We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

172,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Phase Diagramm, Cristallization Behavior and Ferroelectric Properties of Stoichiometric Glass Ceramics in the BaO-TiO₂-B₂O₃ System

Rafael Hovhannisyan, Hovakim Alexanyan, Martun Hovhannisyan,
Berta Petrosyan and Vardan Harutyunyan
*Institute of Electronic Materials
Armenia*

1. Introduction

Binary borate and polytitanates compounds have currently been of considerable interest to the scientific community due to unique properties of barium titanate, barium polytitanates [Kong, 2010; Wakino, 1990], betta barium borate [Chen, C. & Liu, 1986] and recently revealed high negative thermal expansion of crystallized barium di-borate glass samples [Hovhannisyan, 2006]. It has also been revealed recently, that the single crystal of barium di-tanate is high-temperature ferroelectric with Curie temperature equal to 450-500°C [Waghmare et al., 2004; Akishige et al., 2006]. Park with co-authors reported a new barium titanium oxoborate crystal of Ba₃Ti₃O₆(BO₃)₂ and found out that the second harmonic generation (SHG) efficiency of this crystal is equal to 95% of the well known LiNbO₃ [Park et al., 2004]. These data have even strengthened the interest of studying the ternary BaO-TiO₂-B₂O₃ system even more.

Binary BaO-TiO₂ and BaO-B₂O₃ systems are investigated rather in detail by various authors. The following eight binary barium titanates known in the BaO-TiO₂ system are: Ba₂TiO₄ (2BaT), BaTiO₃ (BaT), BaTi₂O₅ (Ba2T), Ba₆Ti₁₇O₄₀ (6Ba17T), Ba₄Ti₁₃O₃₀ (4Ba13T), BaTi₄O₉(Ba4T), Ba₂Ti₉O₂₀(2Ba9T) and BaTi₅O₁₁ (Ba5T) [Rase & Roy, 1955; O'Bryan & Thomson, 1974]. Levin with co-authors have studied the BaO-B₂O₃ system and constructed its melting diagram. They discovered four Ba₃B₂O₆ (3BaB), BaB₂O₄ (BaB), BaB₄O₇(Ba2B) and BaB₈O₁₃ (Ba4B) compounds [Levin & McMurdie, 1949; Levin & Ugrinic, 1953]. Hubner synthesized three new Ba₄B₂O₆ (4BaB), Ba₂B₂O₅(2BaB) and Ba₂B₁₀O₁₇ (2Ba5B) compounds [Hubner, 1969]. However, these compounds are not visible on the BaO-B₂O₃ systems diagram constructed earlier by Levin with co-authors [Levin & McMurdie, 1949; Levin & Ugrinic, 1953].

Pavlikov with co-authors have studied the TiO₂-B₂O₃ system and didn't reveal binary compounds in it [Pavlikov et al., 1976]. Simple eutectic which is very close to B₂O₃ (~2.9 mol% TiO₂) was found and the presence of liquid immiscibility is supposed in the field of compositions containing 25-55 mol% of TiO₂ [Pavlikov et al., 1976]. One binary oxygen containing titanium boron compound- titanium borate, synthesized by Schmid is known now [Schmid, 1964]. Also the formation of TiBO₃ was revealed during interaction between borate glass melts and titanium alloy [Brow & Watkins, 1987].

Vicat & Aleonard for the first time have obtained $\text{BaTi}(\text{BO}_3)_2$ (BaTB) ternary compound related to “Nordenskiöldine” group borates [Vicat & Aleonard, 1968]. Millet and co-authors studied BaTiO_3 - TiO_2 - BaB_2O_4 subsystem in BaO - TiO_2 - B_2O_3 system and have found the second incongruent melting at 950°C ternary $\text{Ba}_2\text{Ti}_2\text{B}_2\text{O}_9$ (2Ba2TB) compound. Between 950 - 960°C it decomposes with formation BaTiO_3 and liquid [Millet et al., 1986]. Authors [Zhang et al., 2003] have studied subsolidus phase relations in the ternary BaO - TiO_2 - B_2O_3 system. They confirmed only the existence of two known BaTB and 2Ba2TB ternary compounds in this system. The pure 2Ba2TB phase has not been obtained under authors experiment conditions [Zhang et al., 2003]. It was in equilibrium with BB, BT, B2T and 4B13T.

However, Park with co-authors considered, that the $\text{Ba}_2\text{Ti}_2\text{B}_2\text{O}_9$ composition was formulated incorrectly and should be re-formulated as $\text{Ba}_3\text{Ti}_3\text{B}_2\text{O}_{12}$, or more precisely $\text{Ba}_3\text{Ti}_3\text{O}_6(\text{BO}_3)_2$ [Park et al, 2004]. Kosaka et al. have confirmed the data of Barbier's group and have shown necessity of reformulation of $\text{Ba}_2\text{Ti}_2\text{B}_2\text{O}_9$ (2Ba2TB) compound as $\text{Ba}_3\text{Ti}_3\text{O}_6(\text{BO}_3)_2$ (3Ba3TB) [Kosaka et al., 2005]. They have synthesized new glass ceramic composition with 3Ba3TB crystalline phase in the BaO - TiO_2 - B_2O_3 system and have found that its powder sample SHG intensities is 68 times as large as a-quartz powders .

Sholokhovitch & Varicheva have studied $[\text{50PbO}+\text{50B}_2\text{O}_3, \text{ mol\%}]-\text{PbTiO}_3$ - BaTiO_3 - $\text{Ba}(\text{BO}_2)_2$ section of PbO - BaO - B_2O_3 - TiO_2 fourfold system and observed eutectic at 32 mol% BaTiO_3 (m.p. 906°C) in the pseudo-binary $\text{Ba}(\text{BO}_2)_2$ - BaTiO_3 system [Sholokhovitch & Varicheva, 1958]. Goto & Cross studied pseudo-binary BaTiO_3 - BaB_2O_4 system for BaTiO_3 single crystals growth and also found simple eutectic with m.p. 942°C at 32 mol% BaTiO_3 [Goto & Cross, 1969]. Simple eutectic with m.p. 1010°C has also been found in BaB_2O_4 - $\text{BaTi}(\text{BO}_3)_2$ pseudo-binary system at 32 mol% $\text{BaTi}(\text{BO}_3)_2$ [Hovhannisyan, 2004].

Interest to glass formation in ternary barium titanium borate system is mainly connected with developing the new composition of glass ceramics on the basis of barium titanates [Matveev et al, 1966; Bhargava et al., 1988a, 1988b, 1988c; Cerchez et al., 2000; Boroica et al., 2004], betta barium borate [Pernice et al., 1998; Feitosa et al., 2006] and 3Ba3TB [Kosaka et al., 2005]. We are fully confident, that experts and researchers will show interest to ceramics and glass ceramics on the basis of binary barium titanates and ternary barium boron titanates for a long time. However, it will be difficult to them to develop new practical compositions without presence of the first of all the phase diagram and glass forming diagram.

Hovhannisyan with co-workers have made the first attempt of the ternary BaO - TiO_2 - B_2O_3 system both glass forming and phase diagram construction [Hovhannisyan et al., 2008]. A large area of glass formation has been revealed in the BaO - TiO_2 - B_2O_3 system depending on melt's cooling ways. The new incongruent melted ternary $\text{Ba}_2\text{TiB}_2\text{O}_7$ (2BaTB) compound has been revealed during the same composition glass crystallization. Clear correlation between glass forming ability and eutectic and peritectic areas has been observed in the investigated BaO - TiO_2 - B_2O_3 system [Hovhannisyan et al., 2008].

However, our further studies of glasses and glass ceramics in this system have shown necessity of both glass forming and phase diagram correction in the ternary BaO - TiO_2 - B_2O_3 system. Another aim of this work is both known and novel stoichiometric ternary barium titanium borates compounds investigations in glassy, glass ceramic and ceramic states. On the other hand we are seriously interested in giving additional information concerning the existence of two $\text{Ba}_2\text{Ti}_2\text{B}_2\text{O}_9$ and $\text{Ba}_3\text{Ti}_3\text{O}_6(\text{BO}_3)_2$ compounds.

2. Experimental

About two hundred samples of various binary and ternary compositions have been synthesized and tested in BaO-TiO₂-B₂O₃ system. Compositions were prepared from “chemically pure” grade BaCO₃, H₃BO₃ and TiO₂ 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 ÷ 7 mm by casting on metallic plate (up to 10³ K/s), as monolithic glass plates with thickness up to 3 mm by casting between two steel plates (~10² K/s), and glass tapes through super cooling method (10³ ÷ 10⁴ K/s). The glass melting was performed at 1400-1500°C for 30-60 min with a 25-30 g batch in a 50 ml uncovered Pt crucible, using an air atmosphere and a “Superterm 17/08” electric furnace. Chemical composition of some glasses was controlled and corrected by results of the traditional chemical analysis. The final analysis results indicate a good compatibility of calculated and analytical values of B₂O₃, BaO and TiO₂.

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 % B₂O₃ 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-TiO₂-B₂O₃ system. The DTA analysis (platinum crucible, powder samples weight ~600 mg, heating rates 7.5 or 15 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, CuKα-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 1-60 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 [ICDD, 2008].

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 (10-5000 Hz) ranges was used. Methodic based on the well known Sawyer - Tower's [Sawyer & Tower, 1930] 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 through 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 of the BaO-TiO₂-B₂O₃ 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 construction.

