About the formation of crystalline compounds in glasses from BaO-TiO2-B2O3 system

Lucica Boroica, Isidor Boroica, Mirela Nicolescu, Emil Rotiu, D. Hülsenberg*
National Glass Institute Th Pallady No. 47 sector 3, Bucharest 74584, Romaniav,
**Technical University Ilmenau, PO BOX 10 05 65, D-98684-Ilmenau, Germany*

The present work is investigating the formation mechanism of the crystalline compounds in the zone of 30-50 mol% BaO and TiO_2mol%/B_2O_3mol%=0.2-2.0. The first melting temperatures were in the range 1100-1350^{O}C. The melts were cooled on metallic plates. The obtained materials were grounded and remelted at 1200-1250 ^{O}C in an electric furnace and rapid quenched between twin roles. The obtained flakes were analyzed by (DTA) in order to determine the crystallization temperatures. The thermal treatments for crystallization were made at different temperature for tow hours. The crystalline phases identified by means of X ray diffraction and IR spectroscopy put into evidence the presence of some barium titanates together with anther compounds.

Introduction

Recently is present an increase interest for their applications in the non-silica oxide glasses and crystallized glasses. The increase use of titanate materials led to the necessity to study more these fields.

Bhargava and co-workers [1].have studied the crystallization of glasses in the BaO-TiO_2-B_2O_3 system. The structural studies on glasses in the from BaO-TiO_2-B_2O_3 system, indicated that the titanium ions may occupy network forming positions.

H**ü**lsenberg and her colleagues [2]., put into evidence the obtaining of $BaTiO_3$ by crystallization of the glass with the following composition: BaO – mol%; TiO_2 – 30 mol% and B_2O_3 – 25 mol%.

Several compositions in the BaO-B_2O_3-TiO_2 system have been studied [3]. The main studied compositions were $BaTi_4O_9$, with an added amount of B_2O_3 =5-50 mol% and $BaTiO_3$ together with B_2O_3 =25-50 mol%. For the compositions with less than 40mol% TiO_2 and more than 20 mol% B_2O_3 the obtained materials were vitreous

The present work is investigating the formation mechanism of the crystalline compounds in the following compositions domains of 30 – 50 mol% B_2O_3 and TiO_2, B_2O_3 mol %= 0.2 – 2.0.

2. Experimental

The studied compositions in the BaO - B_2O_3 - TiO_2 system are presented in table 1.

Table 1 classification of the investigated compositions on the BaO ratio content and on the TiO2/ B2O3

BaO mol%	$M_v = TiO_2/B_2O_3$ (mol%)/No. of compositions				
30	1.3/***10***				
40	2.0/***1***	1.4/***4***	1.0/***8***	0.7/***6***	0.2/***3***
45	1.8/***2***	1.2/***9***	0.8/***5***		
50	1.0/***7***				

The used reagents were of purity. 99 % wt. They were Chimopar BaO– Romania, TiO_2 Fluka – Germany, B_2O_3 Chimopar – Romania. The mixtures were made in two stages, in a polyethylene bottle, with agate balls, first dry for 30 minutes and then with acetone for another 30 minutes. The suspension were dried in air on a porcelain capsules or on a plastic sheet. The dried mixtures were melted in an electric furnace with superkanthal heating elements. The crucibles were from platinum for 0.7 – 1.0-l capacity. The melting temperature was in the range 1100 – 1350 C.

The melts were cooled on metallic plates. The melted samples were grounded and remelted in a special device, an electric cylindrical furnace and then fast quenched between twin rolles [4].

The obtained flakes were analyzed by differential thermal analyses (DTA), in order to determine the crystallization temperatures.

The crystallization thermal treatments were mate in an electric furnace for two hours, at different temperatures in the range (660-800°C).

The crystalline phases were identified by the means of X-ray diffraction electronic microscopy and infrared spectroscopy (IR) in the crystallized samples.

