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Glass–ceramic materials with regulated dielectric properties based on the system $BaO–PbO–TiO_2–B_2O_3–Al_2O_3$

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Abstract

Vitrification and crystallization properties of glasses of the system $BaO–TiO_2–PbO–Al_2O_3$ (B_2O_3) were investigated. The fields of vitrification based on ternary diagrams of $BaTiO_3–PbTiO_3–(TiO_2+Al_2O_3+B_2O_3)$ with varied contents of Al_2O_3 (10, 13, 16 mol.%) and B_2O_3 (3, 15 mol.%) were identified. The glass compositions obtained had relatively low melting temperature (≈1450 °C). These stable glasses could be thermally treated to produce glass-ceramics characterized by fine-crystalline structures and regulated permittivity associated to the contents of ferroelectric phases. The phase composition of such glass-ceramics included different $Pb_xBa_{1-x}TiO_3$ solid solutions depending on the starting chemical composition. Permittivity of the obtained materials ($f=800$ kHz, $T=25$ °C) varied from 20 to 680 relatively to the time of crystallization.

Keywords: Crystallization; Ferroelectric properties; Functional applications; Glass; Glass ceramics

1. Introduction

$BaTiO_3$ and $PbTiO_3$ based glass-ceramics have shown great potential in certain electronic applications. The advantages of ferroelectric glass–ceramic materials, such as lower sintering temperature and homogeneous mixing of ferroelectric phases with glass, have been utilized in ferroelectric and piezoelectric applications.[1,2] In the recent years there have been developments of some new pyroelectric and piezoelectric glass-ceramics (for example Refs. 3–6). Nonetheless, most publications in the field of $BaTiO_3$ and $PbTiO_3$ based glass-ceramic materials, are oriented towards to the use of the sol-gel technique.[7–10] However, some applications in electronics require massive pieces of ferroelectric materials with variable dielectric properties and shapes. Such materials could be used to regulate and homogenize fields in microwave furnaces,[11] which demand variable permittivity within a wide range and with low dielectric loses. Previous research on synthesis of glass–ceramic materials in the $BaO–PbO–TiO_2–B_2O_3–Al_2O_3$ system has shown some problems. The glasses of $BaTiO_3$ and $PbTiO_3$ chemical composition with admixtures of glass-forming oxides (Al_2O_3, SiO_2, B_2O_3) tend to crystallize immediately after a quenching, in addition to the high (1550–1700 °C) melting temperatures displayed.[1,12,13] Some relatively stable glasses have been obtained only with high enough concentration of B_2O_3 and PbO.[18,19] The low content of glass–net formers in the investigated compositions and the fast crystallization creates many problems relative to large-sized glass articles production.

The abovementioned situation has promoted research oriented on production of glass–ceramic composites based on blending $BaTiO_3$, or other types of ferroelectric powders, with molten glasses of different compositions ($PbO–B_2O_3$, $PbO–SiO_2$, $Bi_2O_3–B_2O_3$).[14–16] However, such an approach has met the problem of chemical interaction of ferroelectric powders with glass melt, which resulted in a decrease of the fraction of crystalline particles with size below the critical value.[13,17]

Nonetheless, the utilization of the melting–quenching–crystallization technique is promising for the production of samples with high and regulated contents of ferroelectric phases. The research report here presented had the objective of determining the field of vitrification within the systems $BaO–TiO_2–PbO–Al_2O_3$ and $BaO–TiO_2–PbO–B_2O_3$ which would allow the production of stable glasses featuring regulated crystallization, with homogeneous fine-crystalline structures and variable permittivity.

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2. Experimental procedures

The ternary system $BaTiO_3$–$PbTiO_3$–($TiO_2 + R_2O_3$) with mol% contents of Al_2O_3 of 10, 13, 16 and 19 and B_2O_3 of 3, 6, 10, 15 was selected to identify the fields of vitrification in chemical composition diagrams, which permit to specify the role of the BaO/PbO ratio and the contents of glass-formers in the vitrification process, as well as the phase composition of the resulting glass–ceramic materials. The use of BaO and PbO in the form of titanates is convenient to estimate the extreme contents of crystalline phases and to find the ratio BaO:PbO in solid solutions of their titanates.

Aldrich analytic grade (purity > 99%) TiO_2, $Ba(NO_3)_2$, Pb_3O_4, H_3BO_3 and Al_2O_3 were used as raw materials. All compositions were heated in platinum crucibles and soaked at 1450 °C for 2 h, melt samples were obtained by casting into stainless steel moulds.