3.1.1 Glass forming diagram of the BaO-TiO₂-B₂O₃ system

Figure 1 shows the experimental data on glass formation in the BaO-TiO₂-B₂O₃ system obtained by different authors from 1957 to 2008 [Imaoka & Yamazaki, 1957; Matveev et al., 1966; Bhargava et al., 1987; De Pablos & Duran, 1993; Kusumoto & Sekiya, 1994; Hovhannisyann et al., 2008]. 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. The obtained data are hardly comparable and are “torn away” from the two main factors in glass formation: the liquidus temperature (T_L) and melt cooling rate.

Figure 2 shows corrected glass formation diagram in the BaO-TiO₂-B₂O₃ system based on phase diagrams of the BaO-B₂O₃, BaO-TiO₂, and B₂O₃-TiO₂ 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.

Super cooling technique constructed by our group allowed to expand the borders of glass formation in studied system. The largest glass forming area have been obtained under high melts cooling rates equal to (10^3-10^4) K/s (Fig.2-1). It includes: compositions content 2.5÷3.0 mol% TiO₂ around eutectic area e_9 (~2.9 mol% TiO₂) with m.p. ~450°C in the binary B₂O₃-TiO₂ system [Pavlikov et al., 1976]; compositions content 30÷35 mol% BaO around eutectic area e_7 (~31.5 mol% BaO) with m.p. 1317°C in the binary BaO-TiO₂ system [Rase & Roy, 1955; O'Bryan & Thomson, 1974], which include BaTi₂O₅ composition. Area of glass formation from both these areas moves to eutectic areas e_1 (16,5 mol% BaO) with m.p. 878°C [Levin & McMurdie, 1949; Levin & Ugrinic, 1953] and ~ 31.5 mol% B₂O₃ content compositions in the binary BaO-B₂O₃ system and includes Ba₂B₂O₅ and BaB₂O₄ compositions (Fig.2-1). The transparent glass tapes have been obtained firstly for Ba₃Ti₃B₂O₁₂ (3Ba3TB) composition by

its melt high cooling rate (10^3 - 10^4) K/s (Fig.2-1). The 3Ba3TB glass composition (Table 3) is located practically on the border of glass formation (Fig.2-1).

Fig. 1. Glass forming regions in the BaO-TiO₂-B₂O₃ system according to the data of the authors: 1- [Imaoka & Yamazaki, 1957]; 2- [Matveev et al., 1966]; 3-[Bhargava et al, 1987]; 4- [De Pablos & Duran, 1993]; 5- Kusumoto & Sekiya, 1994]; 6-[Hovhannisyan et al., 2008].

Loss of melts cooling speed to $\sim 10^2$ K/s has naturally led to narrowing of glass formation area (Fig.2-2). However, this cooling rate is enough for monolithic glass plates with thickness up to 3mm fabrication by melts casting between two steel plates. The ternary BaTi(BO₃)₂ (BaTB), Ba₂Ti₂B₂O₉ (2Ba2TB) and Ba₂TiB₂O₇ (2BaTB) compounds have been obtained as bulk glass samples by this way. It was big surprise, that monolithic glass samples have been obtained for ternary glass compositions close to e₅ eutectic area (37.5 mol% B₂O₃) with m.p. 915°C in the binary BaO-B₂O₃ system and containing about 3÷4 mol% TiO₂ (Fig.2-2).

The further reduction of melts cooling rate to ~ 10 K/s has allowed to reveal field of glass compositions with low crystallization ability and stable glass formation in the studied ternary BaO-TiO₂-B₂O₃ system (Fig.2-3).

Fig. 2. Glass forming diagram in the BaO-B₂O₃-TiO₂ system depending of melts cooling rates: (10³-10⁴) K/s; 3~10² K/s; 2-up to 10 K/s;

Earlier we have reported about transparent glass sheets formation in the field of compositions being between eutectic e₁ in the binary B₂O₃-TiO₂ system and ternary eutectic E₁[Hovhannisyan et al., 2008]. However, the present studies have not confirmed previous data. It was possible to obtain transparent glass sheets only in the narrow field of compositions close to eutectic e₁ area (Fig.2).

3.1.2 DTA study of the stoichiometric glass compositions in the BaO-TiO₂-B₂O₃ system

The glass nominal compositions in the BaO-TiO₂-B₂O₃ system examined in the present study and their DTA and dilatometric characteristics are given in Table 1. DTA curves for glasses corresponding to ternary and binary stoichiometric compositions are shown in Fig. 3, giving the peaks due to the glass transition, crystallization, melting, and liquidus temperatures.

On the DTA curve of the 33.33BaO · 33.33TiO₂ · 33.33B₂O₃ (mol%) glass composition strong exothermic effect with maximum at 680°C and endothermic effect with minimum at 1080°C were observed, which show the crystallization and congruent melting of one well known crystalline BaTiB phase (Fig. 3, curve 1).

The similar picture is seen on the DTA curve of the 42.85BaO · 42.85TiO₂ · 14.28 B₂O₃(mol%) glass composition corresponding to stoichiometric 3Ba3TB crystalline compound: we have

strongly expressed exothermic effect at 625 °C and endothermic effects at 975°C, which show the crystallization and melting of one crystalline phase (Fig. 3, curve 3).

Fig. 3. DTA curves (heating rate 7.5K/min) of studied glass compositions (mol%) corresponding to stoichiometric compounds: 1-33.3BaO · 33.3TiO₂ · 33.3B₂O₃ (BaTB), 2-40.0BaO · 40.0TiO₂ · 40.0B₂O₃ (2Ba2TB), 3- 42.85BaO · 42.85TiO₂ · 14.28B₂O₃ (3Ba3TB), 4-50.0BaO · 25.0TiO₂ · 25.0B₂O₃ (2BaTB), and 5-33.3BaO · 66.7TiO₂ (Ba2T)

On the DTA curve of the 40BaO · 40TiO₂ · 20B₂O₃ (mol%) glass composition three exothermic effects clear observed: two effects at 640°C(small) and at 660°C(high) are combined and third is weakly expressed at 690°C, which show processes of glass crystallization and probably of three phases formation (Fig.3, curve 2). Endothermic effect at temperature interval 955-1020 °C (minimum at 975 °C) is connected with the formed crystalline phases melting.

Glass compositions, mol%				Derivatographical characteristics				Dilatometric characteristics	
Sample	BaO	TiO ₂	B ₂ O ₃	T _g , °C	T _{cr} , °C	T _m , °C	T _L , °C	T _g , °C	TEC (α ₂₀₋₃₀₀)· 10 ⁷ K ⁻¹
BaTB	33.33	33.33	33.33	555	680	1080	1080	600	88
2Ba2TB	40.0	40.0	40.0	510	640, 660, 690	975	1090	570	107
3Ba3TB	42.85	42.85	14.30	510	625	975	1260	---	---
2BaTB	50.0	25.0	25.0	475	560, 740	940	1110	512	115
Ba2T	33.33	66.67	---	670	740	1310	1370	---	---

Table 1. Chemical compositions, derivatographical (glass transition -T_g, crystallization peak -T_{cr}, melting -T_m, liquidus temperature-T_L) and dilatometric characteristics (glass transition temperature -T_g, thermal expansion coefficient -TEC) of BaO – TiO₂ – B₂O₃ system glasses.

Two exothermic effects is seen on the DTA curve of the 50BaO · 25TiO₂ · 25B₂O₃ (mol%) glass composition: strongly expressed effect at 585 °C and small diffused effect with maximum at 740°C(Fig. 3, curve 4). Both effects are connected with two crystalline phases formation. According to [Hovhannisyan et al., 2008] the first phase is new crystalline compound, formulated by us as Ba₂TiB₂O₇. The 2BaTiB composition melted incongruently at 940 °C with melt and BaTiO₃ formation. The second weakly expressed endothermic effect on DTA curve at 1110°C is associated with BaTiO₃ dissolution in a melt (Fig. 3, curve 4).

On the DTA curve of the 33.3BaO · 66.67TiO₂ (mol%) glass composition strongly expressed exothermic effect with maximum at 740°C and endothermic effect with minimum at 1320°C were observed, which show the crystallization and melting of one crystalline phase (Fig.3 , curve 5). According to [Rase & Roy, 1955] the 33.3BaO · 66.67TiO₂ (mol%) composition is melted incongruently at 1310°C with melt and BaTiO₃ formation.

3.1.3 TEC study of the stoichiometric glass compositions in the BaO-TiO₂-B₂O₃ system

The isolines diagram of BaO-TiO₂-B₂O₃ system glasses TEC values is given on Fig.4. It is clear observed common regularity, that the increase of barium oxide amounts in glasses of binary BaO-B₂O₃ system leads to increase of glasses TEC values. The same tendency is observed for glasses of ternary compositions: increasing of BaO amounts leads to increase glasses TEC values from 60 to 120 · 10⁻⁷K⁻¹. The substitution of B₂O₃ for TiO₂ in the area of low BaO content glass compositions (20-25 mol%) practically does not influence on the their TEC value. The same tendency is observed for the high BaO content glass compositions (55-60 mol%). It is seen in the central area of compositions that TEC values increase with the substitution of B₂O₃ for TiO₂. However, the major factor influencing on TEC value of studied glasses is the BaO amount in their compositions (Fig.4).

TEC values of glasses corresponding to the ternary barium titanium borates given in Table 3. The glass composition corresponds to BaTiB₂O₆ (33.33BaO-33.33TiO₂-33.33B₂O₃, mol%) has

TEC=88·10⁻⁷K⁻¹ and T_g=555°C calculated from dilatometric curve. Reduction the B₂O₃ and TiO₂ amount together with increasing of BaO amounts in glass compositions leads to increase TEC and reduction T_g values: for glass composition 40BaO·40TiO₂·20B₂O₃, mol % (Ba₂Ti₂B₂O₉) TEC=107·10⁻⁷K⁻¹ and T_g= 570°C; for glass composition 50BaO·25TiO₂·25B₂O₃, mol % (Ba₂TiB₂O₇) TEC=115·10⁻⁷K⁻¹ and T_g=512°C (Table 3).

