bi$_2$O$_3$ systems (Fig.10). There are two eutectics: $E_9$ between BaB$_2$O$_4$ and BaBi$_2$B$_4$O$_7$, $E_{10}$ between BaBi$_2$B$_2$O$_7$ and BaBi$_2$B$_2$O$_{16}$, and peritectic point $P_1$ between BaBi$_2$B$_2$O$_{16}$ and Bi$_2$O$_3$ (Fig.10). The introduction of 26 mol% Bi$_2$O$_3$ in the pseudo-binary system BaB$_2$O$_4$ – Bi$_2$O$_3$ sharp reduced the melting point of initial BaB$_2$O$_4$ on 445°C, and resulted in the formation of a simple eutectic, $E_9$, with melting point 685°C (Fig.10). A maximum of the liquidus with melting point of 725°C is seen at 33.33 mol% of Bi$_2$O$_3$, which indicates the formation of the new congruently melting ternary compound BaBi$_2$B$_2$O$_7$.

Further increase of the Bi$_2$O$_3$ content (42 mol%) leads to a second eutectic, $E_{10}$, formation with melting point 690°C. Increasing of the liquidus temperature is observed in the post eutectic region of composition (more than 42 mol% of Bi$_2$O$_3$) and formation of new incongruent melted at 725°C BaBi$_2$B$_2$O$_{16}$ ternary compound (Fig.10). It is very difficult determined of BaBi$_2$B$_2$O$_{16}$ X-ray characteristics, because they very closed to Bi$_2$O$_3$ characteristics.

Constructed by us this section’s diagram essentially differs from that constructed by Russian researches Egorisheva & Kargin [30] because they could not find out two new compounds revealed by us: congruent melted at 725°C BaBi$_2$B$_2$O$_7$ and incongruent melted at 725°C BaBi$_2$B$_2$O$_{16}$ (Fig.10). At repeated, even more detailed studies they also could not find out these compounds [31].
3.1.2.8. Phase diagram of the pseudo-binary Bi$_3$B$_5$O$_{12}$ – BaBi$_2$B$_4$O$_{10}$ system

It is very simple system with pseudo-binary eutectic E$_{11}$ between two congruent melted Bi$_3$B$_5$O$_{12}$ and BaBi$_2$B$_4$O$_{10}$ compounds. Eutectic E$_{11}$ content 38 mol% of BaBi$_2$B$_4$O$_{10}$ and has melting point 680°C (Fig.11).

3.1.2.9. Phase diagram of the pseudo-binary BaBi$_2$B$_4$O$_{10}$ – BaBiB$_{11}$O$_{19}$ system

Initial BaBi$_2$B$_4$O$_{10}$ has a melting point of 730°C. The second maximum in the liquidus curve (Fig.12) of 807°C is connected with the formation of the ternary compound BaBiB$_{11}$O$_{19}$. There is a simple pseudo-binary eutectic, E$_{12}$, between these two compounds at 65.5 mol% Ba-Bi$_2$B$_4$O$_{10}$ with a melting point of 695°C.
3.1.2.10. Phase diagram of the pseudo-binary system $\text{Bi}_3\text{B}_5\text{O}_{12}$ – $\text{BaBiB}_{11}\text{O}_{19}$ system

Pseudo-binary system $\text{Bi}_3\text{B}_5\text{O}_{12}$ – $\text{BaBiB}_{11}\text{O}_{19}$ has simple eutectic $E_{13}$ formed between two congruent melted $\text{BaBiB}_{11}\text{O}_{19}$ and $\text{Bi}_3\text{B}_5\text{O}_{12}$ compounds. According to DTA eutectic $E_{13}$ has melting point 705°C and content 28 mol% $\text{BaBiB}_{11}\text{O}_{19}$ (Fig. 13).

3.1.2.11. Phase diagram of the pseudo-binary system $\text{BaBiB}_{11}\text{O}_{19}$ – $\text{Ba}_2\text{B}_{10}\text{O}_{17}$ system

Pseudo-binary system $\text{BaBiB}_{11}\text{O}_{19}$ – $\text{Ba}_2\text{B}_{10}\text{O}_{17}$ has simple eutectic $E_{14}$ formed between two congruent melted compounds $\text{Ba}_2\text{B}_{10}\text{O}_{17}$ and $\text{BaBiB}_{11}\text{O}_{19}$. According to DTA eutectic $E_{14}$ has melting point 780°C and content 26 mol% $\text{Ba}_2\text{B}_{10}\text{O}_{17}$ (Fig. 14).
3.1.2.12. Phase diagram of the pseudo-binary \( \text{BaBi}_2\text{B}_4\text{O}_{10} \) – \( \text{Ba}_2\text{B}_{10}\text{O}_{17} \) system

It is very simple system with eutectic \( E_{15} \) formed between two congruent melted \( \text{Ba}_2\text{B}_{10}\text{O}_{17} \) and \( \text{BaBi}_2\text{B}_4\text{O}_{10} \) compounds. Pseudo-binary eutectic \( E_{15} \) content 24 mol% of \( \text{Ba}_2\text{B}_{10}\text{O}_{17} \) and has melting point 710°C (Fig. 15).

3.1.2.13. Phase diagram of the pseudo-binary \( \text{BaBi}_2\text{B}_4\text{O}_{10} \) – \( \text{BaB}_4\text{O}_7 \) system

The same picture is observe for \( \text{BaBi}_2\text{B}_4\text{O}_{10} \) – \( \text{BaB}_4\text{O}_7 \) system: simple eutectic \( E_{16} \) is formed between two congruent melted compounds. Pseudo-binary eutectic \( E_{16} \) content 24 mol% of \( \text{BaB}_4\text{O}_7 \) and has melting point 715°C (Fig. 16).
3.1.2.14. Phase diagram of the pseudo-binary \( \text{BaBiB}_{11} \text{O}_{19} - \text{BaB}_8 \text{O}_{13} \) system

It is simple system with pseudo-binary eutectic \( E_{17} \) between two congruent melted \( \text{BaBiB}_{11} \text{O}_{19} \) and \( \text{BaB}_8 \text{O}_{13} \) compounds. Eutectic \( E_{17} \) content 38 mol\% of \( \text{BaB}_8 \text{O}_{13} \) and has melting point 770°C (Fig. 17).