The regime of glassy specimens crystallization was selected on the base of DTA analysis (Perkin-Elmer DTA-7/DX).

The structure, chemical and phase composition of glass–ceramic materials produced were determined by Scanning Electron Microscopy (Jeol-5800LV) equipped with an X-ray micro-analyzer (EDS-S60 DX90) and also by X-ray diffractometry (Philips X́Pert- MPD). Dielectric measurements were performed on glass–ceramic samples previously ground and polished with SiC slurries with particles down to 0.3 mm. Samples were platinum electroded with masked edges and then silver painted to ensure good electrical contact. A LCR-meter Hewlett-Packard 4274A recorded the capacitance at 800 kHz at 25 °C.

3. Results

The fields of vitrification for different Al_2O_3 contents after fusion of the various compositions at 1450 °C are presented in Fig. 1. The area of glass formation, free from spontaneous bulk or surface crystallization during cooling, was practically the same for Al_2O_3 contents in the range 10–16 mol% and was limited by the following compositions (mol%): $BaTiO_3$ 27–33, $PbTiO_3$ 5–12, $Al_2O_3 + TiO_2 + B_2O_3$ 58–64. At the same time, the field of vitrification with surface crystallization was reduced with increasing contents of Al_2O_3 from 10 to 13 mol%, whereas at 16 mol% Al_2O_3 very intensive surface crystallization took place leaving only a small core of glassy phase. The difference between the samples showing spontaneous bulk crystallization and those showing surface crystallization was the size of crystals and the type of crystalline structure formed. Spontaneous bulk crystallization promoted the formation of gray colored structures with relatively large sized crystals (up to 5 μm) of $Ba_{1.23}Al_{2.46}Ti_{5.54}O_{16}$ and $BaO·2TiO_2$, the formation of pores and micro-cracks was also observed. Intensive surface crystallization resulted in the formation of a fine-crystalline structure of white color (crystals of 90–200 nm) composed of $BaTiO_3$, $PbTiO_3$ and $BaTi(BO_3)_2$ free from large structural defects. The latter this type of glass–ceramic is of little use for the intended application since the crystallization, of the ferroelectric phases, is unregulated, thus its permittivity cannot be controlled

For admixtures of B_2O_3 above 3 mol% it was impossible to obtain transparent glass free from surface crystallization. On this basis the subsequent work concentrated on glasses of BaO-PbO-TiO_2-Al_2O_3 system with 3 mol% of B_2O_3 in order to promote additional stabilization of the glassy structure but without developing surface crystallization.

Glassy samples produced were subjected to DTA analysis to determine the thermal regime in order to regulate the crystallization. Typical DTA scan data is shown in Fig. 2, where it can be noted that the process of crystallization for the BaO–PbO–TiO_2–Al_2O_3 glass system begins at about 640 °C, the main exothermal peaks present in the temperature range of 670–850 °C are related to the formation of different crystalline phases. The phase composition evolution of the glass-ceramics of the composition 1 (mol%: 29 $BaTiO_3$, 17 $PbTiO_3$, 38 TiO_2, 13 Al_2O_3 and 3 B_2O_3 as pointed in Fig. 1) obtained by thermal treatment up to 950 °C for 2 h is presented in Fig. 3. The secondary thermal treatment of cast glass promoted the formation of $BaO·Al_2O_3$ and $BaO·2TiO_2$ crystals at 640–710 °C. Increasing the temperature to 750–850 °C stimulated the crystallization of $PbTiO_3$, and its solid solutions with $BaTiO_3$ that formed the fine-crystalline structure as shown in Fig. 4.

Crystallization of glasses of BaO-PbO-TiO_2-B_2O_3 system takes place only at temperatures above that of glass transition (about 660 °C), as can be observed in Fig. 2.

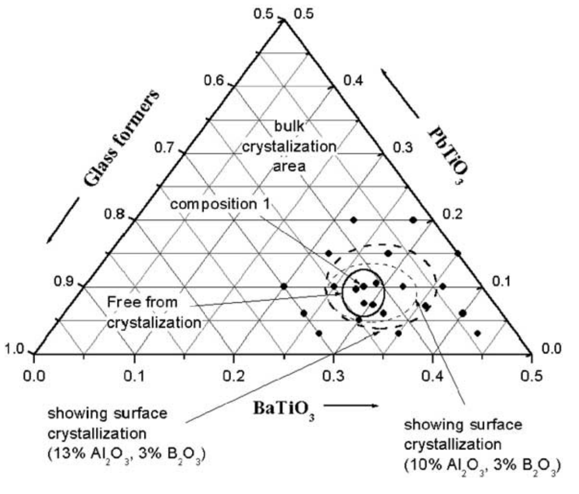

Fig. 1. Chemical composition diagram of the system $BaTiO_3$–$PbTiO_3$–TiO_2–Al_2O_3 showing the fields of vitrification for free from surface and bulk crystallization.

