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Effect of BaO addition on the structure and microstructure of SiO_2–Al_2O_3–Na_2O–K_2O–MgO glass–ceramic composites

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Abstract

We examined the influence of barium oxide addition on the structure and properties of SiO_2–Al_2O_3–Na_2O–K_2O–MgO glass–ceramics. Glass–ceramics were prepared with constant SiO_2/Al_2O_3 and Na_2O/K_2O ratios of 6.5 and 1.04, respectively, and the MgO content was maintained at 10.56 wt%. The barium oxide content was set at 4 wt%, 9 wt%, and 14 wt%. The weight ratios were recalculated from the $BaCO_3$ added. To determine the microstructure of the glassy materials, scanning electron microscopy–energy dispersive spectroscopy (SEM–EDS), X-ray diffraction (XRD), medium (MIR) and far infrared analysis (FIR), and Raman spectroscopy were used. Significant differences were observed in the phase composition and in the silica–alumina-oxide network of the glassy phase, which could be related to changes in the amount of barium oxide. The characteristic temperatures (beginning of sintering, sphere, half-sphere and melting), which were measured by using hot stage microscopy and dilatometry, also showed changes.

Keywords: B. Microstructure; B. Structure; D. Glass–ceramic; Phase; Crystallinity

1. Introduction

Glass–ceramic composite materials are characterized by the presence fine crystalline structures within the fully dense glassy phase [1–3]. The amount of the crystalline phase may vary from 0.5 to 98 vol%; however, usually their content varies from 30 to 70 vol%. The initial oxide composition and the thermal treatment determine the type and quantity of the crystalline phase produced and the chemical composition of the glassy phase bonding the crystallite grains [2,3]. The final phase composition determines the functional properties of the obtained glass–ceramic composites. Here, we report the effect BaO addition on the microstructure and thermal properties of SiO_2–Al_2O_3–Na_2O–K_2O–MgO glass–ceramic composites. The main components, i.e., silica and alumina, form a primary alumino-silico-oxide microstructural network, which is modified by the presence of the alkali metal oxides, Na_2O and K_2O and the alkaline earth oxide, MgO [4–6]. The SiO_2/Al_2O_3 ratio determines the characteristic temperatures such as temperatures of softening and of sphere and of half sphere formation [1,7] of the glass–ceramic materials and therefore, their applications. Characteristic temperatures may be changed by introducing alkaline metal oxides, such as Na_2O and K_2O (low- and medium-temperature fluxing agents) or alkali earth metal oxides MgO, BaO, which are medium and high-temperature fluxing agents. [5–7] Alkali metal oxides Na_2O and K_2O form eutectics with other oxides which enables the melting temperatures to be reduced below 1000 °C [1,2,4]. In the system SiO_2–Al_2O_3–K_2O can be found oxide compositions having a melting at 770, 975 or 1045 °C. In the system SiO_2–Al_2O_3–Na_2O, there are points having melting temperatures of 732 and 740 °C [23]. Similarly, sodium feldspar albite and potassium feldspar orthoclase have an eutectic point with melting temperature at 1063 °C.

MgO is a refractory material with a high melting point of approximately 2800 °C. In the presence of SiO_2, MgO participates in the formation of a liquid phase from ~1170 °C. However, in the presence of alkali metal oxides with which MgO forms eutectics, the process can start below

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1000 °C [5,6]. An increase in the MgO content results in the increased viscosity of the vitreous phase, which influences diffusion processes in the alloy and, in turn, the crystallization process [1,2,6,15]. MgO also reduces the thermal expansion coefficient, resulting in higher resistance to rapid temperature changes. A greater amount of MgO may induce crystallization of solid phases, such as forsterite, cordierite, diopside, and protoenstatite [1,2,6,15].

Barium oxide is the only fluxing agent in the system, which is active in small amounts only at temperatures exceeding 1250 °C. In the presence of alkali metal oxides, BaO begins to co-form the liquid phase below 1000 °C, which is similar to its role in the SiO_2–BaO–K_2O system at 907 °C [6–8] and in the SiO_2–BaO–Na_2O system at 785 °C [6,7]. Further, the addition of BaO effectively improves the mechanical performance and chemical resistance of the glass–ceramic composites [6,7,22].