Fig. 4. BaO-TiO₂-B₂O₃ system's glasses TEC ($\alpha_{20-300} \cdot 10^{-7} \text{K}^{-1}$) values isolines

3.1.4 Phase diagram of the BaO-TiO₂-B₂O₃ system

3.1.4.1 Phase diagram of the pseudo-binary BaTiO₃ -BaTi(BO₃)₂ system

The introduction of BaTB compound in pseudo-binary BaTiO₃ -BaTi(BO₃)₂ system sharply reduced the melting point of initial barium titanate, reduced the crystallization abilities and resulted in the formation of simple eutectic area at 72 mol% BaTB content (38 BaO · 38 TiO₂ · 24 B₂O₃, mol%) with melting point 1020°C (Fig.5 A).

Available inconsistent data about existence of Ba₂Ti₂B₂O₉ crystalline compound promoted more careful study of the BaTi(BO₃)₂ -BaTiO₃ pseudo binary system. High sensitivity of our DTA equipment have allowed to reveal temperatures intervals of processes taking place in initial glass powder samples. Existence on DTA curve of 42.85BaO · 42.85TiO₂ · 14.28B₂O₃ (mol%) glass composition corresponding to stoichiometric 3Ba3TB crystalline compound

only one strongly expressed exothermic (625 °C) and endothermic (975 °C) effects showed on existence of one crystalline phase. Really, X-ray analysis of products of 42.85BaO · 42.85TiO2 · 14.28B2O3 (mol%) glass powder samples crystallized in an interval 600-900 °C has revealed presence of only one 3Ba3TB crystalline phase (Fig.6, curves 1-4). X-ray diffraction patterns of glass crystallization products identification have shown their full conformity with the known references data [Park et al., 2004; ICDD, 2008, File # 074-4273]. 3Ba3TB compound is stable up to 950 °C. It decomposes on BaT and BaTB in temperature interval 950-1020 °C (Fig.5, A; Fig. 6, curve 5). The BaTiO3 and melt formation is the result of 3Ba3TB composition incongruent melting at temperature higher 1020 °C (Fig 6, curve 6). We have revealed that the 3Ba3TiB crystalline compound melted incongruently at 975 °C, with the formation of melt and barium titanate. The dissolution of these phases in a melt lead to the appearance on a DTA curve of the second, weakly expressed endothermic effect in an interval 1020-1260°C (Fig.3, curve 3).

Fig. 5. Phase diagram of the pseudo-binary BaTiO3 - BaTi(BO3)2 system (A) and temperatures intervals of ternary Ba3Ti3B2O12 (B) and Ba2Ti2B2O9 (C) compounds existence on diagram.

Fig. 6. XRD-patterns of the crystallized powder glass samples corresponding to Ba₃Ti₃B₂O₁₂ composition: curve 1- 600°C 60h; curve 2- 660°C 24h, curve 3- 700°C 24h, curve 4- 900°C 24h, curve 5- 950°C 24h, curve 6- 1050°C 24h (samples 2-6 have been water quenched from heat treatment temperature).

The other picture was observed at the 40BaO · 40TiO₂ · 20B₂O₃ (mol%) glass composition crystallization. X-ray identification of products of 40BaO · 40TiO₂ · 20B₂O₃ (mol%) glass crystallization at temperature interval 640÷660 °C (first and second exothermic effects expressed on its DTA curve) within 24h has shown presence of new unknown crystalline phase in both samples. In our point of view it is new crystalline Ba₂Ti₂B₂O₉ compound, which formed as single phase at the same composition glass crystallization. The x-ray powder diffraction patterns of new crystalline Ba₂Ti₂B₂O₉ phase could be indexed on a orthorhombic crystal symmetry with lattice cell as follows : a=9.0404 Å, b=15.1929 Å, c=9.8145 Å; unit cell volume V=1348.02Å³, Z =6, calculated density (D calc.)= 3.99g/cm³; D exp.=3.25g/cm³; α;β;γ =90,00°(Table 2).

2θ	dexp.	I/Io	h k l	2θ	dexp.	I/Io	h k l
8.9821	9.83	9.08	0 0 1	41.1858	2.19	4.92	3 1 3
13.3220	6.65	6.00	1 0 1	41.5752	2.17	30.77	0 7 0
14.7387	6.01	6.46	0 2 1	43.2466	2.09	16.92	3 5 1
17.5044	5.06	6.77	0 3 0	43.4313	2.08	13.39	2 2 4
17.6637	5.02	17.38	1 2 1	43.9115	2.06	20.46	0 4 4
18.0535	4.91	16.77	0 0 2	44.1329	2.05	20.92	4 0 2
20.4821	4.33	5.69	2 1 0	44.8071	2.02	12.77	4 3 1
22.9091	3.88	7.69	2 2 0	45.5586	1.99	8.62	0 7 2
24.6422	3.61	38.46	2 2 1	46.0257	1.97	6.62	0 0 5
25.0566	3.55	41.84	0 4 1	46.2857	1.96	8.92	3 5 2
25.2844	3.52	62.92	0 3 2	46.7837	1.94	8.62	1 7 2
25.4128	3.50	44.77	1 4 0	47.3057	1.92	14.92	2 7 1
26.3303	3.38	17.69	2 3 0	48.6422	1.87	5.38	1 5 4
27.2477	3.27	53.69	0 0 3	48.9274	1.86	13.53	1 2 5
28.0342	3.18	100.00	2 3 1	49.2027	1.85	11.85	4 1 3
28.9573	3.08	38.61	1 0 3	49.4946	1.84	13.54	3 2 4
30.1623	2.96	11.23	3 1 0	49.7898	1.83	10.15	0 3 5
30.7928	2.90	6.52	0 5 1	50.6789	1.80	7.69	2 0 5
31.5856	2.83	9.69	3 1 1	50.9725	1.79	8.62	3 5 3
31.8159	2.81	8.87	3 2 0	51.2844	1.78	10.67	3 3 4
32.6545	2.74	9.85	0 3 3	51.5963	1.77	8.00	0 8 2
33.2727	2.69	10.31	3 2 1	51.9068	1.76	8.46	5 2 0
34.3245	2.61	42.76	2 1 3	52.2224	1.75	8.15	2 8 0
35.0265	2.56	20.31	3 0 2	52.5410	1.74	6.00	1 8 2
36.0357	2.49	5.23	1 5 2	52.8750	1.73	8.46	1 6 4
36.1786	2.48	4.92	0 4 3	53.2055	1.72	7.23	2 8 1
36.9643	2.43	17.23	3 2 2	54.9381	1.67	6.15	4 4 3
37.9464	2.37	12.92	1 0 4	56.7857	1.62	6.92	1 5 5
38.1034	2.36	16.77	3 4 0	57.9443	1.59	9.69	4 5 3
38.2586	2.35	12.15	2 3 3	58.3571	1.58	7.85	4 3 4
40.2124	2.24	21.28	2 5 2	59.1786	1.56	7.23	2 9 1
40.4148	2.23	25.08	0 5 3	59.5971	1.55	4.00	3 7 3
40.6018	2.22	23.38	3 0 3				

Table 2. X-ray characteristics of Ba₂Ti₂B₂O₉ crystalline compound obtained at 40.0BaO · 40.0TiO₂ · 20.0B₂O₃(mol%) glass composition crystallization at 640°C, 24 hours.

3.1.4.2 Phase diagram of the pseudo-binary BaB₂O₄-BaTiO₃ system

Study of pseudo-binary system BaB-BaT has revealed some interesting regularity. The liquidus curve constructed by us is the same as constructed by the Goto & Cross [Goto & Cross, 1969] (Fig.7). We have confirmed presence of pseudo-binary eutectic point with m.p.940°C containing 32 mol% BaTiO₃ (Fig.7). We have confirmed also information about existence of new crystalline Ba₂TiB₂O₇ (2BaBT) compound, which has been reported earlier at this system glasses crystallization [Hovhannisyan et al., 2008]. Strong exothermic effect at narrow temperature interval 560-590°C with maximum at 585°C is observe on DTA curve of 50.0BaO · 25.0TiO₂ · 25.0B₂O₃ (mol%) glass composition (Fig.3, curve 4). The 2BaBT composition has incongruent melting at 940°C and decomposes on BaT and melt. Its liquidus temperature obtained from DTA curve and is equal to 1150°C (Fig.3, curve 4). The 2BaBT compound is not stable and is observed in narrow temperature interval (570-650°C) (Fig.7. A).

Fig. 7. Phase diagram of the pseudo-binary BaB₂O₄- BaTiO₃ system (A) and position of Ba₂TiB₂O₇ compound on it (B).

The pure 2BaBT phase crystallizes from the same glass composition crystallization at 585°C, 24 hours. The X-ray characteristics of Ba₂TiB₂O₇ were determined and are given in Table 3. The X-ray powder diffraction patterns of 2BaBT could be indexed on a rhombic crystal symmetry with lattice cell as follows : a=10.068 Å, b=13.911 Å, c=15.441 Å; unit cell volume V=2629.17Å³, Z =12, calculated density (D calc.)= 4.23g/cm³; D exp.=4.02g/cm³; α;β;γ =90,00°.