3.1.2.15. Phase diagram of the \( \text{BaO-Bi}_2 \text{O}_3-B_2 \text{O}_3 \) ternary system

As result of huge work under project the phase diagram in the ternary \( \text{BaO-Bi}_2 \text{O}_3-B_2 \text{O}_3 \) system has been constructed for the first time and presented on Fig.18. Three new compounds \( \text{BaBi}_{2} \text{B}_2 \text{O}_{7} \), \( \text{BaBi}_{10} \text{B}_6 \text{O}_{25} \) and \( \text{BaBi}_{8} \text{B}_2 \text{O}_{16} \) have been revealed and characterized.
Fields of binary bismuth and barium borates as well as all ternary barium bismuth borates compounds crystallizations have been determined and outlined and sixteen ternary eutectic points E₁-E₁₆ have been revealed as result of phase diagram construction (Fig. 18, table 3). The phase diagram evidently represents interaction of binary and ternary compounds taking place in the pseudo-ternary systems. The ternary eutectic E₁ with m.p. 590°C has been determined among BiBO₃, F and Bi₃B₂O₉ compounds; ternary eutectic E₂ with m.p. 585°C has been formed among BiBO₃, F and C compounds; ternary eutectic E₃ with m.p. 640°C has been formed among F, E and C compounds; ternary eutectic E₄ with m.p. 622°C has been formed among C, BaB₂O₄ and E compounds; ternary eutectic E₅ with m.p. 610°C has been formed among BiBO₃, C and Bi₃B₂O₁₂ compounds; ternary eutectic E₆ with m.p. 675°C has been formed among C, Ba₃B₂O₁₂ and D compounds; ternary eutectic E₇ with m.p. 680°C has been formed among Bi₃B₂O₁₂, D and BiB₂O₆ compounds; ternary eutectic E₈ with m.p. 675°C has been formed among BiB₂O₆, D and Bi₃B₂O₁₅ compounds; ternary eutectic E₉ with m.p. 680°C has been formed among Bi₃B₂O₁₅, D and B₂O₃ compounds; ternary eutectic E₁₀ with m.p. 730°C has been formed among BaB₂O₄, D and B₂O₃ compounds; ternary eutectic E₁₁ with m.p. 750°C has been formed among Ba₂B₁₀O₁₅-D- BaB₈O₁₃ compounds; ternary eutectic E₁₂ with m.p. 680°C has been formed among C, Ba₂B₁₀O₁₇ and D compounds; ternary eutectic E₁₃ with m.p. 690°C has been formed among Ba₂B₁₀O₁₇, C and BaB₂O₄ compounds; ternary eutectic E₁₄ with m.p. 700°C has been formed among BaB₄O₇, C and BaB₂O₄ compounds; ternary eutectic E₁₅ with m.p. 645°C has been formed among G, F and C compounds; ternary eutectic E₁₆ with m.p. 615°C has been formed among Bi₂₄B₂O₃₉, F and Bi₄B₂O₉ compounds (Fig18, Table 3).

Figure 18. Phase diagram of the BaO-Bi₂O₃-B₂O₃ system
<table>
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<th>Point</th>
<th>Composition, mol%</th>
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**Table 3.** The temperature and compositions for ternary eutectic points in the BaO-Bi$_2$O$_3$-B$_2$O$_3$ system

3.2. DTA and X-ray characterisation of ternary stoichiometric glasses and glass ceramics from the BaO-Bi$_2$O$_3$-B$_2$O$_3$ system

The glasses corresponding to known sixth stoichiometric compounds in the BaO-Bi$_2$O$_3$-B$_2$O$_3$ system examined in the present study and following glass compositions (mol%) have been melted: 14.28BaO•7.14Bi$_2$O$_3$•78.57B$_2$O$_3$ (BaBi$_2$O$_{11}$), 25BaO•25Bi$_2$O$_3$•50B$_2$O$_3$(Ba-Bi$_3$O$_{10}$), 33.33BaO•33.33Bi$_2$O$_3$•33.33B$_2$O$_3$(BaBi$_3$B$_2$O$_7$), 11.11BaO•55.55Bi$_2$O$_3$•33.33B$_2$O$_3$ (Ba-Bi$_2$B$_2$O$_{25}$), 50BaO•25Bi$_2$O$_3$•25B$_2$O$_3$ (BaBiBO$_4$) and 60BaO•10Bi$_2$O$_3$•30B$_2$O$_3$ (Ba$_3$Bi$_2$O$_9$). These glasses DTA curves are shown in Fig. 19, giving the peaks due to the glass transition, crystallization, melting, and liquidus temperatures. The glass characteristics points $T_g$ (glass transition), $T_s$ (glass softening), $T_c$ (peak of exothermal effects connected with crystalline phases crystallizations) and $T_m$ (minimum of endothermic effects associated with these phases melting) observed on DTA curves (Fig. 19, curves 1-6) of all tested powder samples summarized on table 4.
Two exothermic effects were observed on DTA curve of $14.28\text{BaO} \cdot 7.14\text{Bi}_2\text{O}_3 \cdot 78.57\text{B}_2\text{O}_3$ (mol %) glass composition: first weak effect at $640^\circ$C and second strong effect at $770^\circ$C (Fig. 19).
The melting temperature \( T_m \) is equal to 807°C and corresponding to Egorisheva and Kargin's data [30]. X-ray patterns of this glass crystallization products show one \( \text{BaBiB}_{11}\text{O}_{19} \) crystalline phase presence [30], which formed at powder samples crystallization in an temperature interval 640-770°C (Fig. 20, curve1). It is possible to assume, that weak exothermic effect at 640°C apparently is connected with pre-crystallisation fluctuations taking place in glass matrix [50]. Diffuse character of second exothermic effect at 770°C testifies about dominating surface crystallisation of the given glass particles.

