

CHEMICAL COMPOSITION, STRUCTURE AND PROPERTIES OF GLASS AND GLASS-CERAMIC MATERIALS IN THE SYSTEM OF BaO(PbO)-B₂O₃-Al₂O₃-TiO₂

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Abstract

The vitrification and crystallization of glasses in the system BaO(PbO)-B₂O₃-Al₂O₃-TiO₂ containing (mol %): BaO (24.6-28.1), PbO (2.8-3.2), B₂O₃ (7.6-24.0), Al₂O₃ (15.9-25.5), TiO₂ (39.1-41.1) were investigated. The batch compositions of different oxide molar ratios were fused in an electric furnace in a platinum crucible at 1450 °C for 2 h and cast into cylindrical-shaped samples. The obtained glasses were crystallized at 950 °C for 2h. BaTiO₃ was recognized as a dominant crystalline phase in the produced glass-ceramic materials. The influence of B₂O₃ and Al₂O₃ contents on the chemical resistance, mechanical strength and dielectric properties was investigated. It is shown that the glass compositions containing (mol %): B₂O₃ 7-25 and Al₂O₃ 16-20 displayed the optimal combinations of exploitation properties. The influence of liquid phase separation on the abovementioned properties was also analyzed.

1. Introduction

Barium titanate is a well known material whose properties are of great interest for electronic and telecommunication applications. Production of BaTiO₃ fine powders necessary to fabricate ceramic materials is actually achieved by very specific methods such as sol-gel, CVD, and hydrothermal synthesis; which are complex and expensive [1-4]. The melting-forming-crystallization process represents a simple and economic way to produce highly densified glass-ceramic materials based on BaTiO₃, starting from parent titanate glasses. Previous research demonstrated that it was possible to obtain stable titanate glasses in different oxide systems [5-9]. The system BaO-Al₂O₃-B₂O₃-TiO₂ with small admixtures of PbO is promising to produce glasses that could be transformed by regulated crystallization into a glass-ceramic material with a predominant crystalline phase of BaTiO₃ [10]; however, the crystallization behavior of such glasses has a very complicated character. On this ground, it was considered important to determine how the relative contents of Al₂O₃ and B₂O₃, as well as the phase composition, influence the properties of the glass-ceramic materials obtained in the abovementioned system. This research could establish the basis, which may allow selecting optimal glass compositions to produce glass-ceramics with high electrical, mechanical and chemical properties.

2. Experimental

Reactive grade chemicals (Aldrich 99.9% purity) of Ba(NO₃)₂, PbO, TiO₂, Al₂O₃ and H₃BO₃ were used as raw materials. In the rest of the document, all percentage compositions of oxide or crystalline phases, quoted for the glass compositions or glass ceramics are expressed in mol%. To determine the role of different R₂O₃ oxides, the glass compositions were prepared with similar contents of BaO (24.6-28.1) and PbO (2.8-3.2). [B₂O₃] was varied in the range of 7.6-24.0, and [Al₂O₃] in the range of 15.9-25.5. At the same time, the total contents of R₂O₃ ranged at 26.9-41.2 and were lower than [TiO₂] at 39.1-44.1. The batches of different chemical composition were fused in platinum crucibles in the electric furnace (Lindberg-BlueM, BF51433) at 1450° during 2 h to obtain homogeneous melts. The melt were cast into cylindrically-shaped graphite moulds to produce glassy samples. SEM and EDS analysis (Philips X'pert MPDPW3040) were conducted for the glasses samples to determine its microstructure. The crystallization behavior was investigated by DTA (Perkin-Elmer TAC7/DX).

Glass-ceramic materials were obtained by the application of an adequate thermal treatment at 950°C during 2 h [10] in an annealing furnace (Lindberg BlueM, BF51800). XRD analysis was used to determine the phase composition of glass-ceramics produced. Chemical durability tests were applied to powdered glasses and glass-ceramics in accordance with the Standards GOST 10134-62 (Russia) and JISR 3520 (Japan). Compression strength tests were conducted for glass-ceramics with a hydraulic press (CONTROLS 65-L1301). Dielectric properties measurements were done with an impedance analyzer (Solartron SI 1260).

3. Results and Discussion

Table 1 reports the data on structure of glass-ceramics obtained with the glasses of different chemical composition. The properties of these materials are presented in Table 2.

Table 1. Chemical and phase composition of the parent glasses and glass-ceramics based thereon. All concentrations in mol %

No	[Al ₂ O ₃]	[B ₂ O ₃]	Contents of the 2 nd glassy phase	Contents of BaTiO ₃ in the glass-ceramics	Additional crystalline phases
1	19.3	7.6	8 (ms)*	23.2	BaO·2TiO ₂ Ba ₄ Ti ₁₀ Al ₂ O ₂₇ Ba ₃ Al ₁₀ TiO ₂₀
2/6	18.6	10.7	6 (ms)	28.7	-
3	16.5	14.5	5 (ms)	25.3	Ba ₄ Ti ₁₀ Al ₂ O ₂₇
4	17.2	24.0	2 (ms)	25.6	BaO·2TiO ₂ Ba ₄ Ti ₁₀ Al ₂ O ₂₇
5	15.9	11.7	4 (ms)	35.8	-
6/2	18.6	10.7	6 (ms)	28.7	-
7	22.2	10.2	22 (sp)	23.2	Ba ₄ Ti ₁₀ Al ₂ O ₂₇ BaAl ₂ O ₄
8	25.5	9.8	42 (sp)	27.9	Ba ₄ Ti ₁₀ Al ₂ O ₂₇ BaAl ₂ O ₄

