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Thermal expansion of glass–ceramics in the system $BaO/Al_2O_3/B_2O_3$

Diana Tauch, Christian Rüssel *

Otto-Schott-Institut, Jena University, Fraunhoferstrasse 6, D 07743 Jena, Germany

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Abstract

Glasses in the system $BaO/Al_2O_3/B_2O_3$ with and without the addition of platinum were melted. In one sample series, the BaO-concentration was varied while the ratio $[Al_2O_3]/[B_2O_3]$ was kept constant. In another sample series, the $[BaO]/[Al_2O_3]$-ratio (= 0.9) was kept constant and the B_2O_3 concentration was varied. The samples were thermally treated at 720 °C for 24 h and subsequently at 780 °C for 4 h. In most thermally treated samples, the crystalline phase $BaO \cdot Al_2O_3 \cdot B_2O_3$ occurred. At some compositions, the platinum-doped samples showed larger concentrations of the crystalline phases. The most remarkable property of the obtained glass–ceramics is their zero or negative thermal expansion coefficient. Here, notable differences were observed: samples with fine grained microstructures showed thermal expansion coefficients approximately zero up to temperatures of around 80 °C. By contrast, samples with coarser microstructures and large spheroidal crystals exhibit negative expansion coefficients up to temperatures of around 280–375 °C. The thermal expansions of these samples were close to those of the mean thermal expansion of the unit cell of the $BaO \cdot Al_2O_3 \cdot B_2O_3$ phase. The thermal expansion of the fine grained samples was approximately equal to that of the crystallographic *a*-axis of the $BaO \cdot Al_2O_3 \cdot B_2O_3$ phase.

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1. Introduction

Recently, it has been shown [1,2] that glass–ceramics in the system $BaO/Al_2O_3/B_2O_3$ may possess negative thermal expansion coefficients. This is due to the crystalline phase $BaO \cdot Al_2O_3 \cdot B_2O_3$ which, as shown by high temperature X-ray diffraction, possesses a strongly negative expansion coefficient in the direction of the crystallographic *c*-axis while it is slightly negative with respect to the *a*-axis [1]. Glass–ceramics with zero thermal expansion coefficients are of great economic importance [2–5], especially with respect to cook top panels [3,4] and numerous applications in micromechanics. These glass–ceramics are industrially produced from $Li_2O/Al_2O_3/SiO_2$ glasses. The crystalline phases formed are β-eucryptite or keatite [6,7]. The glasses the glass–ceramics are made from require high melting temperatures (>1650 °C). The ceramization must be carried out with high temperature accuracy and requires high temperature homogeneity.

The system $BaO/Al_2O_3/B_2O_3$ has first been described by MacDowell [8], here already a comparably small thermal expansion coefficient was reported. Glass–ceramics with zero expansion coefficients based on other systems have scarcely been described in the literature. Recently, the crystallization of the bulk glass, the behavior during sintering of glass powder and the effect of platinum as nucleating agent, as well as the resulting thermal expansion in this system have been reported [1,9]. Here, a notable effect of the preparation procedure and hence the microstructure on the thermal expansion was reported. This is due to the strongly anisotropic thermal expansion coefficient of the rhombohedral phase $BaO \cdot Al_2O_3 \cdot B_2O_3$ which is strongly negative in the direction of the crystallographic *c*-axis.

* Corresponding author. Tel.: +49 3641 948 501; fax: +49 3641 948 502.
E-mail address: ccr@rz.uni-jena.de (C. Rüssel).

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With respect to the *a*-axis, the thermal expansion is approximately zero up to 150 °C and then gets positive. Depending on the preparation procedure, glass–ceramics are obtained which thermal expansion coefficients are zero or, however, negative at room temperature.

In this paper, the crystallization of non-stoichiometric glasses as well as the resulting thermal expansions are described.

2. Experimental procedure

The glasses were melted from reagent grade $BaCO_3$, $Al(OH)_3$ and $B(OH)_3$ at 1500 °C in a platinum crucible. The melt was stirred for 1 h with a platinum stirrer, casted on a steal mould, and then given to a furnace, preheated to 620 °C. Subsequently, the furnace was switched off and the sample allowed to cool. Table 1 summarizes the chemical compositions of the prepared samples. In sample series A to E, the $[Al_2O_3]/[B_2O_3]$-ratio was kept constant (= 1) and the BaO-concentration was stepwise decreased. Sample F is attributed to a [BaO]/$[Al_2O_3]$-ratio of 1 and an increased B_2O_3-concentration. In sample G, 3.3 mol% BaO was replaced by B_2O_3. The resulting [BaO]/$[Al_2O_3]$-ratio (= 0.9) was then kept constant while the B_2O_3-concentration was further increased (sample H and I). As proved by chemical analysis (inductive coupled plasma B_2O_3 evaporation was below 2 mol%. From any obtained glass, a part was thermally treated at 720 °C for 24 h and subsequently at 780 °C for 4 h, using heating and cooling rates of 10 K/min. This temperature time schedule was chosen according to Ref. [1].