3.1.4.3 Phase diagram of the BaO-TiO₂-B₂O₃ ternary system

First of all we have deleted eutectic point e₁, which has been for the first time wrongly put by Levin with co-workers on the binary BaO-B₂O₃ diagram [Levin & McMurdie, 1949; Levin & Ugrinic, 1953], and then is repeated in our recent publications [Hovhannisyan, R. et al, 2008, Hovhannisyan, M. et al, 2009]. Such imperfect data very often committed many authors first of all at binary borate system diagram constructions [ACerS & NIST, 2004]. Because, this point indicate only sharp increase of liquidus temperature which is connected with stable phase separation, typical for many binary borate systems (Fig.8).

2 θ	dexp.	I/Io	h k l	2 θ	dexp.	I/Io	h k l	2 θ	dexp.	I/Io	h k l
8.55	10.328	2.84	0 1 1	37.24	2.412	498	0 2 6	52.22	1.750	276	2 4 7
8.74	10.117	2.04	1 0 0	37.37	2.404	311	3 3 3	52.36	1.745	711	2 2 8
10.57	8.377	1.69	1 0 1	38.24	2.352	871	1 2 6	52.59	1.739	729	0 5 0
10.81	8.176	1.33	1 1 0	38.40	2.342	747	4 2 1	52.74	1.734	507	5 4 1
11.53	7.666	3.20	0 0 2	38.67	2.326	231	2 5 2	53.21	1.720	293	0 6 6
12.27	7.243	1.69	1 1 1	38.96	2.310	231	0 4 5	53.31	1.717	331	0 0 9
12.60	7.028	4.98	0 2 0	39.16	2.296	133	2 4 4	53.42	1.714	409	1 5 0
13.29	6.657	4.00	0 1 2	39.35	2.288	196	2 3 5	53.52	1.711	311	3 6 4
13.63	6.353	4.89	0 2 1	39.50	2.270	178	3 0 5	53.82	1.703	622	0 1 9
14.33	6.100	3.56	1 0 2	39.91	2.236	551	0 5 4	53.98	1.697	898	1 6 6
15.46	5.731	3.02	1 2 0	40.26	2.237	551	1 6 1	54.07	1.695	764	4 6 1
15.90	5.574	1.60	1 1 2	40.45	2.229	1031	4 1 3	54.14	1.693	640	1 0 9
16.49	5.374	3.47	1 2 1	40.57	2.222	960	3 3 4	54.74	1.675	320	5 1 5
16.92	5.236	1.78	0 2 2	40.66	2.207	293	0 0 7	54.91	1.671	276	0 7 5
17.19	5.151	1.87	0 0 3	41.00	2.199	335	2 5 3	55.56	1.635	311	5 4 3
17.31	5.056	1.96	2 0 0	41.16	2.191	249	4 3 1	55.65	1.646	391	1 7 5
18.36	4.828	2222	0 1 3	41.35	2.182	284	0 1 7	55.74	1.648	471	0 8 3
18.69	4.741	924	2 1 0	41.64	2.167	204	1 6 2	55.93	1.642	378	1 2 9
19.12	4.636	2.67	0 3 0	41.85	2.157	924	1 0 7	56.54	1.626	356	3 2 6
19.72	4.498	3.56	2 1 1	41.98	2.152	569	4 2 3	56.66	1.623	284	3 6 5
19.95	4.445	5.51	0 3 1	42.12	2.144	293	3 5 0	56.97	1.615	373	4 2 7
20.34	4.363	3.64	1 1 3	42.40	2.130	187	1 1 7	57.15	1.610	729	0 3 9
20.97	4.281	2.13	2 0 2	42.65	2.107	418	4 0 4	57.37	1.605	631	2 8 2
21.11	4.207	4.00	1 3 0	43.11	2.097	613	2 4 5	57.66	1.597	320	4 5 5
21.56	4.118	2.13	0 2 3	43.24	2.091	738	2 6 1	57.93	1.590	213	1 3 9
21.70	4.092	2.04	2 2 0	43.49	2.080	2376	4 1 4	58.14	1.585	320	5 3 5
22.05	4.026	3.91	2 1 2	43.59	2.075	1799	1 6 3	58.30	1.581	320	2 2 9
22.56	3.936	2.49	2 2 1	43.72	2.069	2347	0 4 6	58.47	1.577	267	6 3 0
22.97	3.870	4.18	0 0 4	43.97	2.058	1475	1 2 7	58.67	1.573	320	0 7 6
23.20	3.831	2.31	1 2 3	44.31	2.043	2556	3 0 6	58.84	1.568	550	1 5 8
23.78	3.739	3.82	0 1 4	44.41	2.038	2231	4 4 0	58.98	1.565	764	2 8 3
24.14	3.694	2.49	1 3 2	45.01	2.013	1511	5 0 0	59.28	1.559	427	4 7 0
24.46	3.636	2.31	2 2 2	45.35	1.998	187	5 0 1	59.51	1.552	773	4 7 1
24.75	3.596	4.00	2 0 3	45.75	1.980	187	3 5 3	59.79	1.546	684	0 9 0
25.19	3.490	10000	1 1 4	45.97	1.973	284	4 4 2	60.09	1.539	284	0 4 9
26.08	3.414	1.96	2 3 0	46.19	1.964	347	3 2 6	60.28	1.534	267	0 1 10
26.24	3.393	1.42	0 4 1	46.64	1.948	1902	5 0 2	60.50	1.529	249	4 7 2
26.36	3.378	1.78	0 2 4	47.12	1.927	222	0 7 2	60.76	1.523	178	2 6 7
26.67	3.341	1.60	2 3 1	47.44	1.915	1627	2 4 6	60.93	1.519	222	3 1 9
27.15	3.280	2.49	3 0 1	47.56	1.910	1653	0 1 8	61.41	1.508	187	6 3 3
27.71	3.215	3615	1 4 1	47.70	1.905	1529	3 6 0	61.79	1.500	373	5 3 6
28.57	3.089	9860	0 0 5	47.85	1.900	1120	3 4 5	61.98	1.496	373	3 7 5
29.50	3.025	2.49	1 4 2	48.12	1.890	204	0 5 6	62.14	1.493	142	4 7 3
29.69	3.008	1.24	3 1 2	48.35	1.881	124	4 2 5	62.36	1.488	311	5 0 7
29.95	2.982	4.35	2 1 4	48.54	1.874	142	3 5 1	62.72	1.480	124	0 9 3
30.56	2.923	2.31	1 0 5	48.89	1.861	222	0 2 6	62.95	1.475	133	6 0 5
30.80	2.910	1.42	1 1 5	49.08	1.855	160	0 6 5	63.24	1.471	160	2 4 9
31.06	2.875	6.04	0 4 3	49.19	1.851	284	2 6 4	63.24	1.469	187	2 1 10
31.64	2.825	2.76	0 2 5	49.35	1.844	640	3 0 7	63.43	1.465	178	0 3 10
31.95	2.800	3.91	2 2 4	49.63	1.835	1191	2 7 1	63.66	1.461	133	6 3 4
32.71	2.736	8.33	0 5 1	49.70	1.833	1324	5 3 1	63.74	1.459	169	5 6 3
32.88	2.722	2.67	3 3 0	49.85	1.828	1511	3 1 7	63.93	1.455	267	4 3 8
33.45	2.677	3615	3 3 1	49.97	1.824	1120	1 6 3	64.14	1.451	320	2 8 5
33.95	2.639	3615	1 5 1	50.08	1.820	631	1 7 3	64.26	1.448	293	1 3 10
34.36	2.605	21.06	3 2 3	50.19	1.817	613	4 5 2	64.51	1.444	213	5 4 6
34.98	2.563	2.13	3 3 2	50.62	1.802	231	2 0 8	64.72	1.439	276	7 0 0
35.62	2.515	4.50	4 0 0	51.51	1.772	160	5 1 4	64.96	1.436	578	6 5 0
35.85	2.503	5.16	1 4 4	51.65	1.769	189	2 5 6	64.97	1.434	669	3 5 8
36.21	2.479	1.78	4 1 0	51.85	1.762	604	3 4 6	65.77	1.418	391	4 0 9
36.47	2.462	1.78	2 2 5	51.96	1.758	515	3 5 3				
36.84	2.436	2.40	2 5 0	52.12	1.753	222	1 3 6				

Table 3. X-ray characteristics of Ba₂TiB₂O₇ crystalline compound obtained at 50.0BaO · 25.0TiO₂ · 25.0B₂O₃(mol%) glass composition crystallization at 585°C, 24 hours

Fig. 8. Phase diagram of the BaO-TiO₂-B₂O₃ system

Seven ternary eutectic points E₁-E₇ have been revealed as result of phase diagram construction (Fig.8, 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. 850°C has been determined among Ba₄B and BaTB compounds and TiO₂; ternary eutectic E₂ with m.p. 835°C has been formed among Ba₄B, 2Ba₅B and BaTB compounds; ternary eutectic E₃ with m.p. 850°C has been formed among 2Ba₅B , Ba₂B and BaTB compounds; ternary eutectic E₄ with m.p. 860°C has been formed among Ba₂B, BaB and BaTB compounds; ternary eutectic E₅ with m.p. 865°C has been formed among BaT, 2BaB and BaB compounds; ternary eutectic E₆ with m.p. 930°C has been formed among BaT, BaB and BaTB compounds; ternary eutectic E₇ with m.p. 1000°C has been formed among BaT, BaTB compounds and TiO₂ (Fig8, Table 4). Clear correlation between glass forming ability and both binary and ternary eutectic areas has been observed in the investigated ternary system (Fig.2).

