International Journal of the Physical Sciences Vol. 6(36), pp. 8164 - 8170, 30 December, 2011
Available online at http://www.academicjournals.org/IJPS
DOI: 10.5897/IJPS11.762
ISSN 1992 - 1950 ©2011 Academic Journals

Full Length Research Paper

Glass-forming tendency in the K_2O-BaO-B_2O_3-Al_2O_3-TiO_2 system

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Accepted 05 December, 2011

Vitrification in the system of K_2O-BaO-B_2O_3-Al_2O_3-TiO_2 containing (mol%): K_2O (0 to 28), BaO (0 to 28), B_2O_3 (5 to 24), Al_2O_3 (7 to 25) and TiO_2 (33 to 60) was investigated by fusion at 1450°C for 2 h. The fields of vitrification were analyzed with different forms of diagrams. It is shown that stable glasses can be produced with batchs containing 62 to 75 mol% of glass-formers ([TiO_2]+[B_2O_3]+[Al_2O_3]) including (TiO_2) up to 48 mol% and (R_2O_3)>20 mol%. For those compositions with (TiO_2)=35 to 47 mol%, the molar ratio of (Al_2O_3) / (B_2O_3) can be varied in the range of 1 to 2.5. The structure of obtained glasses was characterized by scanning electron microscope (SEM) and infrared (IR); the investigated glasses contained one or two vitreous phases depending on their chemical composition. One-phase glasses can be obtained with compositions of (Al_2O_3) / (B_2O_3)≥1.75. The vitreous phase of one-phase glasses and the main glassy phase of two-phase glasses are formed by octahedra of $TiO_{6/2}$ and $AlO_{6/2}$ as well as $(B_3O_6)^{3-}$ rings; the droplets of the second vitreous (borate) phase was formed by $BO_{3/2}$, $TiO_{4/2}$ and $BO_{4/2}^-$, $AlO_{4/2}^-$ groups combined with Ba^{2+} and K^+ cations.

Key words: Vitrification, borate, titanate, two-phase glasses.

INTRODUCTION

Glasses with high TiO_2 content are of great interest in basic research and technologic applications because of their optical properties and good chemical resistance (Cheng and Chen, 1986). Also, the titanate glasses are interesting for obtaining of glass-ceramics with crystalline phases of barium and lead titanates, which present good dielectric properties, by techniques such as quenching and heat treatment (Golezardi et al., 2010; Shankar and Deshpande, 2011) or glass irradiated by laser pulse (Bo et al., 2005). The main problem is the produce of stable glasses, since it is well known that TiO_2 into glasses increases spontaneous crystallization tendency during the cooling (Ruiz-Valdés et al., 2005), however, it is reported that additions of glass formers and modifiers such as SiO_2 and B_2O_3 (Aronne et al., 2003), Al_2O_3 and Na_2O (Kokubo et al., 1987), B_2O_3, K_2O, Cs_2O and BaO (Sakka et al., 1990), PbO and P_2O_5 (Koudelka et al., 2003), etc., into the glassy network, stabilizes it against bulk or superficial crystallization.

On one hand, glass ceramics based on titanate glasses, containing crystalline phases of $K_2Ti_6O_{13}$ (Gonzales-Lozano et al., 2009), and/or perovskites of $BaTiO_3$ (Sarkar and Sharma, 1989; Thakur et al., 1995; Gorokhovskii et al., 2002; Takahashi et al., 2006), are very promising in structural and electronic applications. The crystals of $K_2Ti_6O_{13}$ have a fibrous tunnel-like structure and exhibit high thermal insulation, mechanical