Another part was crushed into pieces <1 mm and then mixed with a $PtCl_4$ acetone solution in order to obtain a Pt-concentration of 0.01 wt%. Sample G was also prepared with Pt-concentrations of 0.005 and 0.02 wt%. The mixture was then homogenized, dried, remelted at 1480 °C and stirred at 1480 °C for 30 min. Then the melt was casted and cooled as described above. In the following platinum containing samples are denoted e.g. as 'sample A_{Pt}', those without platinum e.g. as 'A'.

The glasses were characterized by dilatometry (Netzsch 402E). Crystallized samples were studied by X-ray diffraction (Siemens D5000). The thermal expansion coefficient of crystallized samples was measured by dilatometry (Netzsch 402E), densities were measured with a helium pycnometer (Accupyc 1330). The microstructures of the thermally treated samples were characterized by optical microscopy.

3. Results

Glass transformation temperatures, T_g, and softening temperatures, T_D, of the glassy samples studied are summarized in Table 1. The decrease in the BaO-concentration results in an increase in both T_g, and the softening temperature. Increasing the B_2O_3-concentration results in a decrease of T_g and T_D. The densities of the glassy samples are summarized in Table 1, column 7. They are all in the range from 3.19 to 3.45 g cm^{-3}. Samples with higher BaO-concentrations show larger densities.

Fig. 1 shows XRD-patterns of crystallized samples. In the patterns of samples A, I and I_{Pt} low intensities lines

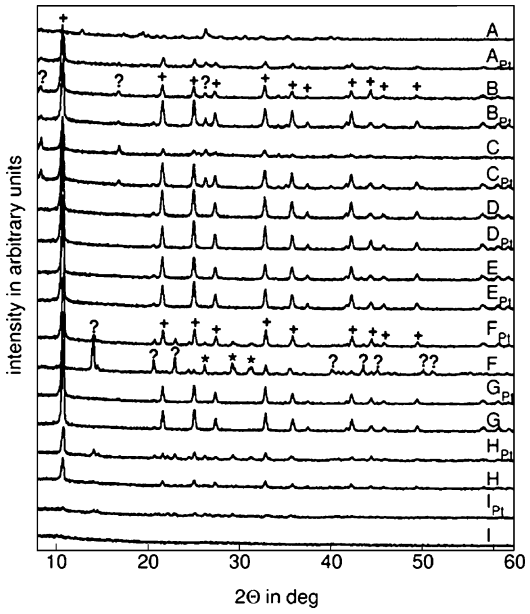

Fig. 1. XRD-patterns of the samples A to I and A_{Pt} to I_{Pt}.

Table 1
Chemical composition (in mol%), glass transformation, softening temperature and densities of the prepared glasses, densities and thermal expansion coefficients of the prepared glass–ceramics

Sample	[BaO]	$[Al_2O_3]$	$[B_2O_3]$	T_g (°C)	T_D (°C)	Density (g cm^{-3})			α (10^{-7} K^{-1}) (100–300 °C)	
						Glass	Glass–ceramics	Pt–glass–ceramics	Glass–ceramics	Pt–glass–ceramics
A	35.5	32.25	32.25	573	634	3.45	3.44	3.29	–	44
B	33.3	33.3	33.3	585	660	3.37	3.10	3.10	−12	19
C	32.3	33.9	33.9	600	667	3.34	3.29	3.07	–	21
D	31	34.5	34.5	600	660	3.33	3.07	3.06	7	−6
E	28.6	35.7	35.7	604	674	3.24	3.05	3.10	26	24
F	32.1	32.1	35.7	566	642	3.33	3.20	3.12	–	−8
G	30	33.3	36.7	585	644	3.25	3.07	3.06	24	16
H	29.3	32.7	38	583	641	3.23	3.20	3.15	–	13
I	28.3	31.7	40	574	629	3.19	3.17	3.15	–	–