3.2 Crystallization behavior of the stoichiometric glass compositions in the BaO-TiO₂-B₂O₃ system

3.2.1 Crystallization behavior of the stoichiometric glass BaTi(BO₃)₂ composition

The BaTi(BO₃)₂ ternary compound (BaTB) is related to “Nordenskiöldine” group borates with common formula Me²⁺Me⁴⁺B₂O₆ with well known dolomite-type structure [Vicat & Aleonard, 1968; Bayer, 1971]. The “layer-type” structure of calcite and dolomite is

Point	T _m , (°C)	Composition, mol% B ₂ O ₃ :BaO:TiO ₂
E ₁	850	76.0:20.0:4.0
E ₂	835	75.0:21.0:4.0
E ₃	850	63.5:32.0:4.5
E ₄	860	58.0:38.0:4.0
E ₅	865	35.0:62.0:3.0
E ₆	930	31.5:45.0:23.5
E ₇	1000	22.6:32.1:45.3

Table 4. The melting temperature (T_m) and compositions for ternary eutectic points in the BaO-B₂O₃-TiO₂ system

responsible for the strong anisotropy of the “Nordenskiöldine” group borates [Bayer, 1971]. It is very stable compound occupied dominating position in BaO-TiO₂ -B₂O₃ system phase diagram (Fig.8). It has congruent character of melting at 1080°C (Fig.3, curve1). We have given a preference to study the process of directed crystallization of BaTiB composition based on above stated.

Thermal treatment at 670-690°C, 1 h is enough for full crystallization of the pressed powder glass samples. X-ray diffraction patterns of crystallization products (Fig.9, curve1) are identical to the references data [Vicat & Aleonard, 1968; ICDD, 2008, File # 35-0825].

The other pictures were observed for monolithic samples (Fig.9, curve 2). X-ray diffraction patterns determined from crystallized (630°C 4h+ 690°C 24h) tape samples surface indicated reorientation of crystalline structure, leading to increase of intensity of following reflexes : 5.47 Å (003) from 7% up to 70% (10 time), 2.51 Å (110) from 35 to 100%(3 time), 3.85 Å (102) from 75 to 100%.

At monolith glass sample crystallization at 630°C 4h+ 690°C 12h under direct current (DC) voltage 3.0 kV/cm X-ray diffraction patterns of samples surface again indicate reorientation of crystalline structure: reflexes 5.47 Å (003) decrease from 70% to 46%, 3.85 Å (102) decrease from 100 to 60%, 2.51 Å (110) from 100 to 42%, and reflex 2.97 Å (003) again began 100% (Fig.9, curve3).

X-ray diffraction patterns of BaTB glass tape sample surface crystallized at 630°C 12h+ 690°C 12h (Fig.8, curve4) indicate very strongly change of crystalline structure in relation to a sample received by a traditional powder method: reflex 5.47 Å (003) increase from 7% to 100 %, 3.85 Å (102) decrease from 100 to 10%, 2.51 Å (110) decrease from 100 to 42%, 2.97 Å (003) decrease from 100 to 35%, 2.73 Å increase from 3 to 51% , 1.82 Å increase from 3 to 43% again began 100% (Fig.9, curve4). Part of reflexes practically disappeared (are not visible) at the given regime of X-ray record: 2.73, 2.28, 2.15, 2.10, 2.06, 1.92, 1.61, 1.52 Å.

X-ray diffraction patterns of BaBT glass tape sample surface crystallized under DC 3kV/cm at 630°C 1h+ 690°C 4h again indicate reorientation of crystalline structure (Fig.9, curve5).

Processes of reorientation of the crystal structure, similar occurring with a monolithic sample are observed: reflexes 5.47 Å (003) sharply decrease from 100% to 38%, reflex 2.97 Å (003) again began 100%, 3.85 Å (102) increase from 10 to 58%, 2.51 Å (110) increase from 42 to 78% (Fig.9, curve5). Well observable reflexes 2.72, 2.62, 2.15, 2.10, 1.92, 1.61, 1.60, 1,52 Å have again appeared. Such impression is created, that under DC action the re-oriented structure tends to return to structure inherent in the initial sample received on powder technology.

Fig. 9. XRD-patterns of the BaTB samples and $[hkl]$ -indices attributed to the peaks of the BaTiB₂O₆ crystallized glasses:

curve 1- pressed powder sample crystallized at 690°C 1h.

curve 2- monolithic glass sample crystallized at 630°C 4h+ 690°C 12h;

curve 3- monolithic glass sample crystallized at 630°C 4h+ 690°C 12h under DC 3kV/cm

curve 4- tape glass sample crystallized at 630°C 12h+ 690°C 12h

curve 5- tape glass sample crystallized at 630°C 1h+ 690°C 4h under DC 3kV/cm

3.2.2 Crystallization behavior of the stoichiometric glass Ba₃Ti₃O₆(BO₃)₂ composition

Having confirmed existence of 3Ba₃TiB there was a necessity to study temperature intervals of its stability. We'll try to do it through glass powder samples crystallization using its DTA data (Fig.3, curve 3). Formation of pure 3Ba₃TiB compound clear observed on X-ray diffraction patterns of the same composition glass powder samples crystallization at 600°C 60h - temperature of the crystallization beginning on the DTA curve (Fig.6, curve 1). The further increasing of thermal treatment temperatures (660, 700, 800 and 900°C) lead to indication only pure 3Ba₃TiB crystalline compound in products of glass crystallization (Fig.6, curves 2-4). X-ray diffraction patterns of crystallization products (Fig.6, curves 1-4) are identical to the references data [Park et al., 2004; ICDD, 2008, File # 074-4273]. We have revealed that the 3Ba₃TiB compound in an interval 950-1020°C decomposes with BaTiO₃ and BaTB formation (Fig.6, curve5). The 3Ba₃TiB compound is melted incongruently at 975°C (Fig.3, curve 3), with formation of melt and BaTiO₃ at temperatures higher 1020 °C (Fig.6, curve 6).

3.2.3 Crystallization behavior of the stoichiometric glass $\text{Ba}_2\text{Ti}_2\text{B}_2\text{O}_9$ composition

Denying of existence of $(2\text{Ba}_2\text{TiB})$ stoichiometric compounds from Barbier group [Park et al., 2004] after $\text{Ba}_3\text{Ti}_3\text{B}_2\text{O}_{12}$ ($3\text{Ba}_3\text{TiB}$) synthesis and characterization have increased an intrigue around $2\text{Ba}_2\text{TiB}$ compound. According to references data both compounds had Hexagonal cell and very closed cell parameters: $a = 8.7110 \text{ \AA}$, $c = 3.9298 \text{ \AA}$ for $3\text{Ba}_3\text{TiB}$ [ICDD, 2008, File#074-4273] and $a = 8.7210 \text{ \AA}$, $c = 3.933 \text{ \AA}$ for $2\text{Ba}_2\text{TiB}$ [Millet et al., 1986]. It was impossible to pure synthesis of both compounds through solid phase reaction. We'll try to do it through glass tapes crystallization.

It was big surprising for us, when on the DTA curve of the $40\text{BaO} \cdot 40\text{TiO}_2 \cdot 20\text{B}_2\text{O}_3$ (mol%) glass composition three exothermic effects have been observed: two effects at 640°C (small) and at 660°C (high) are combined and third is weakly expressed at 690°C (Fig.3, curve 2). X-ray identification of products of $40\text{BaO} \cdot 40\text{TiO}_2 \cdot 20\text{B}_2\text{O}_3$ (mol%) glass composition crystallization at temperatures 640 and 660°C within 24h has shown presence of new unknown $\text{Ba}_2\text{Ti}_2\text{B}_2\text{O}_9$ crystalline phase in both samples (Fig.10, curves 2, 3). Its X-ray characteristics have been determined and are given in Table 2. X-ray identification of crystallization products have shown of $2\text{Ba}_2\text{TB}$ phase formation starting from 600°C (Fig.10, curve1).

The third exothermic effect on $2\text{Ba}_2\text{TiB}$ glass DTA curve (Fig.3, curve 2) at 690°C is connected with its decomposition and $3\text{Ba}_3\text{TiB}$, BaTiB compounds formation (Fig.10, curves 4, 5). Process of $2\text{Ba}_2\text{TB}$ sample decomposition is continues up to 950°C 24h. At this temperature the $3\text{Ba}_3\text{TiB}$ phase is disappear and the BaTiO_3 phase starts to appear together with BaTiB phase (Fig.10, curve 6). And finally we observed disappearance of both $3\text{Ba}_3\text{TB}$ and BaTB phases at temperatures higher 1020°C (Fig.10, curve7).

The strong endothermic effect of melting with minimum at 975 is observed on DTA curve (Fig.3, curve 2). According to references data [Millet et al., 1986] the $2\text{Ba}_2\text{TiB}$ composition between $950\text{-}960^\circ\text{C}$ decomposes with BaTiO_3 and liquid formation. In our cases together with BaTiO_3 we have identified the BaTB in temperature interval $950\text{-}1020^\circ\text{C}$ (Fig.10, curve 6) , and BaTiO_3 + melt us results of incongruent melting at temperatures higher 1020°C (Fig.10, curves 7).

The same picture as for powder samples is observed for crystallized glass tapes of $2\text{Ba}_2\text{TB}$ composition. We have X-ray amorphous transparent tape glass sample after thermal treatment at 600°C 6h (Fig.11, curve1). Only new, pure $2\text{Ba}_2\text{TB}$ phase is formed at next steps of thermal treatment: 640°C 24h, and 660°C 24h (Fig.11, curves 2,3). The $2\text{Ba}_2\text{TB}$ compound decomposes with $3\text{Ba}_3\text{TB}$ and BaTB phases formation at thermal treatment at 700°C 24h (Fig.11, curve 4).