One sharp exothermic effect at 640°C and sharp endothermic effect at 730°C were observed on DTA curve of \( \text{BaBiB}_2\text{O}_{10} \) glass composition (Fig. 19, curve2). The melting temperature \( T_m \) is equal to 730°C and corresponding to Egorisheva’s data [30]. X-ray diffraction patterns of this glass crystallization products show one \( \text{BaBiB}_2\text{O}_{10} \) crystalline phase crystallization[30], which formed at glass powder samples crystallization at temperature 640°C (Fig. 20, curve2) and its melting. \( T_m \) is equal to 730°C and corresponding to Egorisheva’s data [30]. Hardly visible pre-crystallisation fluctuation exothermal effect is observed also at 545°C (Fig. 19, curve2).

Figure 20. XRD-patterns of the crystallized glasses corresponding to ternary \( \text{BaBiB}_{11}\text{O}_{19} \) (1- 760 °C 24h,cooling in the muffle) and \( \text{BaBiB}_2\text{O}_{10} \) (2- 640°C 24h,cooling in the muffle) compounds

On the DTA curves of stoichiometric \( \text{BaBiB}_2\text{O}_7 \) and \( \text{BaBi}_{10}\text{B}_6\text{O}_{25} \) glass compositions observed two exothermal effects at 570 and 645°C for \( \text{BaBiB}_2\text{O}_7 \) and at 460 and 620°C for \( \text{BaBi}_{10}\text{B}_6\text{O}_{25} \) (Fig. 19, curves 3,4). But both compositions have one endothermic effect of melting at 725 and 690°C respectively for \( \text{BaBiB}_2\text{O}_7 \) and \( \text{BaBi}_{10}\text{B}_6\text{O}_{25} \) testifying to one formed crystalline phase melting (Fig. 19, curves 3,4). X-ray data of these samples confirmed monophase crystallizations in each samples (Fig. 21, curves 1,2; Fig.22, curves 1,2).

According to [34] the X-ray powder diffraction patterns of formed \( \text{BaBiB}_2\text{O}_7 \) crystalline phase at stoichiometric glass composition (33.33BaO•33.33Bi_2O_3• 33.33B_2O_3 mol%) at second
exothermic peaks temperature (640°C 24h) was indexed on an orthorhombic cell with following lattice parameters: a=11.818 Å, b=8.753 Å, c=7.146 Å, cell volume V=739.203 Å, Z=4 (Fig. 21, curve 2). XRD-patterns of products of same glass crystallization at 570°C 24h keeps all diffraction lines of its analogue obtained at 640°C 24h (Fig. 21, curve 1). Difference is observed only in sharp increasing of intensity (I/I_0) of [030] diffraction line from 4 to 43 at high temperature crystallization. That leads to reorientation of crystal structure, decreasing [030] diffraction line and accompanied with occurrence of the second exothermal effect on DTA curve (Fig. 19, curve 3).

Figure 21. XRD-patterns of the crystallized glasses corresponding to ternary BaBi_2B_2O_7 composition:

1-570°C 24h, cooling in the muffle; 2-640°C 24h, casting in the cold water

X-ray powder diffraction patterns of BaBi_{10}B_6O_{25} single crystals was indexed on an orthorhombic cell with following lattice parameters: a=6.434 Å, b=11.763 Å, c=29.998 Å, cell volume V=2270.34 Å, Z=8 [34]. XRD-patterns of products of same compositions (11.11BaO•55.55Bi_2O_3•33.33B_2O_3 mol%) glass crystallization at both exothermal effects (420°C 24h and 620°C 24h) have all diffraction lines of the BaBi_{10}B_6O_{25} single crystals (Fig. 22, curves 1-3). Naturally, BaBi_{10}B_6O_{25} single crystal has well generated planes and clear observed diffraction lines on XRD-patterns in contrast to crystalline phases formed at same composition glasses crystallization. However, the most intensive diffraction line (I/I_0=100) of single crystals is [133], whereas products of glass crystallizations have [203] strongest diffraction line and [133] diffraction line became 5-10 times less (Fig. 22, curves 1-3). Now it is difficult to us only on the basis of XRD-patterns analysis of glass crystallizations products to assume the nature of the second exothermal effect at 620°C on DTA curve of BaBi_{10}B_6O_{25} of glass composition (Fig. 19, curve 4). Their XRD-patterns are identical each other and to single crystals,
but contain slightly quantity of not indexed reflexes, which are absent in X-ray powder diffraction patterns of $\text{BaBi}_{10}\text{B}_6\text{O}_{25}$ single crystals (Fig. 22, curves 1-3).

Figure 22. XRD-patterns of the crystallized glasses corresponding to ternary $\text{BaBi}_{10}\text{B}_6\text{O}_{25}$ composition: (1-460°C 24h, cooling in the muffle; 2-620°C 24h, casting in the cold water) and $\text{BaBi}_{10}\text{B}_6\text{O}_{25}$ single crystals (3).