Table 2. Properties of the glass-ceramic materials produced in the system of BaO(PbO)-Al₂O₃-B₂O₃-TiO₂

No	Contents of R ₂ O ₃ , mol. %		Strength, MPa	Dielectric properties		Weight losses in		
	[Al ₂ O ₃]	[B ₂ O ₃]		ε	tan δ	H ₂ O	1N HCl	1N NaOH
1	19.3	7.6	116	339	0.066	0.050	0.145	0.061
2/6	18.6	10.7	91	377	0.064	0.041	0.192	0.072
3	16.5	14.5	112	388	0.058	0.033	0.200	0.055
4	17.2	24.0	120	766	0.087	0.067	0.226	0.081
5	15.9	11.7	71	803	0.062	0.025	0.168	0.070
6/2	18.6	10.7	91	377	0.064	0.041	0.192	0.072
7	22.2	10.2	49	353	0.066	0.056	0.143	0.145
8	25.5	9.8	380	709	0.089	0.170	0.371	0.271

It is possible to note the change of properties for two groups of compositions. The first, for compositions 1-4 corresponding to the glasses of similar [Al₂O₃] of 17.2-19.3 and [B₂O₃] in the range of 7.6-24.0; the second, for compositions 5-8 with similar [B₂O₃] of 9.8-11.1 and [Al₂O₃] in the range of 15.9-25.5. The dielectric losses of all obtained glass-ceramic materials have similar values; however the maximum values were for the glass-ceramics based on glass compositions with lowest and highest level of liquid phase immiscibility, i.e. compositions No 4 and 8. In the first group, an increase of [B₂O₃] promoted increased permittivity, especially significant in the compositions with [B₂O₃] > 20 (No 4). In the second group, this characteristics initially increased from 766 (for [Al₂O₃] = 15.9) up to 804 (for [Al₂O₃] = 22.2); however, such values decreased intensively in the compositions with [Al₂O₃] = 25.5. Dielectric properties of glass-ceramic materials produced in the investigated system correspond to the contents of BaTiO₃ in the glass-ceramics in their structure (Table 1), regardless of the contents of the second vitreous phase.

On the other hand, the mechanical strength of glass-ceramics was related to the intensity of liquid phase separation. In the glass compositions with low level of metastable liquation (2-8 vol % of the secondary vitreous phase) the compression strength was not high (91-120 MPa); nonetheless, acceptable. The appearance of extended areas with spinodal liquid phase separation in the glass structure (for content of the secondary vitreous phase of about 22 vol %) reduced the mechanical strength (composition No 7), since micro-cracks appeared in the interface of the main glassy matrix and the areas with spinodal liquation. However, the compression strength intensively increased for the compositions that presented spinodal liquid phase separation in all volume of the glass (composition No 8, Fig. 1).

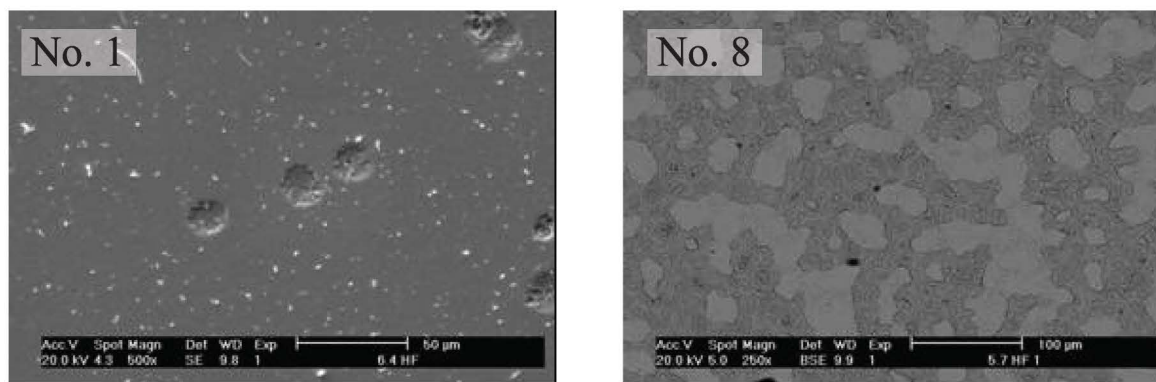


Figure 1. Micrographs of some investigated glasses etched in 3% aqueous solution of HF.

An increase of $[B_2O_3]$ in the glass compositions of the first group (as defined above) influenced very little the chemical resistance to water and alkaline solutions; however, reduced the acid resistance. In the second group, increased $[Al_2O_3]$ reduced the chemical durability, especially for the glass compositions characterized with spinodal liquid phase separation. Taking into account that, in accordance with [11], the secondary glassy phase is characterized with high $[B_2O_3]$, it is possible to assume that this vitreous phase has lower chemical resistance.

4. Conclusions

In the system investigated, the glass compositions characterized with $[B_2O_3] = 7-25$ and $[Al_2O_3] = 16-20$ ($[R_2O_3] = 26-31$) resulted with the optimal combination of exploitation properties which allows their application as dielectrics of the Class I. The compositions with increased contents of Al_2O_3 (up to 24-26) allowed increased mechanical and dielectric properties; however, are characterized with much lower chemical durability.

5. References

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