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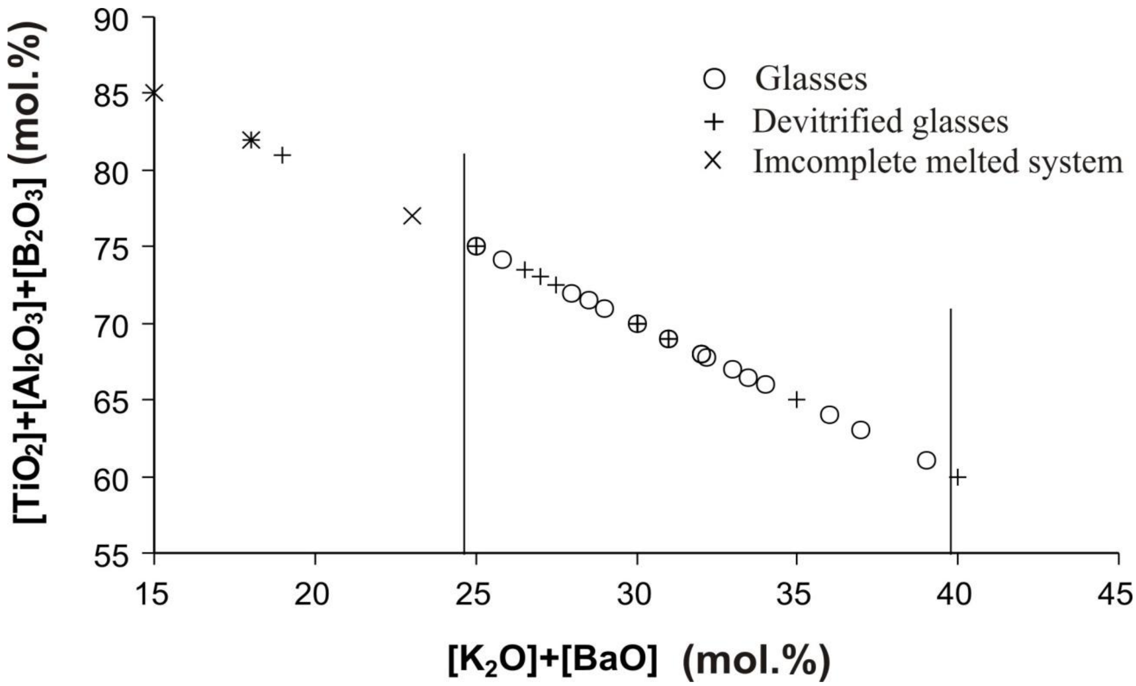

Figure 1. Influence of glass-net formers and modifiers content (mol %) on vitrification.

and chemical resistance (Wu et al., 2000). Potassium hexatitanate whiskers are used as reinforcing agent for plastics and metallic alloys because their price ranges from one-tenth to one-twentieth of the cost of SiC whiskers (Tjong and Meng, 1999). On the other hand, $BaTiO_3$ is used most extensively in manufacturing of ceramic capacitors because of its high dielectric properties (Kobayashi et al., 2008). Thus, the glass-ceramics containing potassium hexatitanate altogether with $BaTiO_3$ could be applied as reinforced functional materials.

However, vitrification and crystallization processes of titanate glasses, using melting-casting technique have been studied in a few systems, such as K_2O-TiO_2 (Kokubo et al., 1987), K_2O-Al_2O_3-TiO_2 (Gonzáles-Lozano et al., 2009) and BaO-PbO-TiO_2-B_2O_3-Al_2O_3 (Ruiz-Valdés et al., 2004); the introduction of K_2O in the latter vitreous system instead of PbO (as flux) could permit obtaining stable glasses and possibly glass-ceramics with potassium titanates and barium titanate altogether, after regulated crystallization. This research presents the results on vitrification processes in the K_2O-BaO-B_2O_3-Al_2O_3-TiO_2 system, acceptable to produce reinforced glass-ceramic ferroelectrics.

MATERIALS AND METHODS

Commercial chemicals (analytic grade purity >99%) used as raw materials were K_2CO_3, H_3BO_3, Al_2O_3, $Ba(NO_3)_2$ and TiO_2. The nominal composition of the investigated mixtures varied in the range of mol%: K_2O (0 to 27), BaO (2.5 to 27), B_2O_3 (5 to 24), Al_2O_3 (7 to 25) and TiO_2 (33 to 60). All mixtures were thermally treated and melted in platinum crucibles in two stages: initially were heated slowly up to 400°C with 1 h at this temperature to decompose the H_3BO_3 and avoid B_2O_3 losses by volatilization (Pernice et al., 1999); then heated up to 1450°C and held for 2 h to homogenize the melt. The melts were poured onto a steel plate at room temperature and the solidified products were classified depending on their physical features as transparent glasses, devitrified glasses or unmelted mixtures.