The DTA curve of 50$\text{BaO}\cdot 25\text{Bi}_2\text{O}_3\cdot 25\text{B}_2\text{O}_3$ mol% ($\text{BaBiBO}_4$) glass composition contain exothermic effect of glass crystallization at 450°C and endothermic effect of this crystalline phase melting at 680°C (Fig. 19, curv. 5). X-ray diffraction patterns of this glass crystallization products show one $\text{BaBiBO}_4$ crystalline phase formation at glass powder samples crystallization at temperature interval 450-640°C (Fig. 23, curve 1), which completely correspond to Barbier with co-authors data [29]. A second endothermic effect within the interval of 745-775°C with minimum at 760°C is associated with $\text{BaBiBO}_4$ incongruent melting (Fig. 19, curve 5).

We have revealed also, that the crystalline $\text{BaBiBO}_4$ compound is melted incongruently at 680°C with the melt and crystalline $\text{BaBiO}_3$ formation (Fig. 23, curve 2). The $\text{BaBiO}_3$ crystalline phase was observed on XRD-patterns of thermal treated at 720 °C and fast freeze in cold
water products and identified according to X-ray database [43, fail # 01-074-7523]. The dissolution of this BaBiO$_3$ phase in a melt leads to the appearance on a DTA curve the second endothermic effect in an interval 745-775°C (Fig. 19, curve 5). Above 775°C we have glass-forming BaBiBO$_4$ composition melt without presence of any crystalline phase.

![XRD-patterns of the crystallized glasses corresponding to ternary BaBiBO$_4$ composition](http://dx.doi.org/10.5772/52405)

**Figure 23.** XRD-patterns of the crystallized glasses corresponding to ternary BaBiBO$_4$ composition:

1-450°C 24h, cooling in the muffle; 2-720°C 3h, casting in the cold water

Two exothermal effects of glass crystallization at 540 and 670°C and one endothermic effect of crystalline phase melting at 827°C are seen on the DTA curve of the 60BaO•10Bi$_2$O$_3$•30B$_2$O$_3$ mol% (Ba$_3$BiB$_3$O$_9$) glass composition (Fig. 19, curve 6). X-ray diffraction patterns of this glass crystallization products at 540 and 670°C show one Ba$_3$BiB$_3$O$_9$ crystalline phase formation (Fig. 24, curves 1,2) at glass powder samples crystallization at 540 and 670°C and fully correspond to Egorisheva with co-authors data, which synthesized for the first time and have describe Ba$_3$BiB$_3$O$_9$ compound [31]. However, we didn’t indicate polymorphic transition of Ba$_3$BiB$_3$O$_9$ at 850°C as reported in [31]. Presence of second endothermic effect within the interval of 840-890°C with minimum at 865°C is associated with Ba$_3$BiB$_3$O$_9$ incongruent melting (Fig. 19, curve 6). We have revealed that the crystalline Ba$_3$BiB$_3$O$_9$ compound is melted incongruently at 827°C with the glass forming melt and crystalline phase formation (Fig. 24, curve 3). The Ba$_3$B$_2$O$_5$ crystalline phase was observed in amorphous matrix on XRD-patterns of thermal treated at 830 °C and fast freeze in cold water products and identified according to X-ray database [43, fail # 024-0087]. For clear Ba$_3$B$_2$O$_5$ observation on XRD-patterns the preliminary crystallized at 670°C 24h sample have been exposed at 830°C 3 h (Fig. 23, curve 3). Dissolution of this Ba$_3$B$_2$O$_5$ phase in a melt leads to the appearance on a DTA curve the second endothermic effect in an interval 840-890°C (Fig. 19, curve 6). Above 890°C we have glass-forming Ba$_3$BiB$_3$O$_9$ composition melt without presence of any crystalline phase at cooling rate 10$^2$ K/s.
3.3. TEC study of the stoichiometric compositions glasses in the BaO-Bi$_2$O$_3$-B$_2$O$_3$ system

The isolines diagram of BaO-Bi$_2$O$_3$-B$_2$O$_3$ system glasses TEC values is given on Fig. 25. It is clear observed common regularity, that the increase of barium and bismuth oxides amounts in glasses of binary BaO-Bi$_2$O$_3$ and Bi$_2$O$_3$-B$_2$O$_3$ systems leads to increase TEC of glasses. The same tendency is observed for glasses of ternary system: joint presence of BaO and Bi$_2$O$_3$ and increase their amounts leads to increase glasses TEC values from 70 to 127•$10^{-7}$K$^{-1}$ (Fig. 25).
The high boron content glass composition corresponds to BaBiB_{19}O_{19} (14.28BaO•7.14Bi_{2}O_{5}•78.57B_{2}O_{3} mol %) have TEC=72•10^{-7}K^{-1} and Tg=498°C calculated from dilatometric curve (Table 4). Reduction the B_{2}O_{3} amount together with increasing of BaO and Bi_{2}O_{3} amounts in glass compositions lead to increase TEC and reduction Tg values: for glass composition 25BaO•50Bi_{2}O_{5}•25B_{2}O_{3} mol % (BaBi_{5}B_{2}O_{10}) TEC=96•10^{-7}K^{-1} and Tg=445°C; 33.3BaO•33.3Bi_{2}O_{5}•33.3B_{2}O_{3} mol % (BaBi_{3}B_{2}O_{10}) TEC=108•10^{-7}K^{-1} and Tg=415°C; 11.1BaO•55.5Bi_{2}O_{3}•33.3B_{2}O_{3} mol % (BaBi_{11}B_{2}O_{13}) TEC=97•10^{-7}K^{-1} and Tg=350°C; 16.67BaO•66.67Bi_{2}O_{5}•16.67B_{2}O_{3} mol % (BaBi_{4}B_{2}O_{11}) TEC=110•10^{-7}K^{-1} and Tg=415°C. However, for 50BaO•25Bi_{2}O_{5}•25B_{2}O_{3} mol % (BaBiBO_{1}) and 60BaO•10Bi_{2}O_{5}•30B_{2}O_{3} mol % (Ba_{2}BiB_{2}O_{9}) glass compositions simultaneous increase both TEC and Tg values were observed: TEC=120•10^{-7}K^{-1} and Tg=400°C; TEC=127•10^{-7}K^{-1} and Tg=460°C respectively for BaBiBO_{4} and Ba_{2}BiB_{2}O_{9} (Fig. 25, Table 4).