3.2.4 Crystallization behavior of the stoichiometric glass $\text{Ba}_2\text{TiB}_2\text{O}_7$ composition

X-ray identification of glass powder samples of $50\text{BaO} \cdot 25\text{TiO}_2 \cdot 25\text{B}_2\text{O}_3$ (mol%) compositions thermal treated in an interval $570\text{-}650^\circ\text{C}$ 24 h have shown pure 2BaTB compound formation (Fig.12, curve1). The 2BaTB compound decomposes on two phases: BaTiO_3 and BaB_2O_4 at temperature interval $650\text{-}940^\circ\text{C}$ (Fig.12, curves 2, 3).

3.2.5 Crystallization behavior of the stoichiometric glass BaTi_2O_5 composition

Using our super cooling technique and special two step melting technology we have obtained BaTi_2O_5 (B_2T) compound in glass state (glass tapes with thickness $0.03 - 0.4\text{mm}$) and have studied processes of it crystallization. The initial glass tape sample thermal treated

Fig. 10. XRD-patterns of the crystallized powder glass samples corresponding to Ba₂Ti₂B₂O₉ composition:
 curve 1- 600°C 60h;
 curve 2- 640°C 24h;
 curve 3- 660°C 24h;
 curve 4- 700°C 24h;
 curve 5- 740°C 24h;
 curve 6- 950°C 24h;
 curve 7- 1020°C 24h (samples 2-7 have been water quenched from heat treatment temperature).

Fig. 11. XRD-patterns of the crystallized tape glass samples corresponding to $\text{Ba}_2\text{Ti}_2\text{B}_2\text{O}_9$ ($2\text{Ba}_2\text{TiB}$) composition:

curve 1- 600°C 6h;

curve 2- 640°C 24h;

curve 3- 660°C 24h;

curve 4- 700°C 24h

Fig. 12. XRD-patterns of the crystallized powder glass samples corresponding to Ba₂TiB₂O₇ composition:

curve 1- 585°C 24h;

curve 2- 730°C 24h;

curve 3- 800°C 24h;

at 680°C 12h is X-ray amorphous (Fig.13, curve1). The further increase of crystallization temperature (680°C 12h +740°C 12h) results in occurrence of BaTi₂O₅ peaks [ICDD, 2008, File # 34-0133] with preservation of a transparency of a tape sample (Fig.13, curves 2,3). The BaTi₂O₅ is dominating crystalline phase at studied crystallization regimes (Fig.13, curves 3-

4). However, we do not exclude presence of barium polytitanates in glass crystallization products in quantities not influencing on the end-product properties. We have observe on X-ray patterns strongly reorientation of formed barium di-titanate crystalline phase: reflex 8.247 Å (hkl 002) increase from 9% and become 100% and 3.47 Å (hkl 401) decrease from 100% to 0 (Fig.13, curves 2,3).

Fig. 13. XRD-patterns of the crystallized BaTi_2O_5 glass tape samples obtained by super cooling technique:

curve 1- initial tape sample thermal treated at 680°C 12h -transparent;

curve 2- tape sample (680°C 12h + 740 °C 12h)-transparent;

curve 3- tape sample 740 °C 12h- transparent;

curve 4- tape sample 900-1000 °C 12h, casting in water

4. Ferroelectric properties of stoichiometric glasses in $\text{BaO-TiO}_2\text{-B}_2\text{O}_3$ system

The ferroelectric (polarization - electric field) hysteresis, is a defining property of ferroelectric materials. In the last twenty years it has become a subject of intensive studies due to potential applications of ferroelectric thin films in nonvolatile memories. In ferroelectric memories the information is stored as positive or negative remanent polarization state. 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 remanent polarization, $P_R - (-P_R)$), dependence of the coercive field E_c on sample thickness, decrease of remanent or switchable polarization with number of switching cycles, polarization imprint, endurance, retention [Damyanovich, 2005]. Electric field induced polarization measurement was used for ferroelectric characterization of known and revealed first time new ternary $\text{BaTi}(\text{BO}_3)_2$, $\text{Ba}_2\text{Ti}_2\text{B}_2\text{O}_9$, $\text{Ba}_3\text{Ti}_3\text{B}_2\text{O}_{12}$, $\text{Ba}_2\text{TiB}_2\text{O}_7$ and binary BaTi_2O_5 stoichiometric compositions glass ceramics.

4.1 Polarization behavior of BaTi(BO₃)₂, Ba₃Ti₃B₂O₁₂, Ba₂Ti₂B₂O₉, Ba₂TiB₂O₇ glass ceramics

Electric field induced polarization (P) and remanent polarization (P_r) were measured at room temperature for BaBT, 3Ba3TiB, 2Ba2TiB, 2BaTiB glass tape samples crystallized using various regimes (Fig.14).

Linear P-E curves are observed up to fields of 40-120 kV/cm for all measured samples with thickness 0.04-0.08mm. The polarization becomes nonlinear with increasing of applied electric field, and at 140-400 kV/cm the remanent polarization 2P_r values were found 0.35, 3.89, 0.6 and 0.12 μC/cm² for the BaBT (Fig.14, A), 3Ba3TiB (Fig.14, B), 2Ba2TiB (Fig.14, C) and 2BaTiB (Fig.14, D) crystallized glass tape samples respectively. According to obtained results it is possible to conclude that samples are ferroelectrics. The highest remanent polarization value (2P_r=3.89 μC/cm²) has 3Ba3TiB crystallized glass tape sample (Fig.14, B).

Fig. 14. Dependence of polarization (P) on electric field (E) for crystallized stoichiometric glass compositions:

BaTiB₂O₆ glass tape sample of 0.08 mm in thickness crystallized at 700°C 24h

Ba₃Ti₃B₂O₁₂ glass tape sample of 0.07 mm in thickness crystallized at 900°C 12h

Ba₂Ti₂B₂O₉ glass tape sample of 0.08 mm in thickness crystallized at 640°C 24h

Ba₂TiB₂O₇ glass tape sample of 0.04 mm in thickness crystallized at 580°C 12h

4.2 Polarization behavior of BaTi₂O₅ glass ceramic

Electric field induced polarizations were measured at room temperature for BaTi₂O₅ glass tape samples crystallized at various regimes. The high value of polarization (P~10μCu/cm²)

and remanent polarization ($2P_r = 6,2 \mu\text{Cu}/\text{cm}^2$) we observe for strongly oriented transparent glass ceramic at applied field $220 \text{ kV}/\text{cm}$ (Fig.15).

Fig. 15. Dependence of polarization (P) on electric field (E) for BaTi_2O_5 crystallized glass tape (740°C 12h) of 0.08 mm in thickness

5. Discussion

Revision of phase diagrams of very complex ternary $\text{BaO-TiO}_2\text{-B}_2\text{O}_3$ system has allowed us to study it more precisely. For this purpose glass samples have been used as initial testing substance for phase diagram construction. It is a very effective method, because it is possible 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.

On the other hand super cooling technique created by our group allowed us to expand borders of glass formation from stable glass forming barium tetra borate up to binary di-barium borate and up to barium di-titanates which, together with compositions corresponding to ternary BaTB , 2BaTB , $2\text{Ba}_2\text{TB}$, $3\text{Ba}_3\text{TB}$ compounds, have been obtained as glass tape with thickness of 30-400 microns (Fig.2). Large area of glass formation has allowed to have enough quantity of samples for DTA and X-ray investigations and $\text{BaO-TiO}_2\text{-B}_2\text{O}_3$ system phase diagram construction.

There are very stable congruent melted binary barium titanate and barium borate and ternary barium boron titanate (BaTB) compounds in the ternary system. They have dominating positions in ternary diagram and occupied the biggest part of it (Fig.8). However, mutual influence of these stable compounds and not-stable binary (Ba_2T) and ternary compounds ($2\text{Ba}_2\text{TB}$, $3\text{Ba}_3\text{TB}$ and 2BaTB) lead to formation of seven ternary eutectic points (Table2), which have essential influence on liquidus temperature decrease and glass formation. Ternary eutectics E_5 , E_6 and E_7 together with binary eutectics e_7 and e_6 have allowed to outline the field of barium titanate crystallization on the $\text{BaO-TiO}_2\text{-B}_2\text{O}_3$ system phase diagram. The BaTiO_3 is very stable compound and occupies dominating position on the phase diagram (Fig.8). Ternary eutectics E_5 , E_6 and E_4 together with binary eutectics e_4

and e_5 have allowed to outline the field of barium borate crystallization. The BaB₂O₄ is very stable compound also and occupied enough position on the studied ternary phase diagram (Fig.8). Ternary eutectics E_1 , E_2 , E_3 , E_4 , E_6 and E_7 have allowed to determine the field of crystallization of BaTB ternary compound. The BaTB is very stable compound also and occupies dominating position in the central part of the studied ternary BaO-TiO₂-B₂O₃ system phase diagram (Fig.8).

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 and 8). It is possible to ascertain confidently, that glass formation can serve as the rapid test method for phase diagram construction.

Common regularities of bulk glass samples TEC changes in studied BaO-TiO₂-B₂O₃ system have been determined: increase of BaO amounts leads to increase glasses TEC values from 60 to 120 · 10⁻⁷K⁻¹. The substitution of B₂O₃ for TiO₂ practically doesn't influence glasses TEC value (Fig.4).