The glass microstructure was characterized on polished samples recovered with graphite by Scanning Electron Microscopy (SEM, Philips XL30ESEM, equipped with an X-ray microanalyzer, EDS, EDAX Pegasus). The structural features of glass samples were also investigated by Infrared spectroscopy (IR, Nicolet, Avatar 320 ESP), pellets of 15 mm diameter of a mixture with 3.0 mg of glass and 300 mg of KBr were prepared by pressing, and they were used to obtain infrared (IR) absorption spectra.

RESULTS AND DISCUSSION

Glass-forming tendency

Figures 1 to 3 present several diagrams that allowed delimiting the fields of vitrification of the system in different coordinates. Figure 1 indicates the limits of glass-net formers and glass-net modifiers contents which allowed vitrifying the system investigated. Glassy samples were attainable with (K_2O+BaO) contents in the range of 25 to 40 mol%, while the (TiO_2+B_2O_3+Al_2O_3) acceptable range was from 60 to 75 mol%. Nonetheless, some compositions within such range, presented

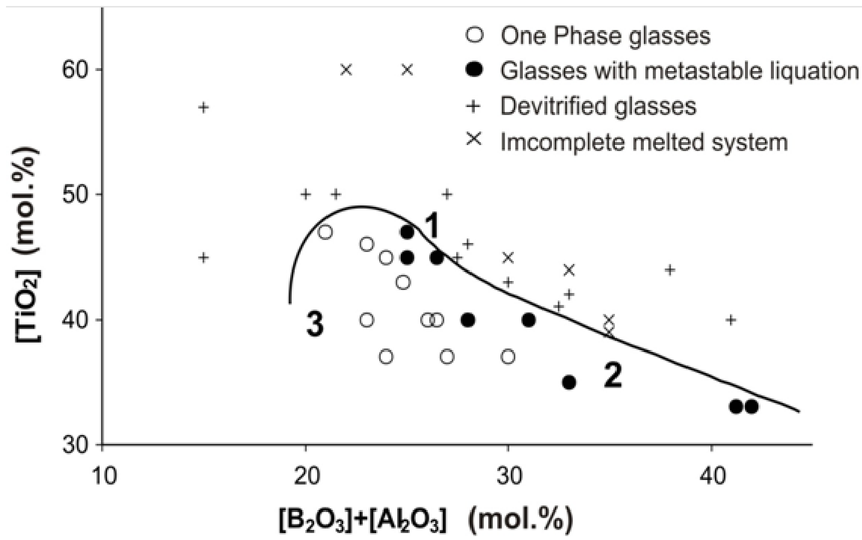

Figure 2. Influence of TiO_2 and R_2O_3 contents (mol %) on the vitrification 1, 2 and 3 groups of compositions with different character of IR spectra (Figure 4).