TEC values of crystallized glasses corresponding to the ternary barium bismuth borates given in Table 4. Crystallized barium bismuth borate glass samples have TEC values lower, than initial glasses and equals to: 49•10^{-7}K^{-1} for BaBi_{11}O_{19} sample (750°C 24h), 78•10^{-7}K^{-1} for BaBi_{5}B_{2}O_{10} sample (630°C 24 h), 96•10^{-7} K^{-1} for BaBi_{3}B_{2}O_{10} sample (640°C 24h), 97•10^{-7}K^{-1} for BaBi_{4}B_{2}O_{10} sample (610°C 24h), 110•10^{-7} K^{-1} for BaBiBO_{1} sample (450°C 24h) and 109•10^{-7} K^{-1} for Ba_{2}BiB_{2}O_{9} sample (690°C 24h). The same tendency, as well as for their glassy analogues, is observed for crystallized glass samples: increase of barium and bismuth oxides amounts in ternary compounds leads to their TEC values increase.

4. Ferroelectric properties of new ternary BaBi_{2}B_{2}O_{7} and BaBi_{10}B_{6}O_{25} stoichiometric compositions glass ceramics.

The ferroelectric (polarization - electric field) hysteresis, is a defining property of ferroelectric materials. Thus, the most widely studied characteristics of ferroelectric hysteresis were those of interest for this particular application: the value of the switchable polarization (the difference between the positive and negative remanant polarization, P_{R} = (−P_{R})), dependece of the coercive field Ec on sample thickness, decrease of remanent or switchable polarization with number of switching cycles, polarization imprint, endurance, retention [51].

Electric field induced polarization (P) and remanent polarization(P_{r}) were measured at room temperature for BaBi_{2}B_{2}O_{7} and BaBi_{10}B_{6}O_{25} glass tape samples crystallized using various regimes (Fig. 26).

a. BaBi_{2}B_{2}O_{7} glass tape sample of 0.07 mm in thickness crystallized at 450°C 24h, 2P_{r} = 0.15 μC/cm²;

b. BaBi_{10}B_{6}O_{25} glass tape sample of 0.06 mm in thickness crystallized at 380 °C 12h, 2P_{r} = 0.32 μC/cm²;

c. BaBi_{10}B_{6}O_{25} glass tape sample of 0.06 mm in thickness crystallized at 410°C 12h, 2P_{r} = 0.62 μC/cm²;
d. BaBi$_{10}$B$_6$O$_{25}$ glass tape sample of 0.05 mm in thickness crystallized at 410°C 24h, $2P_r = 0.9$ μC/cm$^2$

**Figure 26.** Dependence of polarization ($P$) on electric field ($E$) for crystallized stoichiometric glass compositions:

Linear $P$–$E$ curves are observed up to fields of 40-120 kV/cm for all measured samples with thickness 0.05-0.07mm. The polarization becomes nonlinear with increasing of applied electric field, and at 140-380 kV/cm the remanent polarization $2P_r$ values were found 0.15 μC/cm$^2$ for the BaBi$_{10}$B$_6$O$_{25}$ (Fig. 26, A). The remanent polarization $2P_r$ value for BaBi$_{10}$B$_6$O$_{25}$ crystallized glass tape samples increasing with termal treatment temperature from 0.32 to 0.64 μC/cm$^2$ (Fig. 26, B & C) and time (Fig. 26, D). The highest remanent polarization value ($2P_r = 0.9$ μC/cm$^2$) has BaBi$_{10}$B$_6$O$_{25}$ glass tape sample crystallized at 410°C 24h (Fig. 26, D). According to obtained results it is possible to conclude that samples are ferroelectrics.

5. Discussion

The principal difference of our methodology from traditional is a glass samples using as initial testing substance for phase diagram of very complex ternary BaO-Bi$_2$O$_3$-B$_2$O$_3$ system construction. It is a very effective method, due possibility to indicate temperature intervals of all processes taking place in glass samples: glass transition, crystallization, quantity of formed crystalline phases and their melting. Whereas, samples prepared by traditional solid phase synthesis are less informative and often lose a lot of information. Super cooling technique created by our group allowed us both to expand borders of glass formation and to have enough quantity samples for DTA and X-ray investigations and BaO-Bi$_2$O$_3$-B$_2$O$_3$ system phase diagram construction (Fig.2).