We have tried also to answer in discussion among various scientific groups about the existence of 2Ba2TB and 3Ba3TB compounds [Millet et al., 1986; Zhang et al., 2003; Park et al., 2004; Kosaka et al., 2005]. We have revealed for the first time through glass samples of stoichiometric 3Ba3TB composition examination, that 3Ba3TB compound is very stable in an interval of 600-950°C. It decomposes in temperature interval 950-1020°C with BaTiO₃ and BaTB phase formation. Then, at temperature higher than 1020°C, it has incongruent melting with melt and BaTiO₃ formation (Fig.5A).

The next unexpected result was obtained at glass samples corresponding to 2Ba2TB composition crystallization. First of all we have revealed on its DTA curve the presence of three exothermic effects with maximums at 640, 660 and 690°C. We have confirmed the existents of 2Ba2TB compound in temperature interval 600-670°C. Its new X-ray powder diffraction patterns could be indexed on a orthorhombic crystal symmetry with lattice cell as follows : $a=9.0404$ Å, $b=15.1929$ Å, $c=9.8145$ Å; unit cell volume $V=1348.02$ Å³, $Z=6$, calculated density ($D_{calc.}$)= 3.99g/cm³; $D_{exp.}$ = 3.25 g/cm³; $\alpha;\beta;\gamma=90,00^\circ$ (Table 2). However, its X-ray characteristics don't coincide with earlier reported data [Millet et al., 1986].

As a result of the pseudo-binary BaB₂O₄-BaTiO₃ system reinvestigation, a new ternary Ba₂TiB₂O₇ compound has been revealed and characterized at the same composition glass crystallization in the temperature interval of 570-650°C. The X-ray powder diffraction patterns of 2BaBT could be indexed on a rhombic crystal symmetry with lattice cell as follows : $a=10.068$ Å, $b=13.911$ Å, $c=15.441$ Å; unit cell volume $V=2629.17$ Å³, $Z=12$, calculated density ($D_{calc.}$)= 4.23g/cm³; $D_{exp.}$ =4.02 g/cm³ ; $\alpha;\beta;\gamma=90,00^\circ$. X-ray characteristics of both 2Ba2TB and 2BaTB compounds were determined and are given in Tables 2 and 3.

Study of the directed crystallization processes have allowed to reveal, that at the given way of casting the oriented germs are induced in the glass tape, which at the further heat treatment results in oriented transparent and opaque GC formation (Fig.9). The impact of external electric field changes the direction of crystalline BaTiB₂O₆ phase growth, i.e. reorients them (Fig.9).

Electric field induced polarization (P) and remanent polarization(P_r) were measured at room temperature for BaBT, 3Ba3TiB, 2Ba2TiB, 2BaTiB glass tape samples crystallized at various regimes. All tested samples are ferroelectrics and shown loop of hysteresis.

Linear P - E curves are observed up to fields of 40-120 kV/cm for all measured samples with thickness 0.04-0.08mm. 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 0.35, 3.89, 0.08 and 0.12 $\mu\text{C}/\text{cm}^2$ for the BaBT (Fig.14, A), 3Ba3TiB (Fig.14, B), 2Ba2TiB (Fig.14, C) and 2BaTiB (Fig.14, D) crystallized glass tape samples respectively. According to obtained results it is possible to conclude that samples are ferroelectrics. The 3Ba3TiB crystallized glass tape sample (Fig.14, B) has the highest remanent polarization value ($2P_r=3.89 \mu\text{C}/\text{cm}^2$).

Studies of crystallization processes of barium di-titanate compositions glass tapes also have led to unexpected results. As far as it is difficult to receive this composition in glassy state as appeared so difficultly to crystallized it. All time we obtained transparent glass ceramics, which has residual polarization equal to 6,2 $\mu\text{C}/\text{cm}^2$ comes nearer to barium di-titanate single crystal (6,8 $\mu\text{C}/\text{cm}^2$ [Akishige et al., 2006]). For comparison the value of residual polarization of known barium titanate is equal to 25 $\mu\text{C}/\text{cm}^2$. However, the barium di-titanate has $T_c=470^\circ\text{C}$ [Akishige et al., 2006] as for BaT its value equal to 124°C .

6. Conclusion

The earlier published phase and glass forming diagrams of the ternary BaO-TiO₂-B₂O₃ system have been revised and reconstructed. Seven ternary eutectics have been determined in it. Existence of three ternary Ba₂TiB₂O₇, Ba₂Ti₂B₂O₉ and Ba₃Ti₃B₂O₁₂ incongruently melted compounds have been confirmed at the same glass compositions crystallization, temperatures borders of their existence and their X-ray characteristics have been determined.

The new Ba₂TiB₂O₇ and Ba₂Ti₂B₂O₉ compounds have been characterized. The X-ray powder diffraction patterns of Ba₂TiB₂O₇ could be indexed on a rhombic crystal symmetry with lattice cell as follows: $a=10.068 \text{ \AA}$, $b=13.911 \text{ \AA}$, $c=15.441 \text{ \AA}$; unit cell volume $V=2629.17 \text{ \AA}^3$, $Z=12$, calculated density ($D_{\text{calc.}}$)= 4.23g/cm³; $D_{\text{exp.}}=4.02\text{g}/\text{cm}^3$; $\alpha;\beta;\gamma=90,00^\circ$. It is stable in temperature interval 570-650 °C. The Ba₂Ti₂B₂O₉ X-ray powder diffraction patterns could be indexed on a orthorhombic crystal symmetry with lattice cell as follows $a=9.0404 \text{ \AA}$, $b=15.1929 \text{ \AA}$, $c=9.81455 \text{ \AA}$; unit cell volume $V=1348.02 \text{ \AA}^3$, $Z=6$, calculated density ($D_{\text{calc.}}$)= 3.99g/cm³; $D_{\text{exp.}}=3.25\text{g}/\text{cm}^3$; $\alpha;\beta;\gamma=90,00^\circ$. It is stable in temperature interval 600-670 °C. The Ba₃Ti₃B₂O₁₂ is very stable compound in temperature interval 600-900°C.

The influence of various methods of melts casting on glass forming ability in the ternary BaO-TiO₂-B₂O₃ system is investigated. The expanded glass formation area changes from stable glass forming barium tetra borate up to binary di-barium borate and up to barium di-titanate. Clear correlation between glass forming ability and eutectic areas have been revealed in investigated system.

Common regularities of bulk glass samples TEC changes in studied BaO-TiO₂-B₂O₃ system have been determined: increasing of BaO amounts leads to increase glasses TEC values from 60 to 120 · 10⁻⁷K⁻¹. The substitution of B₂O₃ for TiO₂ practically don't influence on glasses TEC value.

All synthesized tapes glass ceramics are ferroelectrics. The transparent barium di-titanate glass ceramics has high residual polarization value equal to 6,2 $\mu\text{C}/\text{cm}^2$.

7. Acknowledgement

This work was supported by the International Science and Technology Center (Projects # A-952 & A-1486).

8. References

- Akishige, Y., Shigematsu, H., Tojo, T., Kawaji, H & Atake, T. (2006). Thermal properties on single crystals of ferroelectric barium dititanate. *Ferroelectrics*, Vol.336, pp. (47-56).
- The American Ceramic Society & National Institute of Standards and Technology [ACerS & NIST]. (2004). Phase Equilibria Diagrams. CD-ROM Database, Version 3.0, ISBN: 1-57498-215-X.
- Bayer, G. (1971). Thermal Expansion Anisotropy of Dolomite-type Borates $Me^{2+}Me^{4+}B_2O_6$. *Zeitschrift Fur Kristallographie*. Vol.133, pp. (85-90).
- Bhargava A., Snyder R.L., Condrate R.A. (1987). The Raman and infrared spectra of the glasses in the system BaO-TiO₂-B₂O₃. *Mater.Res.Bull.*, vol. 22, No. 12, pp. (1603-1611).
- Bhargava, A., Snyder, R.L. & Condrate, R.A. (1988). Preparation of BaTiO₃ glass-ceramics in the system Ba-Ti-B-O. I. *Materials Letter*, Vol.7. No. 5-6, pp. (185-189).
- Bhargava A., Snyder, R.L. & Condrate, R.A. (1988). Preparation of BaTiO₃ glass-ceramics in the system Ba-Ti-B-O. II. *Materials Letter*, Vol.7. No. 5-6, pp. (190-196).
- Bhargava, A., Shelby, J.E. & Snyder, R.L. (1988). Crystallization of glasses in the system BaO-TiO₂-B₂O₃. *J. Non-Cryst. Solids*, Vol.102, pp. (136-142).
- Boroica, L. et al. (2004). Study of titanates formed by crystallization in BaO-TiO₂-B₂O₃ system. Proceedings of the XX ICG in Kyoto, Sep. 27th-Oct 1st, 2004, PDF file No O-08-014, ISBN: 4-931298-43-5 C3858.
- Brow, R.K. & Watkins, R.D. (1987). In: *Technology of Glass, Ceramics or Glass Ceramics to Metal Sealing*, edited by Moddeman W.E. et al., Proceedings of the Winter Annual Meeting of Amer. Soc. Mech. Eng., Boston, MA, 1987, pp. (25-30).
- Cerchez, M., Boroica, L. & Huelsenberg, D. (2000). Glasses and crystallised glasses in the BaO-TiO₂-B₂O₃ system. *Phys. Chem. Glasses*, Vol.41, No. 5, pp. (233-235).
- Chen, C. & Liu, G. (1986). Recent Advances in Nonlinear Optical and Electro-Optical Materials. *Annual Review of Materials Science*, Vol.16, pp. (203-243).
- Damjanovic, D. (2005). Hysteresis in Piezoelectric and Ferroelectric Materials, In: *The Science of Hysteresis*, Mayergoyz, I & Bertotti, G., Vol. 3, pp.(337-465), Elsevier, ISBN: 0-1248-0874-3.
- De Pablos A. & Duran A. (1993). Glass forming and properties in the system B₂O₃-TiO₂-MnOm (M= Li, Ba, Pb). Proceedings of the 2nd Intern. Conf. Fundamentals of Glass Science and Technology, Venice, 1993, pp. (363-368).
- Feitosa, C.A.C., Mastelaro, V.R., Zanatta, A.R., Hernandez A.C. & Zanotto, E.D. (2006). Crystallization, texture and second harmonic generation in TiO₂-BaO-B₂O₃ glasses. *Optical Mater.*, Vol.28, No. 8-9, pp.935-943.
- Goto, Y. & Cross, L.E. (1969). Phase Diagram of the BaTiO₃-BaB₂O₄ system and growth of BaTiO₃ crystals in the Melt. *Yogyo-Kyokai-shi*, Vol. 77, pp. (355-356).
- Hovhannisyan, R.M. (2004). BaB₂O₄, BaAl₂B₂O₇, BaTi(BO₃)₂: glasses and glass ceramics on their basis. Proceedings of the XX ICG in Kyoto, Sep. 27th-Oct 1st, 2004, PDF file No O-07-056, ISBN: 4-931298-43-5 C3858.
- Hovhannisyan, R.M. (2006). Binary alkaline-earth borates: phase diagrams correction and low thermal expansion of crystallized stoichiometric glass compositions. *Phys.Chem.Glasses: Eur. J.Glass Sci. Technol. B*, Vol. 47, No. 4, pp. (460-465).
- Hovhannisyan, R.M. et al. (2008). Mutual influence of barium borates, titanates and borontitanates on phase diagram and glass formation in the BaO-TiO₂-B₂O₃ system. *Phys.Chem.Glasses: Eur. J.Glass Sci. Technol. B*, Vol. 49, No. 2, pp. (63-67).
- Hovhannisyan, M.R. et al. (2009). A study of the phase and glass forming diagrams of the BaO-Bi₂O₃-B₂O₃ system. *Phys. Chem.Glasses: Eur. J.Glass Sci. Technol. B*, Vol.50, No. 6, pp. (323-328).