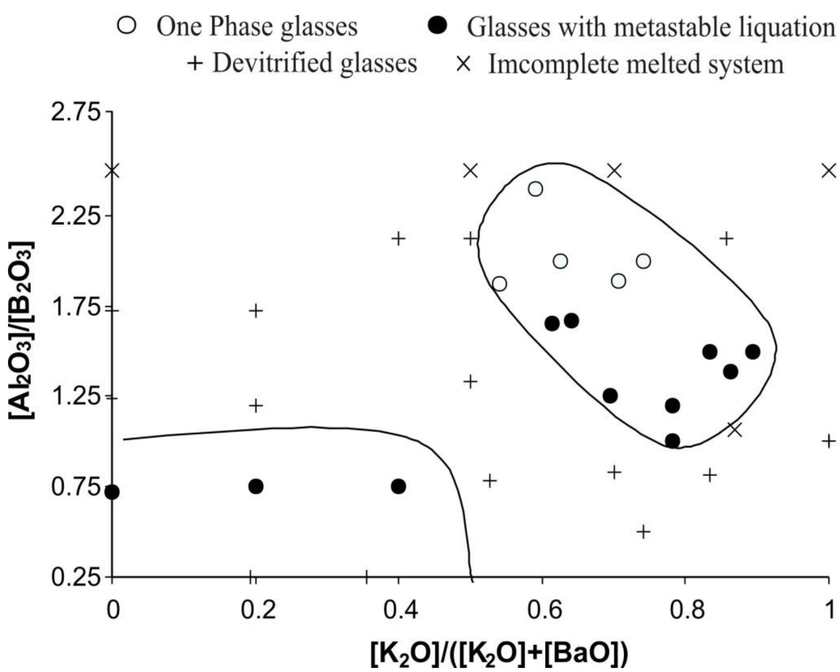

Figure 3. Influence of (Al_2O_3) / (B_2O_3) and (K_2O) / ([K_2O]+[BaO]).

devitrified samples, indicating the high importance of the individual contents of each oxide. The influence of TiO_2 and R_2O_3 contents on the vitrification behaviour are presented in Figure 2. It is shown that the highest TiO_2 content to obtain glasses in the investigated system were 48 mol% and corresponded to (R_2O_3) in the range of 20 to 25 mol%. Higher or lower (R_2O_3) promoted reduced (TiO_2) in the glasses produced. Figure 3 shows how the molar ratios of (Al_2O_3) / (B_2O_3) and (K_2O) / ([K_2O]+[BaO]) influenced the processes of vitrification in the system investigated; two fields of vitrification can be considered, which are shown with line boundaries. The first is characterized with relatively high concentration of K_2O (0.5<[K_2O]/([K_2O]+[BaO]) < 0.9). The optimal molar ratio of 9Al_2O_3) / (B_2O_3), promoting vitrification of such compositions, located between 1 and 2 ([Al_2O_3]>[B_2O_3]).