The dielectric constant of glass–ceramic, obtained by regulated crystallization of the glass of composition 1 (Fig. 1), as a function of the time of treatment at 900 °C is presented in Fig. 5. The dielectric losses (tg δ) of the materials investigated changed from 0.01 (glass) to 0.03 (glass–ceramics).

4. Discussion

The results confirmed that glasses of the system $BaTiO_3$–$PbTiO_3$–R_xO_y tend to spontaneously crystallize in bulk and/or surface fashion. In order to inhibit such processes the contents of additional glass-formers in the system must be regulated. Aiming to formulate stable glass compositions, different approaches have been considered in the literature with the problems discussed in the introduction.

The results from this work demonstrated that the combined admixture of Al_2O_3 (13–16 mol%) or B_2O_3 with excess of TiO_2 (as R_xO_y) was successful to synthesize stable glasses with low fusion temperatures. However, in Al_2O_3 free glasses of the system BaO–PbO–TiO_2–B_2O_3 the abundant contents of boro-titanate glass structural units could have favored decreased glass transition temperatures (<650 °C) below that of crystallization (650–750 °C, see Fig. 2); under this conditions the rate of the initial crystallization was insufficiently fast before deformation of the glass articles took place. On the other hand, high concentrations of B_2O_3 (6–15 mol%) promoted surface crystallization.

In this way, it seems that the system $BaTiO_3$–$PbTiO_3$–TiO_2–Al_2O_3–B_2O_3 with relatively small contents of B_2O_3 (2–3 mol.%) is quite acceptable to prepare stable glass with relatively low fusion temperature, acceptable temperature range of regulated crystallization and thus

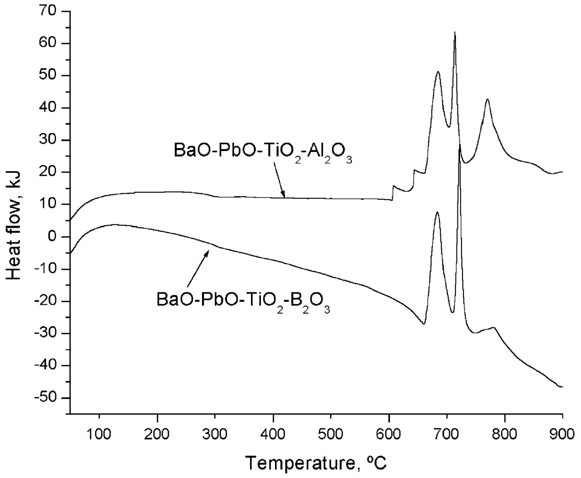

Fig. 2. DTA curves for the glasses of the following chemical compositions (mol.%): $BaTiO_3$(29)–$PbTiO_3$(17)–TiO_2(38)–Al_2O_3 (13)–B_2O_3(3) and $BaTiO_3$(29)–$PbTiO_3$(17)–TiO_2(37)– B_2O_3(15).

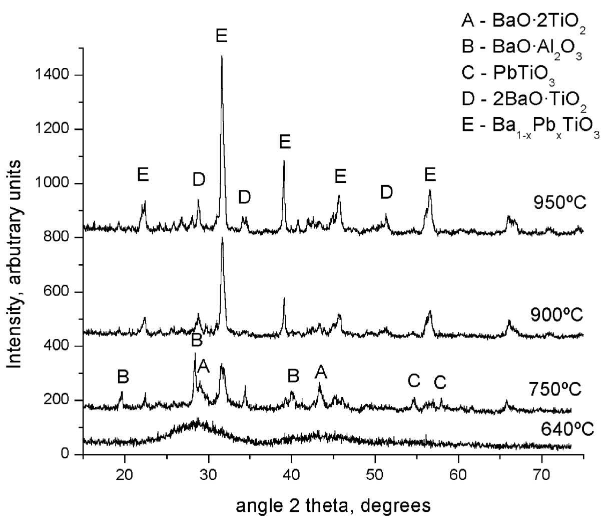

Fig. 3. X-ray diffraction patterns for the glass of composition 1 showing the evolution of crystallization structure as a function of the temperature of treatment.