- Hubner, K.-H. (1969). Ueber die Borate $2\text{BaO} \cdot 5\text{B}_2\text{O}_3$, tief- $\text{BaO} \cdot \text{B}_2\text{O}_3$, $2\text{BaO} \cdot \text{B}_2\text{O}_3$ und $4\text{BaO} \cdot \text{B}_2\text{O}_3$. *Neues Jahrb. Mineral., Monatsch.*, pp. (335-343).
- International Center for Diffraction Data [ICDD]. (2008). Powder Diffraction Fails, PDF-2 release database, Pennsylvania, USA, ISSN 1084-3116.
- Imaoka M. & Yamazaki T. (1957). Glass formation range borate systems between a-group elements. *Rep. Inst. Ind. Sci. Univ. Tokyo*, Vol. 6, No. 4, pp. (127-183).
- Kong, L.B., Li, S., Zhang, T.S., Zhai, J.W., Boey, F.Y.C. & Ma, J. (2010). Electrically tunable dielectric materials and strategies to improve their performances. *Progress in Materials Science*, Vol. 55, No. 8, pp. (840-893).
- Kosaka, S. et al. (2005). Synthesis and nonlinear optical properties of $\text{BaTi}(\text{BO}_3)_2$ and $\text{Ba}_3\text{Ti}_3\text{O}_6(\text{BO}_3)_2$ crystals in glasses with high TiO_2 contents. *J. Solid State Chem.*, Vol. 178, pp. (2067-2076).
- Kusumoto K. & Sekiya T. (1994). Preparation of barium titanate particles by glass crystallization method. *Rep. Governm. Ind. Res. Inst. Nagoya*, Vol. 43, No. 4-5, pp. (156-162).
- Levin, E.M. & McMurdie, H.F. (1949). The System $\text{BaO}-\text{B}_2\text{O}_3$. *J. Res. Nat. Bur. Standards*, Vol. 42, pp. (131-138).
- Levin, E.M. & Ugrinic, G.M. (1953). The System Barium Oxide-Boric Oxide- Silica. *J. Res. Nat. Bur. Standards*, Vol. 51, pp. (37-56).
- Matveev M.A., Khodskii L.G., Fisyuk G.K., Bolutenko A.I. & Strugach L.S. (1966). Some properties of glasses on the base of the systems $\text{BaO}-\text{TiO}_2-\text{B}_2\text{O}_3$, $\text{BaO}-\text{TiO}_2-\text{P}_2\text{O}_5$ and $\text{BaO}-\text{TiO}_2-\text{SiO}_2$. *Neorg.Mater.*, Vol. 2, No. 6, pp. (1119-1123).
- Millet, J.M., Roth, R.S. & Parker H.S. (1986). Phase relation between polytitanates of barium and the barium borates, vanadates, and molybdates. *J. Am.Ceram. Soc.*, Vol. 69, No.11, pp. (811-814).
- O'Bryan, H.M. & Thomson, J. (1974). Phase equilibria in the TiO_2 – rich region of the system $\text{BaO}-\text{TiO}_2$. *J. Am.Ceram. Soc.*, Vol. 57, No. 12, pp. (522-526).
- Park, H., Bakhtiarov, A., Zhang, W., Vargas-Baca, I. & Barbier, J. (2004). Non-centrosymmetric $\text{Ba}_3\text{Ti}_3\text{O}_6(\text{BO}_3)_2$. *J. Solid State Chem.*, Vol. 177, pp. (159-164).
- Pavlikov, V.N., Yurchenko, V.F. & Tresvyatskiy, S.G. (1976). The $\text{B}_2\text{O}_3-\text{TiO}_2$ system. *Zh. Neorg. Khim.*, Vol. 21, pp. (233-236).
- Pernice, P., Esposito, S. & Aronne, A. (1998). Structure and nonisothermal crystallization of glasses in the $\text{BaO}-\text{TiO}_2-\text{B}_2\text{O}_3$ system. *Phys. Chem. Glasses*, Vol. 39, No. 4, pp. (222-227).
- Rase, D.E. & Roy, R. J. (1955). Phase equilibria in the system $\text{BaO}-\text{TiO}_2$. *J. Am.Ceram. Soc.*, Vol. 38, No. 3, pp. (102-113).
- Sawyer, C.B. & Tower, C. H. (1930). Rochelle Salt as a Dielectric. *Phys. Rev.*, Vol. 35, No.3, pp. (269 -273).
- Schmid H. (1964). X-ray evidence for CrCO_3 , VBO_3 and TiBO_3 with calcite structure. *Acta Cryst.*, Vol. 17, pp. (1080-1081).
- Sholokhovich, V.L. & Varicheva, V.I. (1958). The system $\text{PbO}-\text{BaO}-\text{B}_2\text{O}_3-\text{TiO}_2$ study. *Izv. Akad. Nauk SSSR, Ser. Fiz.*, Vol. 22, pp. (1449-1452).
- Vicat, J. & Aleonard, S. (1968). Etude de borates $\text{MeMe}^1(\text{BO}_3)_2$ de structure dolomite. *Materials Research Bulletin*, Vol.3, pp. (611-620).
- Waghmare, U., Sluiter, M. H.F., Kimura, T., Goto, T. & Kawazoe.Y. (2004). A lead-free high-TC ferroelectric BaTi_2O_5 : a first-principles study, *Applied Physics Letter*, Vol. 84, No. 24, pp.(4917-4919).
- Wakino, K., Nishikawa, T., Ishikawa, Y. & Tamura, T. (1990). Dielectric resonator materials and their applications for mobile communication system. *Br. Ceram. Trans.*, Vol. 89, pp. (39-43).

Ferroelectrics - Physical Effects

Edited by Dr. Mickaël Lallart

ISBN 978-953-307-453-5

Hard cover, 654 pages

Publisher InTech

Published online 23, August, 2011

Published in print edition August, 2011

Ferroelectric materials have been and still are widely used in many applications, that have moved from sonar towards breakthrough technologies such as memories or optical devices. This book is a part of a four volume collection (covering material aspects, physical effects, characterization and modeling, and applications) and focuses on the underlying mechanisms of ferroelectric materials, including general ferroelectric effect, piezoelectricity, optical properties, and multiferroic and magnetoelectric devices. The aim of this book is to provide an up-to-date review of recent scientific findings and recent advances in the field of ferroelectric systems, allowing a deep understanding of the physical aspect of ferroelectricity.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Rafael Hovhannisyan, Hovakim Alexanyan, Martun Hovhannisyan, Berta Petrosyan and Vardan Harutyunyan (2011). Phase Diagramm, Cristallization Behavior and Ferroelectric Properties of Stoichiometric Glass Ceramics in the BaO-TiO₂-B₂O₃ System, *Ferroelectrics - Physical Effects*, Dr. Mickaël Lallart (Ed.), ISBN: 978-953-307-453-5, InTech, Available from: <http://www.intechopen.com/books/ferroelectrics-physical-effects/phase-diagramm-cristallization-behavior-and-ferroelectric-properties-of-stoichiometric-glass-ceramic>

INTECH
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the [Creative Commons Attribution-NonCommercial-ShareAlike-3.0 License](https://creativecommons.org/licenses/by-nc-sa/3.0/), which permits use, distribution and reproduction for non-commercial purposes, provided the original is properly cited and derivative works building on this content are distributed under the same license.

IntechOpen

IntechOpen