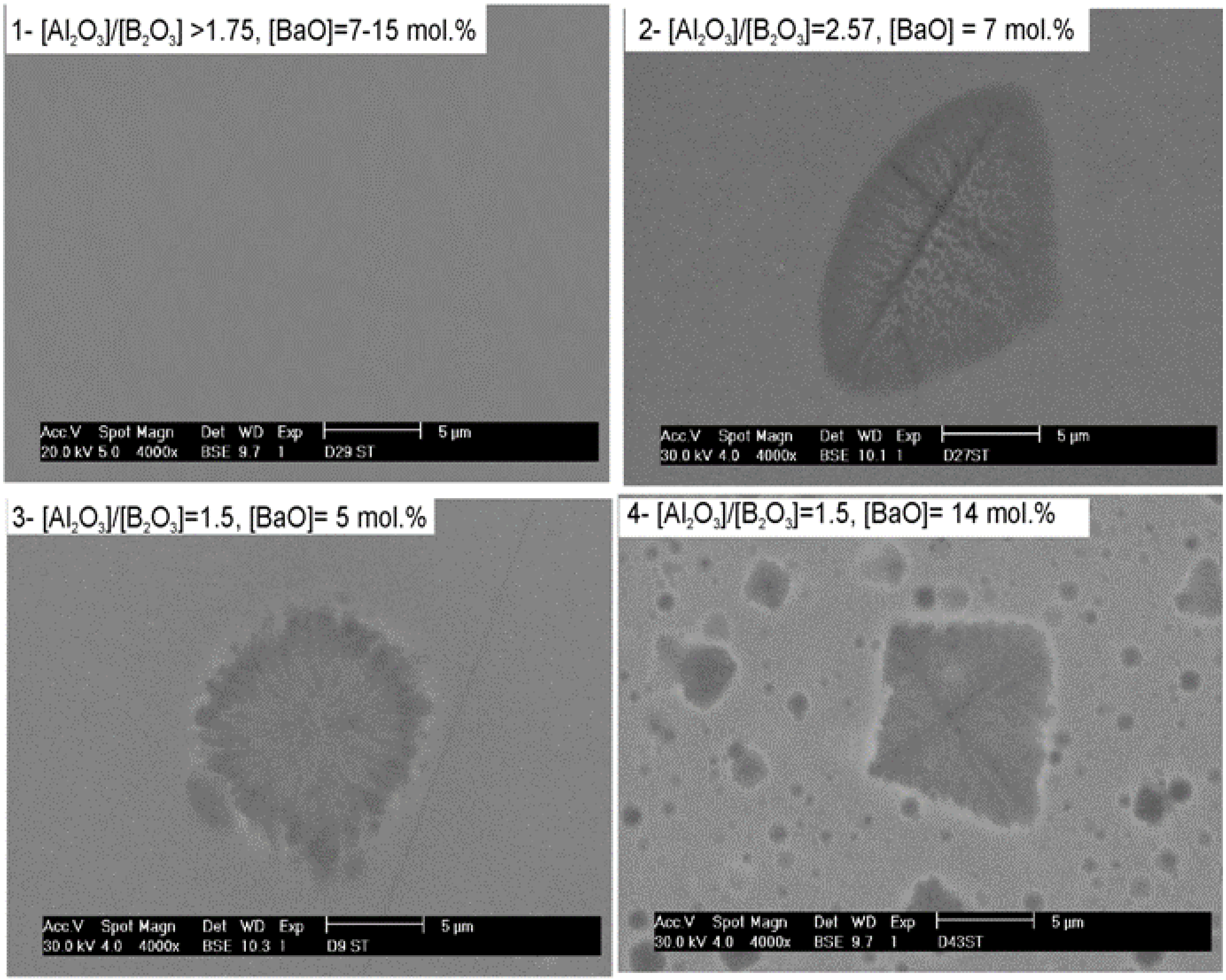

Figure 4. Micrographs of some obtained glasses (magnification 4000x).

The second field was characterized by a relatively low (K_2O) (K_2O) / ([K_2O]+[BaO]) < 0.5), stable glasses could be obtained for compositions with (Al_2O_3) < (B_2O_3).

In accordance with the obtained results, complete vitrification took place in the compositions of ([TiO_2]+[B_2O_3]+[Al_2O_3])=60 to 75 mol%; however, the relations among these three oxides was important to define the formation of one or two phase glasses. Increasing concentration of glass net modifiers above 30 mol% promoted higher contents of the second vitreous phase inclusions, which could be formed by B_2O_3, similar to those glasses investigated in the K_2O free system of BaO-PbO-B_2O_3-Al_2O_3-TiO_2 (Ruiz-Valdes et al., 2005). Thus, glass-net modifiers supported the formation of the borate glassy phase; however, this effect was inhibited increasing (Al_2O_3) or diminishing (B_2O_3), which stabilized the titanate glassy phase, without formation of a second glassy phase (Figure 3); for those reasons, the compositions with (Al_2O_3) / (B_2O_3) > 1.75 tended to form one phase glasses.

Glass structure

According to the scanning electron microscope (SEM) results, glasses with one and two vitreous phases were observed (Figure 4). In the latter, the main glassy matrix contained droplets of the secondary vitreous phase (metastable liquid phase separation). One phase glasses were obtained with (R_2O_3)<32 mol% and (Al_2O_3) / (B_2O_3) > 1 (Figures 3 and 4), whereas two-phase glasses were produced with (Al_2O_3) / (B_2O_3) < 1.75 and (R_2O_3) > 23 to

Table 1. General composition of glasses calculated from the batch (without B_2O_3) and EDS data for the main (titanate) glassy phase (without B_2O_3).

Characteristics of glass		**Oxide contents (mol %)**			
		Al_2O_3	**K_2O**	**BaO**	**TiO_2**
(Al_2O_3) / (B_2O_3)=1.5 (BaO)= 5 mol.%*	Based on batch	16.7	27.8	5.5	50.0
	EDS	15.1	18.5	1.0	65.5
(Al_2O_3) / (B_2O_3)=1.5 (BaO)= 14 mol.%*	Based on batch	16.7	27.8	15.5	40
	EDS	14.7	18.4	5.2	61.8
(Al_2O_3) / (B_2O_3)=1.88	Based on batch	16.3	21.7	18.5	43.5
(BaO)= 17 mol.%**	EDS	15.5	18.7	17.1	48.7

*, Two-phase glass; **, one-phase glass.