3.Results. Discussion

3.1. Systematization of the researched compositions

To obtain a logic connection between the structure characteristics of the glasses, these were grouped after the molar content of BaO and molar ratio of the vitrifiants (TiO_2/B_2O_3) denominated as Mv considering, in accordance to the literature information, that TiO_2 presents 4 coordination.

3.2 sample aspect

The samples obtained after classic cooling on metallic plates were transparent and yellow colored. By x-ray diffraction analyze were put into evidence the presence of some crystalline compounds as presented in figure 1, only sample number 3 was amorphous.

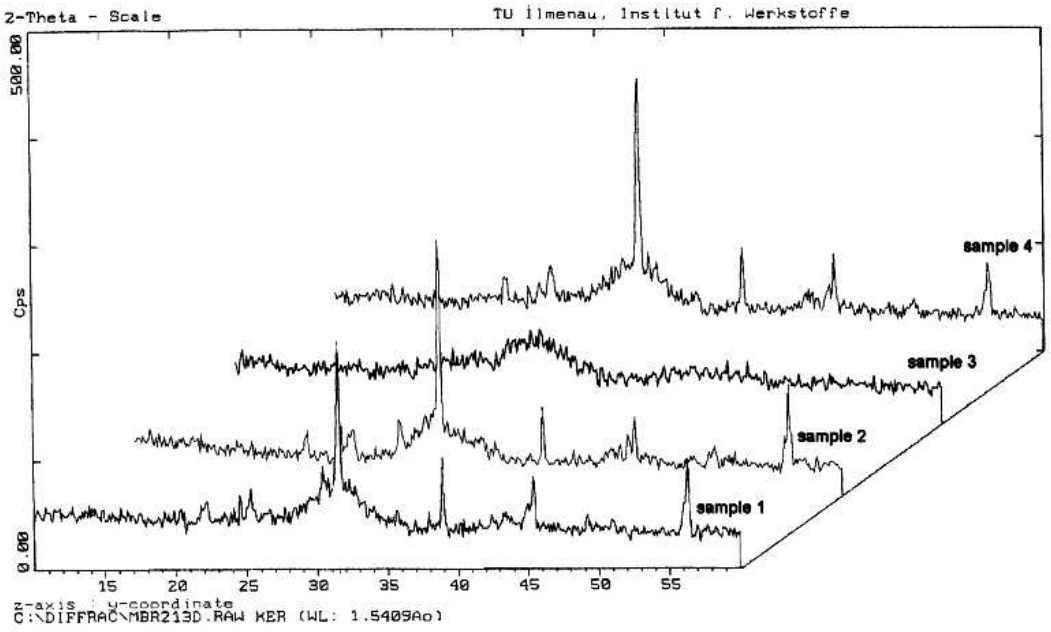

Fig 1 X-ray diffraction for sample cooped on metallic plate.

After the ultra fast quenching, the flakes for all compositions were vitreous, only one, composition 2, being partly crystallized.

In figure 2 are presented the optic microscopy of the sample 3 cooled on metallic plate (a) ultra fast-quenched (b) and flakes sample 2 (c).

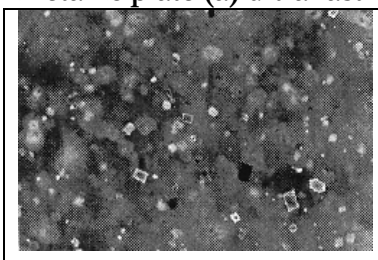

Fig 2 a

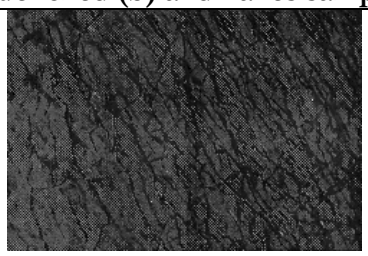

Fig 2 b

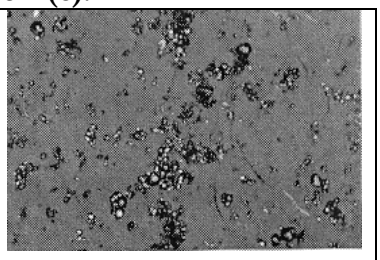

Fig 2 c

3.3. DTA analyses

The DTA determinations made in tow laboratories established the following results as are presented in table 2.