The region of stable glasses includes the binary compounds BaB$_2$O$_7$, Ba$_2$B$_{10}$O$_{17}$, BaB$_3$O$_{13}$, Bi$_2$B$_2$O$_y$, BiBO$_3$, Bi$_5$B$_9$O$_{12}$, BiB$_2$O$_y$, and Bi$_2$B$_4$O$_{15}$ in the BaO–B$_2$O$_3$ and Bi$_2$O$_3$–B$_2$O$_3$ systems (Fig.
2. Binary BaB\(_2\)O\(_4\), Ba\(_2\)B\(_{10}\)O\(_{17}\), and BaB\(_3\)O\(_{13}\) barium borates have melting temperatures (T\(_m\)) of 910, 905, and 890°C and can be found between the eutectics e\(_{12}\), e\(_{14}\), and e\(_{19}\) with T\(_m\) = 878, 869, 895, and 899°C, respectively. The transition to a crystallization field of barium metaborate is accompanied by a sharp increase of liquidus temperature (T\(_L\)) and a decrease of the glass forming ability of the melts. The final compound, forming a stable glass, contains ~43 mol %BaO and has T\(_L\) = 950°C. Compounds BaB\(_2\)O\(_4\) and Ba\(_2\)B\(_{10}\)O\(_{17}\), having higher T\(_m\), are found in the region of the compounds obtained in the form of glasses with a cooling rate of (10\(^3\)–10\(^4\)) K/s. Glass formation in the BaO–B\(_2\)O\(_3\) binary system is limited by the eutectic e\(_{12}\) with T\(_m\) = 1025°C (Fig. 2) because of the sharp increase of the liquidus temperature during the transition to a field of crystallization of the Ba\(_2\)B\(_{10}\)O\(_{17}\) compound (T\(_m\) = 1383°C). BaB\(_2\)O\(_4\) (T\(_m\) = 1095°C) is the dominating compound in the system and does not form stable glasses. Its considerable crystallization field narrows the region of stable glasses in the ternary system, which is only restricted by compounds with T\(_L\) ~ 950°C (Fig. 2).

Binary bismuth borates Bi\(_2\)B\(_4\)O\(_9\), BiBO\(_3\), Bi\(_2\)B\(_{12}\)O\(_{25}\), Bi\(_3\)B\(_6\)O\(_{19}\), and Bi\(_2\)B\(_{15}\)O\(_5\) have T\(_m\) 675, 685, 722, 708, and 715°C can be found between the eutectics e\(_1\), e\(_3\), e\(_4\), e\(_5\), e\(_6\), e\(_8\), e\(_9\), e\(_10\), e\(_11\), e\(_12\), e\(_13\), e\(_14\), e\(_15\), and e\(_16\) with a T\(_m\) of 622, 646, 665, 698, 695, and 709°C, respectively [2, 34]. The region of stable glasses in the Bi\(_2\)O\(_3\)–B\(_2\)O\(_3\) system is limited by a compound containing ~70%mol Bi\(_2\)O\(_3\) and having T\(_L\) = 670°C. Compounds that are found in the range of 70–80mol% Bi\(_2\)O\(_3\) (before the e\(_i\) point) are obtained in the form of glasses during cooling at a rate of ~10\(^2\) K/s. During the transition to the crystallization field of Bi\(_2\)B\(_2\)O\(_3\) and Bi\(_2\)O\(_3\), T\(_L\) increases to 825°C (T\(_m\) of Bi\(_2\)O\(_3\)). Glasses in this part of the system are obtained during melt cooling at a rate of (10\(^3\)–10\(^4\)) K/s. These compounds have a low liquidus temperature; however, the structure factor essentially influences their glass forming ability, not allowing glass formation at low melt cooling rates.

Six ternary compounds are known in the BaO–Bi\(_2\)O\(_3\)–B\(_2\)O\(_3\) system: Ba\(_3\)BiB\(_2\)O\(_9\), BaBiBO\(_3\), BaBiB\(_2\)O\(_{10}\), and BaBiB\(_3\)O\(_{19}\) synthesized by Barbie and Egorysheva in 2005–2006, and BaBiB\(_2\)O\(_7\) and BaBiB\(_2\)O\(_{19}\) revealed by our research group in 2008–2009. BaBiB\(_2\)O\(_7\), BaBiB\(_2\)O\(_{19}\), BaBiB\(_3\)O\(_{19}\), and BaBiB\(_3\)O\(_{25}\) melt congruently at 730, 807, 725, and 695°C respectively, and BaBiBO\(_3\) melts incongruently at 680°C and has T\(_L\) = 760 °C. All these five ternary compounds along with the eutectics formed between each other and with binary barium and bismuth borates form a “plateau” with low T\(_L\), which is responsible for the formation of the region of stable glasses in the ternary system BaO–Bi\(_2\)O\(_3–B_2O_3\). Compounds joining low temperature eutectic e\(_1\) (622°C) [2] in the Bi\(_2\)O\(_3–B_2O_3\) binary system and the eutectics e\(_{13}\) (~790°C) and e\(_{14}\) (~750°C) in the BaO–Bi\(_2\)O\(_3\) binary system 26 - 28] form glasses only at higher cooling rates of their melts (10\(^3\)–10\(^6\)) K/s. Glass formation in the BaO–Bi\(_2\)O\(_3\) binary system stops at 45 mol% BaO content (T\(_L\) ~930°C) [26 - 28]. Along with the factor of the liquidus temperature [52], a considerable contribution to the glass formation of the pointed compositions is made by the structural factor of the melt. The combination of the structural factors of the melt and the liquidus temperature is also considerable during the transition to the vitreous state of the compositions, which are found in the crystallization fields of BaB\(_2\)O\(_4\) and Ba\(_2\)B\(_{10}\)O\(_{17}\), where they show the tendency towards glass formation only at high rates of melt cooling.
There are very stable congruent melted binary BaB$_2$O$_4$ and ternary BaBi$_2$B$_4$O$_{10}$, BaBiB$_3$O$_{11}$, and BaBi$_2$B$_4$O$_{25}$ compounds in the studied ternary BaO-Bi$_2$O$_3$-B$_2$O$_3$ system. They have dominating positions in ternary diagram and occupied the biggest part of it (Fig.18). Mutual influence of these compounds and other binary and ternary compounds (BaB$_2$O$_4$, BaBi$_2$O$_4$, BaB$_4$O$_{12}$, Bi$_2$BO$_3$, Bi$_3$B$_2$O$_{12}$, Bi$_2$B$_4$O$_{15}$, BaBi$_2$B$_4$O$_{25}$, and BaBi$_3$B$_4$O$_{25}$) lead to formation of sixteen revealed at present time ternary eutectics (Fig.18 & Table 3), which have essential influence on liquidus temperature decrease and to assist in glass formation. Ternary BaBi$_2$B$_4$O$_{10}$ compound forms eight eutectics with binary and ternary compounds, its neighbors: E$_1$(622°C), E$_2$(640°C), E$_3$(610°C), E$_4$(675°C), E$_5$(680°C), E$_{12}$(690°C), and E$_{14}$(700°C) (Fig.18 & Table 3). BaBi$_3$B$_4$O$_{25}$ compound forms seven eutectics with its neighbors: E$_1$ (675°C), E$_2$ (680°C), E$_3$ (655°C), and E$_{12}$ (680°C) (Fig.18 & Table 3). BaBi$_4$B$_3$O$_9$ compound forms five eutectics with its neighbors: E$_4$ (590°C), E$_5$ (590°C), E$_6$ (585°C), E$_8$ (645°C), and E$_{16}$ (615°C) (Fig.18 & Table 3). Determined ternary eutectics together with binary eutectics E$_1$, E$_2$, E$_3$, E$_4$, E$_5$, and E$_6$ of Bi$_2$O$_3$-B$_2$O$_3$ system have allowed to outline the fields of binary Bi$_2$B$_4$O$_{15}$, BiBO$_3$, Bi$_3$B$_2$O$_{12}$, Bi$_2$BO$_3$, and Bi$_2$B$_4$O$_{15}$ bismuth borates crystallisation, as well as together with binary eutectics E$_4$, E$_5$, and E$_6$ of BaO-B$_2$O$_3$ system have allowed to outline the fields of binary BaB$_2$O$_4$, Ba$_2$B$_2$O$_5$, and BaBi$_2$O$_3$ barium borates and partly Ba$_2$B$_4$O$_4$ crystallization on the BaO-Bi$_2$O$_3$-B$_2$O$_3$ system phase diagram (Fig.18).