30 mol.% (depending on $[TiO_2]$, Figure 2). On the other hand, the (BaO) influenced the intensity of liquid phase separation. The comparison of microstructure for two glasses with the same (Al_2O_3) / (B_2O_3)=1.5 and ([BaO]+$[K_2O]$)=31 mol% but different (BaO) of 5 and 14 mol%, indicated that higher (BaO) increased the quantity of vitreous droplet inclusions. The energy-dispersive (EDS) data for the main glassy phase from these two-phase glasses, in comparison with the homogeneous glass ($[Al_2O_3]/[B_2O_3]$=1.88), as well as the general chemical composition calculated from the batch (without B_2O_3), are reported in Table 1. Taking into account that EDS measurements for one-phase glasses were similar to those calculated from the batch composition. We can infer that in the two-phase glasses, the main glassy phase tends to TiO_2, whereas considering the decrement in the contents of potassium oxide and barium oxide; it can be assumed that these tended to locate in the second vitreous phase.

On the other hand, the IR absorption spectra of some produced glasses are shown in Figure 5. Regardless of the presence of one or two vitreous phases, all spectra showed intensive absorption bands in the range of 1100 to 1500 cm^{-1} (associated to the vibration of the B-O bond constituting the linkage of $(B_3O_6)^{3-}$ rings (Tossell, 1995) as well as an absorption band at 600 to 900 cm^{-1} which is ascribed to the Ti-O stretching mode of octahedral $(TiO_{6/2})$ (Aronne et al., 2003; Cheng and Chen, 1986); and $(AlO_{6/2})$ units (Ruiz-Valdés et al., 2005); however, the relation of their intensities differ. In the group 1, an intense absorption band appeared at 900 and 1150 cm^{-1} which corresponds to Al-O and B-O units of the groups (AlO_4) and $(BO_4)^-$, whereas, the absorption bands in the 1150 and 1300 and 1300 and 1500 cm^{-1} regions are due to B-O stretching of trigonal (BO_3) units (Pernice et al., 1999); indicating the presence of a second borate vitreous phase formed by polyhedrons in six fold coordination. On the other hand, the intensity of the 600 and 900 cm^{-1} band was lower than the band at 1100 and 1500 cm^{-1}, and the contrary effect was noted for the glasses of groups 2 and 3. The differences between the IR spectra of the glasses from groups 2 and 3 related to the intensities of the additional absorption bands appearing at 1400 and 1550 cm^{-1}; these are usually related to B-O stretching vibration of (BO_3) units in the structure of borate glasses without and with other glass-net formers (Verhoef and Den. 1995; El-Damrawi and El-Egili, 2001). The glasses of the group 2 have the intensity of these bands of lower intensity for the band characterized with maximal absorption intensity at 1230 cm^{-1}($(B_3O_6)^{3-}$ rings), while for the glasses of the group 3, the intensity of the absorption band appeared at 1230 cm^{-1} which is higher than those related to $BO_{3/2}$ groups. In accordance with Ruiz-Valdés et al. (2005), the $(B_3O_6)^{3-}$ rings can be incorporated by means of Ba^{2+} ions, in the structure of the titanate glassy phase formed in the glasses of the system $BaO-Al_2O_3-B_2O_3-TiO_2$. Therefore, it is possible to propose that the one-phase glasses related to group 3 have a structure similar to that of the glasses obtained in similar K_2O-free system; while the glasses of group 2 also contain B_2O_3 polyanions of another structure, which are incorporated in the titanate glassy matrix (one-phase glasses characterized with (TiO_2)>43 mol% and (R_2O_3)<23 mol% (Figure 2) or are integrated in the structure of the second borate vitreous phase in two-phase glasses with (TiO_2)<43 mol% and (R_2O_3) > 27 mol% (Figure 2).

The coordination of titanium atoms in titanate glasses is a discussion object, since, while some authors affirm that the tetrahedral coordination is dominant (Kokubo et al., 1987; Sakka et al., 1990), another authors have reported octahedral coordinations where the structure of titanate glasses is postulated that it consists of a three-dimensional network where octahedra share corners with one another (Cheng and Chen, 1986; Ruiz-Valdés et al., 2004, 2005; Sigaev et al., 2001). In this work, it is proposed that the glass structure of the one-phase glasses is constituted by octahedral groups of $TiO_{6/2}$ forming a three-dimensional network similar to the reported one in previous works, but also contains $(B_3O_6)^{3-}$ rings and $AlO_{6/2}$ octahedra.

