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CHEMICAL COMPOSITION, STRUCTURE AND PROPERTIES OF GLASS AND GLASS-CERAMIC MATERIALS IN THE SYSTEM OF BaO(PbO)-B_2O_3-Al_2O_3-TiO_2

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Abstract

The vitrification and crystallization of glasses in the system BaO(PbO)-B_2O_3-Al_2O_3-TiO_2 containing (mol %): BaO (24.6-28.1), PbO (2.8-3.2), B_2O_3 (7.6-24.0), Al_2O_3 (15.9-25.5), TiO_2 (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 ºC for 2 h and cast into cylindrical-shaped samples. The obtained glasses were crystallized at 950 ºC for 2h. $BaTiO_3$ was recognized as a dominant crystalline phase in the produced glass-ceramic materials. The influence of B_2O_3 and Al_2O_3 contents on the chemical resistance, mechanical strength and dielectric properties was investigated. It is shown that the glass compositions containing (mol %): B_2O_3 7-25 and Al_2O_3 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 $BaTiO_3$ 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 $BaTiO_3$, 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-Al_2O_3-B_2O_3-TiO_2 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 $BaTiO_3$ [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 Al_2O_3 and B_2O_3, 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 $Ba(NO_3)_2$, PbO, TiO_2, Al_2O_3 and H_3BO_3 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 R_2O_3 oxides, the glass compositions were prepared with similar contents of BaO (24.6-28.1) and PbO (2.8-3.2). [B_2O_3] was varied in the range of 7.6-24.0, and [Al_2O_3] in the range of 15.9-25.5. At the same time, the total contents of R_2O_3 ranged at 26.9-41.2 and were lower than [TiO_2] 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_2O_3]**	**[B_2O_3]**	**Contents of the 2nd glassy phase**	**Contents of $BaTiO_3$ in the glass-ceramics**	**Additional crystalline phases**
1	19.3	7.6	8 (*ms*)*	23.2	$BaO{\cdot}2TiO_2$ $Ba_4Ti_{10}Al_2O_{27}$ $Ba_3Al_{10}TiO_{20}$
2/6	18.6	10.7	6 (*ms*)	28.7	-
3	16.5	14.5	5 (*ms*)	25.3	$Ba_4Ti_{10}Al_2O_{27}$
4	17.2	24.0	2 (*ms*)	25.6	$BaO{\cdot}2TiO_2$ $Ba_4Ti_{10}Al_2O_{27}$
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	$Ba_4Ti_{10}Al_2O_{27}$ $BaAl_2O_4$
8	25.5	9.8	42 (*sp*)	27.9	$Ba_4Ti_{10}Al_2O_{27}$ $BaAl_2O_4$

Table 2. Properties of the glass-ceramic materials produced in the system of $BaO(PbO)$-Al_2O_3-B_2O_3-TiO_2

No	**Contents of R_2O_3, mol.%**		**Strength, MPa**	**Dielectric properties**		**Weight losses in**		
	[Al_2O_3]	**[B_2O_3]**		**ε**	**tan δ**	**H_2O**	**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 [Al_2O_3] of 17.2-19.3 and [B_2O_3] in the range of 7.6-24.0; the second, for compositions 5-8 with similar [B_2O_3] of 9.8-11.1 and [Al_2O_3] 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 [B_2O_3] promoted increased permittivity, especially significant in the compositions with [B_2O_3] > 20 (No 4). In the second group, this characteristics initially increased from 766 (for [Al_2O_3] = 15.9) up to 804 (for [Al_2O_3] = 22.2); however, such values decreased intensively in the compositions with [Al_2O_3] = 25.5. Dielectric properties of glass-ceramic materials produced in the investigated system correspond to the contents of $BaTiO_3$ 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).

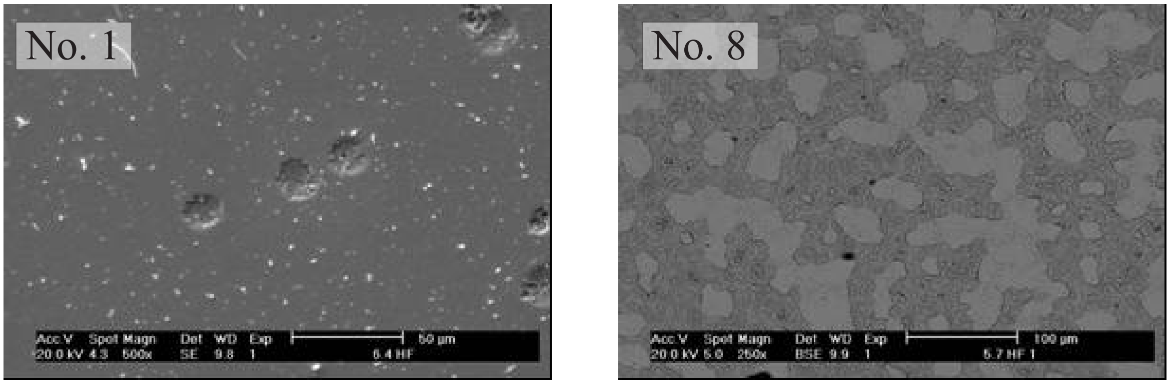

Figure 1. Micrographs of some investigated glasses etched in 3% aqueous solution of HF.

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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