The clear correlation between glass forming and phase diagrams has been observed in studied system. The glass melting temperature and level of glass formation depending on the cooling rate of the studied melts are in good conformity with boundary curves and eutectic points (Fig.2 & 18).

The phase diagram of the well known binary Bi$_2$O$_3$-B$_2$O$_3$ system has been corrected in the interval between the Bi$_4$B$_2$O$_9$ and Bi$_2$B$_5$O$_{12}$ compounds. The eutectic composition, 48.5Bi$_2$O$_3$•51.5B$_2$O$_3$ (mol%), between BiBO$_3$ and Bi$_2$B$_5$O$_{12}$ with m.p. 665±5°C, has been determined. It is shown that the compound BiBO$_3$ is congruently melting with a m.p. of 685±5°C.

The next unexpected results were obtained at phase diagram construction: two new ternary BaBi$_2$B$_4$O$_7$ and BaBi$_3$B$_4$O$_{25}$ compounds have been revealed at the same glass compositions crystallisation. X-ray characteristics of the new ternary compound BaBi$_2$B$_4$O$_7$, synthesized at the 33.33BaO•33.33Bi$_2$O$_3$•33.33B$_2$O$_3$ (mol%) glass composition crystallisation at 640°C, 20 h. The x-ray powder diffraction patterns of BaBi$_2$B$_4$O$_7$ could be indexed on an orthorhombic cell with lattice parameters as follows: BaBi$_2$B$_4$O$_7$: a=11.818 Å, b=8.753 Å, c=7.146 Å, cell volume V=739.203 Å$^3$, Z=4.

Single crystals of BaBi$_3$B$_4$O$_{25}$ were obtained by cooling of a melt with the stoichiometric composition. Glass powder of composition 11.11BaO•55.55Bi$_2$O$_3$•33.33B$_2$O$_3$ (mol%) was heated in a quartz glass ampoule up to 750°C at a rate 10 K/min. After 2 h at high temperature, the melt was cooled at a rate 0.5 K/h. Single crystals with sizes up to 1.66×0.38×0.19 mm$^3$ were grown. The x-ray powder diffraction patterns of BaBi$_3$B$_4$O$_{25}$ could be indexed on an orthorhombic cell with lattice parameters as follows: a=6.434 Å, b=11.763 Å, c=29.998 Å, cell volume V=2270.34 Å$^3$, Z=8.
Common regularities of bulk glass samples TEC changes in studied BaO-Bi$_2$O$_3$-B$_2$O$_3$ system have been determined: the increase of barium and bismuth oxides amounts in glasses of binary BaO-Bi$_2$O$_3$ and Bi$_2$O$_3$-B$_2$O$_3$ systems leads to increase TEC of glasses. The same tendency is observed for glasses of ternary BaO-Bi$_2$O$_3$-B$_2$O$_3$ system: joint presence of BaO and Bi$_2$O$_3$ and increase their amounts leads to increase glasses TEC values from 70 to $127 \times 10^{-7}$ K$^{-1}$ (Fig. 25).

Crystallized barium bismuth borate glass samples have TEC values lower, than initial glasses and equals to: $49 \times 10^{-7}$ K$^{-1}$ for BaBi$_{11}$O$_{19}$ sample (750°C 24h), $78 \times 10^{-7}$ K$^{-1}$ for BaBi$_{2}$B$_{4}$O$_{10}$ sample (630°C 24 h), $96 \times 10^{-7}$ K$^{-1}$ for BaBi$_{2}$B$_{4}$O$_{7}$ sample (640°C 24h), $97 \times 10^{-7}$ K$^{-1}$ for BaBi$_{10}$B$_{6}$O$_{25}$ sample (610°C 24h), $110 \times 10^{-7}$ K$^{-1}$ for Ba$_3$Bi$_2$O$_9$ sample (690°C 24h). The same tendency, as well as for their glassy analogues, is observed for crystallized glass samples: increase of barium and bismuth oxides amounts in ternary compounds leads to their TEC values increase.