On the other hand, for two-phases glasses, the main vitreous phase has the same above mentioned structure; additionally, the droplets of the second vitreous phase

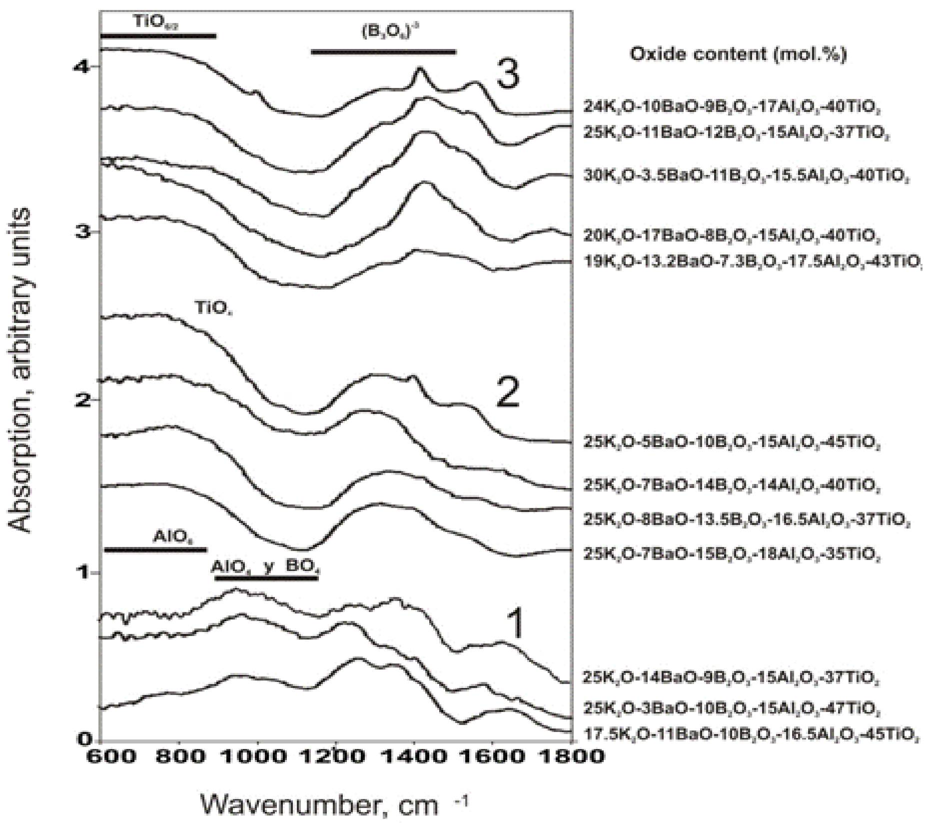

Figure 5. IR absorption spectra of some glasses obtained. The number of group corresponds to the group of compositions marked in Figure 2.

are constituted by $BO_{3/2}$ units$(B_3O_6)^{3-}$ rings as well as $TiO_{4/2}$, $AlO_{4/2}^-$ and $BO_{4/2}^-$ tetrahedrons with electrical charge compensated by Ba^{2+} and/or K^+ ions.

Conclusion

Stable one- and two-phase titanate glasses were obtained in the PbO-free system of K_2O-BaO-B_2O_3-Al_2O_3-TiO_2 containing 62 to 75 mol% of glass-formers ($[TiO_2]+[R_2O_3]$) including up to 48 %mol TiO_2 and (R_2O_3) >20 mol%. The glass compositions containing mol%: $43<(TiO_2)<48$, $18<([B_2O_3]+[Al_2O_3])<23$ and (Al_2O_3) / $(B_2O_3)>1.75$ are considered more promising to produce glass-ceramics based on different crystalline titanates due to the absence or low contents of the second (borate) glassy phase and the structure well prepared to form $BaTiO_3$ (functional component) and $K_2Ti_4O_9$ or $K_2Ti_6O_{13}$ (reinforcement), by heat treatment.

ACKNOWLEDGEMENT

María Azucena González Lozano acknowledges the scholarship from CONACYT, México.

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