Table 2

Sample	Transf. Temp. ^{O}C	Lost weight %	Exothermal ^{O}C	Endothermic ^{O}C
1	556	-1.3	679.7; 719.6	977,4
2	531.8	-0.1	624.1; 661,9; 734.0	946.2; 966.2
3	571.3	-0.4	665.0; 702,5; 732.9	873.0; 978.2
4	561.0	-0.1	672.7; 683.2	947.4; 991.4; 1008.8; 1033.4
5	540	-0.1	633.1; 683; 697.2	956.0
8	570	-0.1	663.6; 700.7	954.6; 972.8; 1012.4
10	596.4	-0.5	681.2	1064.7

3.4 X ray diffractometry

The diffraction analyses were made on flakes crystallized for tow hours at the following temperature 660; 690; 730; 780; 800°C.

The results are presented in table 3

Table 3 crystalline compounds

Code sample	Temp. ^{O}C	color	*Compound*
1	780	cream	$Ba_2Ti_2B_2O_9$; Ba Ti $(BO_3)_2$; BaB_2O_4
1	800	cream	$Ba_2Ti_2B_2O_9$; Ba Ti $(BO_3)_2$
2	660	yellow	$Ba_2Ti_2B_2O_9$; $BaTiO_3$
2	690	yellow	$BaTiO_3$; BaB_2O_4; Ba_2TiO_4
2	730	yellow	$BaTiO_3$; $Ba_2Ti_2B_2O_9$
2	780	yellow	$Ba_2Ti_2B_2O_9$; $BaTiO_3$
3	660	grey	Ba Ti $(BO_3)_2$
3	690	white	Ba Ti $(BO_3)_2$
3	730	white	$BaTiO_3$; $BaTi_4O_9$; BaB_2O_4
3	800	white	Ba Ti $(BO_3)_2$; BaB_2O_4; $Ba_2Ti_2B_2O_9$
4	660	slightly yellow	Ba_2TiO_4; $Ba_2Ti_9O_{20}$; $BaTi_4O_9$

4	690	slightly yellow	$Ba_2Ti_2B_2O_9$; Ba_2TiO_4, $BaTi_4O_9$; Ba Ti $(BO_3)_2$
4	780	cream	Ba Ti $(BO_3)_2$; $Ba_2Ti_2B_2O_9$; $BaTiO_3$
4	800	yellow	$Ba_2Ti_2B_2O_9$; Ba Ti $(BO_3)_2$
5	690	white	$Ba_2Ti_2B_2O_9$; $BaTi_2O_5$; BaB_2O_4
5	780	cream	$BaTiO_3$; $Ba_2Ti_2B_2O_9$; Ba Ti $(BO_3)_2$
5	800	cream	BaB_2O_4; $Ba_2Ti_2B_2O_9$; Ba Ti $(BO_3)_2$
6	690	cream	$Ba_2Ti_9O_{20}$; Ba Ti $(BO_3)_2$
6	730	slightly yellow	Ba Ti $(BO_3)_2$; $BaTiO_3$
7	780	slightly yellow	$Ba_2Ti_2B_2O_9$; Ba Ti $(BO_3)_2$; $BaTiO_3$
8	690	white	Ba Ti $(BO_3)_2$; $Ba_2Ti_2B_2O_9$; $BaTi_2O_5$
8	780	slightly yellow	Ba Ti $(BO_3)_2$; $BaTiO_3$; $Ba_2Ti_2B_2O_9$
8	800	cream	$Ba_2Ti_2B_2O_9$; Ba Ti $(BO_3)_2$;
9	690	cream	$Ba_2Ti_2B_2O_9$; Ba_2TiO_4; Ba Ti $(BO_3)_2$; $BaTi_2O_5$
9	780	slightly yellow	$Ba_2Ti_2B_2O_9$; $BaTiO_3$
10	690	cream	Ba Ti $(BO_3)_2$;
10	780	slightly yellow	Ba Ti $(BO_3)_2$;