Electric field induced polarization ($P$) and remanent polarization ($P_r$) were measured at room temperature for BaBi$_2$B$_2$O$_7$ and BaBi$_{10}$B$_6$O$_{25}$ glass tape samples crystallized at various regimes. All tested samples shown loop of hysteresis.

Linear $P$–$E$ curves are observed up to fields of 40-120 kV/cm for all measured samples with thickness 0.05-0.07mm. The polarization becomes nonlinear with an increase of applied electric field, and at 140-400 kV/cm the remanent polarization $2P_r$ values were found 0.15 $\mu$C/cm$^2$ for the BaBi$_2$B$_2$O$_7$ (Fig.26, A), and 0.32-0.9 $\mu$C/cm$^2$ for the BaBi$_{10}$B$_6$O$_{25}$ (Fig.26, B-D), crystallized glass tape samples. According to obtained results it is possible to conclude that all tested samples are ferroelectrics.

5. Conclusion

Effective way of new system investigation and new compounds and characteristic points revealing via simultaneous glass forming and phase diagrams construction have been shown. Phase diagram of the ternary BaO-Bi$_2$O$_3$-B$_2$O$_3$ system have been constructed for the first time us result of fourteen pseudo-binary systems and sections phase diagrams investigations.

The phase diagram of the well known binary Bi$_2$O$_3$-B$_2$O$_3$ system has been corrected in the interval between the Bi$_4$B$_2$O$_9$ and Bi$_3$B$_5$O$_{12}$ compounds. The eutectic composition, $48.5\%$Bi$_2$O$_3$•$51.5\%$B$_2$O$_3$ (mol%), between BiBO$_3$ and Bi$_3$B$_5$O$_{12}$, with m.p. 665±5°C, has been determined. It is shown that the compound BiBO$_3$ is congruently melting with a m.p. of 685±5°C.

Two new ternary BaBi$_2$B$_2$O$_7$ and BaBi$_{10}$B$_6$O$_{25}$ compounds have been revealed at the same glass compositions crystallisation. The new ternary compound BaBi$_{10}$B$_6$O$_{25}$ synthesized at the 33.33BaO•33.33Bi$_2$O$_3$•33.33B$_2$O$_3$ (mol%) glass composition crystallization at 640°C, 20 h. The x-ray powder diffraction patterns of BaBi$_2$B$_2$O$_7$ could be indexed on an orthorhombic cell with lattice parameters as follows: BaBi$_2$B$_2$O$_7$, $a=11.818$ Å, $b=8.753$ Å, $c=7.146$ Å, cell volume $V=739.203$ Å$^3$, $Z=4$.

Single crystals of BaBi$_{10}$B$_6$O$_{25}$ were obtained by cooling of a melt with the stoichiometric composition. Glass powder of composition 11.11BaO•55.55Bi$_2$O$_3$•33.33B$_2$O$_3$ (mol%) was
heated in a quartz glass ampoule up to 750°C at a rate 10 K/min. After 2 h exposition at high temperature, the melt was cooled at a rate 0.5 K/h. Single crystals with sizes up to 1.66×0.38×0.19 mm$^3$ were grown. The x-ray powder diffraction patterns of BaBi$_{10}$B$_6$O$_{25}$ could be indexed on an orthorhombic cell with lattice parameters as follows: a=6.434 Å, b=11.763 Å, c=29.998 Å, cell volume V=2270.34 Å$^3$, Z=8.

Ternary BaBi$_2$B$_4$O$_{10}$, BaBiB$_{11}$O$_{19}$, and BaBi$_{10}$B$_6$O$_{25}$ compounds have dominating positions in ternary diagram and occupied the biggest part of it. Mutual influence of these and other binary and ternary compounds (BaB$_4$O$_7$, Ba$_2$B$_{10}$O$_{17}$, BaB$_8$O$_{15}$, Bi$_4$B$_2$O$_9$, BiBO$_3$, Bi$_3$B$_5$O$_{12}$, Bi$_2$O$_6$, Bi$_2$B$_6$O$_{15}$, BaBi$_2$B$_2$O$_7$, and BaBi$_{12}$B$_4$O$_{16}$) lead to formation of sixteen ternary eutectics, which have essential influence on liquidus temperature decrease and to assist in glass formation.

The clear correlation between glass forming and phase diagrams has been observed: glass melting temperature and level of glass formation depending on the cooling rate of the studied melts are in good conformity with boundary curves and eutectic points.

Common regularities of bulk glass samples TEC changes in studied BaO-Bi$_2$O$_3$-B$_2$O$_3$ system have been determined: the increase of barium and bismuth oxides amounts in glasses of binary BaO-Bi$_2$O$_3$ and Bi$_2$O$_3$-B$_2$O$_3$ systems and their joint amounts increasing in ternary compositions leads to increase glasses TEC values from 70 to 127×10$^{-7}$K$^{-1}$.

Crystallized barium bismuth borate glass samples have TEC values lower, than initial glasses. Increase of barium and bismuth oxides amounts in ternary compounds leads to their TEC values increasing from 49 to 109×10$^{-7}$K$^{-1}$.

Electric field induced polarization ($P$) and remanent polarization ($P_r$) were measured at room temperature for BaBi$_2$B$_2$O$_7$ and BaBi$_{10}$B$_6$O$_{25}$ glass tape samples crystallized at various regimes. The remanent polarization $2P_r$ values were found 0.15 μC/cm$^2$ for the BaBi$_2$B$_2$O$_7$, and 0.32- 0.9 μC/cm$^2$ for the BaBi$_{10}$B$_6$O$_{25}$ crystallized glass tape samples. According to obtained results it is possible to conclude that all tested samples are ferroelectrics.

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