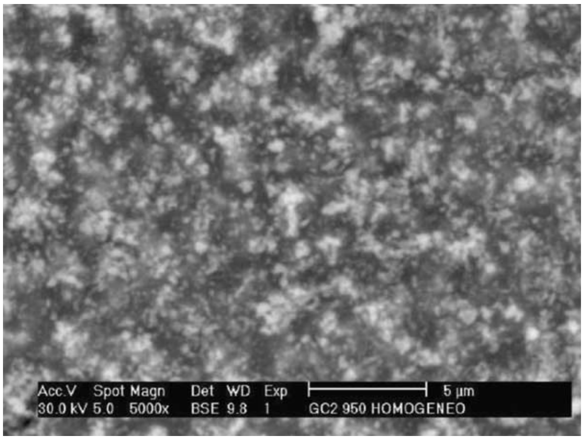

Fig. 4. Scanning electron microphotograph of glass–ceramic material obtained from the glass of composition 1 after the thermal treatment at 950 °C during 1 h.

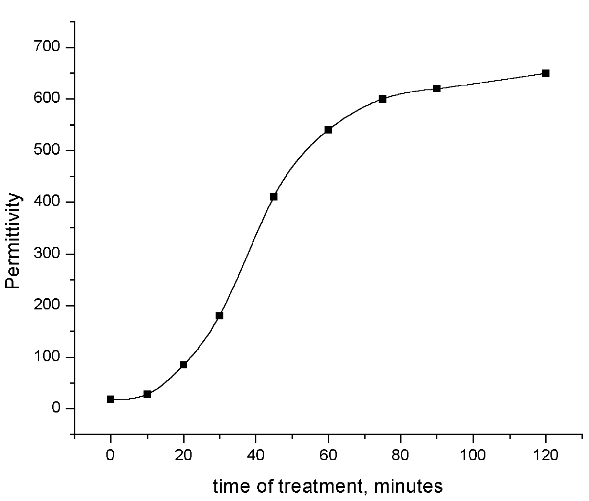

Fig. 5. Permittivity values vs time of crystallization for the glass–ceramics of the composition 1.

potentially controllable crystallization properties. The small additions of B_2O_3 favored the additional stabilization of the glass structure from spontaneous crystallization without stimulating surface crystallization.

The diffractograms obtained for the glass samples of this system after the treatment at 710–850 °C showed reflections typical for $Pb_{1-x}Ba_xTiO_3$ ($x = 0.1$–0.3) and $PbTiO_3$, in agreement with the report by Meng et al.[13] At the same time, after crystallization at 900–950 °C the diffractograms showed stronger reflections of $Pb_{1-x}Ba_xTiO_3$ ($x = 0.4$–0.9).[17] Taking into account the slight modification of the X-ray diffractograms as a result of the variation of the x-parameter in the solid solution of $Pb_{1-x}Ba_xTiO_3$,[17] it was difficult to estimate the values of x by means of this technique. On the other hand, EDS data is not acceptable in view of the nanometric character of the crystalline structure that was formed. Thus, it is only possible to suppose that the use of higher temperatures in the secondary treatment conveniently results in the formation of higher amounts of $Pb_{1-x}Ba_xTiO_3$ solid solutions of higher BaO contents, hence less free $PbTiO_3$. That is important since the presence of $PbTiO_3$ crystals leads to lower structural density (higher dielectric losses) due to the large tetragonality of the crystal lattice,[20] for this reason crystallization at 900–950 °C is preferable.

The size of crystals observed in the glass–ceramics structure obtained by regulated crystallization is quite acceptable for ferroelectric properties since it is above the critical level of 20–60 nm for $BaTiO_3$ and $PbTiO_3$;[9] moreover, the crystal size is also lower than 1500 nm, allowing the formation of structural micro-cracks, which in turn promote an increase of dielectric losses.

By controlling the crystallization time it is possible to obtain glass–ceramic samples with relatively low dielectric losses and variable permittivity in the range 30–650, which would allow its application as elements regulating the intensity fields in microwave furnaces.[7]

5. Conclusions

The glass with the composition (mol.%): $BaTiO_3$ 27–33, $PbTiO_3$ 5–12, Al_2O_3 12–14, B_2O_3 2–3; is characterized by relatively low melting temperature of 1450 °C and allows the production of large sized glassy articles stable from spontaneous crystallization. Secondary thermal treatment of such glasses results in the formation of a glass–ceramic material featuring a fine-crystalline structure (crystal size of 90–200 nm). The variation of the regime of crystallization permits the regulation of the phase composition and properties of glass–ceramics produced.

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