The X-ray diffraction show out the presence of some ternary compounds as $Ba_2Ti_2B_2O_9$ and Ba Ti $(BO_3)_2$ together with barium titanates $BaTiO_3$; $BaTi_4O_9$; and $Ba_2Ti_9O_{20}$.

These results are conffirmed by the electronic microscopy (figure 3) and the IR determinations.

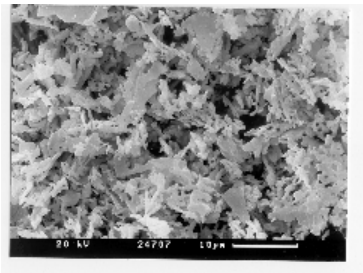

Fig 3 a sample 1

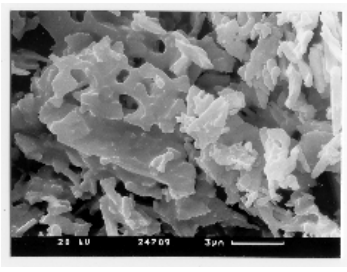

Fig 3 b sample 3

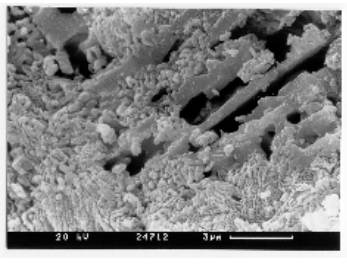

Fig 3 c sample 5

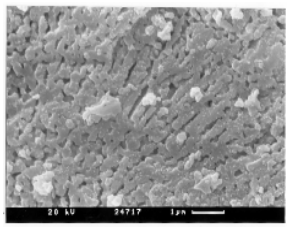

Fig 3 d sample 7

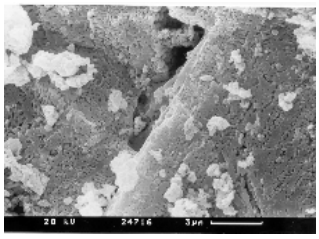

Fig 3 e sample9

Conclusions

Were investigated the formation mechanism of the crystalline compounds in the following compositions domains of 30 – 50 mol% B_2O_3 and TiO_2, B_2O_3 mol %= 0.2 – 2.0.The glasses were obtained in tow steps, first melt and cooled on metalic plates and the remelt and ultra fast quenched.

After the ultra fast quenching, the flakes for all compositions were vitreous, only one, composition 2, being partly crystallized.

The flakes were thermal treated for crystallization for tow hours at the following temperature 660; 690; 730; 780; 800°CThe X-ray diffraction show out the presence of some ternary compounds as $Ba_2Ti_2B_2O_9$ and Ba Ti $(BO_3)_2$ together with barium titanates $BaTiO_3$; $BaTi_4O_9$; and $Ba_2Ti_9O_{20}$.

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[1] Bhargava, A. Shelly, J. L. Snyder, R. L. *Crystalisation of glasses in system BaO - B_2O_3 - TiO_2* J. Non. Cryst. Colids. 1988,**102**,136

[2] Knauf, O. Hamman B. H**ü**lsenberg, D. Patent DE 4038729171-1994

[3] Cerchez, M. Boroica, L. H**ü**lsenberg, D. *Glasses and crystallized glasses in the BaO-B_2O_3-TiO_2 system* Phys. Chem. Glasses, 2000,41 (5), 233

[4] Masahiro Tatsumisago, Tsutomu Minami, Masami Tanaka *Rapid quenching technique using thermal image furnace for glass preparation* J. Am. Ceram. Soc. 1981 C 97-98