2. Experimental procedure

In this work, the SiO_2–Al_2O_3–Na_2O–K_2O–MgO + BaO glass–ceramic composite system was used. The CaO/MgO molar ratio was fixed at 0.04; consequently, MgO was the major component (nearly 100 wt%). Barium oxide was then introduced into the system at 4 wt%, 9 wt%, and 14 wt%. These values were recalculated on the basis of the amount of barium carbonate added as the raw material. Other raw materials included were sodium feldspar (Na600) and potassium feldspar (K600) (supplied by SIBELCO), quartz (MK40, sourced from the SKSM Sobótka), kaolin (KOC, SURMIN), talcum A10H from Luzenac, and barium carbonate ($BaCO_3$, supplied by Avantor Polska). Then, each batch was milled using a planetary mill to obtain a residue of approximately 1 wt% through a 56 μm sieve, which was then dried to obtain the raw powder. Each raw powder was examined by hot stage microscopy (HSM) to determine the various characteristic temperatures. Then, raw materials were fired in porcelain crucibles in a single cycle at a maximum temperature of 1230 °C for 14 h. Samples for scanning electron microscopy (SEM) and Raman spectroscopy were prepared by slicing out cubes from the fired material. The cubes were then polished to obtain the samples with dimensions $10 \times 10 \times 6$ mm^3. Samples for structural examination and chemical analysis were prepared by grounding the material in an agate mortar to obtain a powder with grain sizes lower than 63 μm.

Chemical analysis was carried out using a wavelength dispersive X-ray fluorescence (WDXRF) spectrometer Axios mAX, Phillips-PANalytical (Table 1). All the characteristic temperatures were determined by HSM on a Misura 3 microscope, EES Expert System Solution S.r.l. (Table 2). The internal structure of the samples was analyzed by X-ray diffraction XRD, PANalytical X-ray diffractometer X'Pert Pro for phase composition determination (Table 3, Fig. 1), SEM Nova Nano SEM 200 with an energy dispersive spectrometer microanalyzer EDS-EDAX (Figs. 1–7), mid-infrared MIR, 4000–400 cm^{-1} and far-infrared FIR, 400–40 cm^{-1} analyses carried out on a Bruker Vertex 70v spectrometer (Figs. 8 and 9), Raman spectroscopy with excitation was carried out with Ar^+ (514 nm) and He–Cd (325 nm) lasers, Jobin Yvon (Fig. 10).

Table 1
Oxide compositions of the tested glazes (wt%).

SiO_2	Al_2O_3	CaO	MgO	$Na_2O + K_2O$	BaO	SiO_2/Al_2O_3
70.92	11.04	0.42	10.85	6.78	0	6.42
67.65	10.55	0.43	10.64	6.88	3.85	6.41
64.58	10.11	0.46	10.27	6.70	7.88	6.39
59.03	9.15	0.38	10.48	6.75	14.20	6.45

3. Results and discussion

The oxide composition of the glass–ceramic materials with and without barium oxide was analyzed to verify whether the introduction of various amounts of barium oxide would be the only factor influencing changes in the phase composition and the structure of this material.

The presence of a very small amount of calcium oxide can be attributed to the addition of materials, such as feldspar and kaolin, which contain a small amount of CaO. Barium oxide was gradually introduced in amounts close to the assumed values of4 wt%, 9 wt%, and 14 wt%.

Characteristic temperatures describe the behavior of the ceramic materials during heat treatment. The HSM measurement technique is particularly suitable for designing the firing curves. Using this technique, various characteristic temperatures, such as sintering, sphere, hemisphere, and full melt temperatures, which are related to the increase in the amount of the liquid silica–alumina phase, can be measured. Measurements using HSM are compatible with the ISO 540:1995 and DIN 51730-1998 standards. Using dilatometric measurements, two other characteristic temperatures, including the transformation temperature (T_g) and dilatometric softening temperature (T_d), can be obtained. T_g characterizes the transition from an elastic brittle state to a viscous glassy state and corresponds to a dynamic viscosity of the order of 10^{13} Pa s. T_d is the temperature at which the length of a sample in the dilatometer, with a considerable external force applied to the sample during heating at a constant rate, reaches a maximal value and begins to decrease with further increase in temperature. The appearance of a maximum on the dilatometric curve can be correlated with the parallel influence of sample dilatation with increasing temperature and sample deformation due to the viscous flow. The position of the maximum can correspond to a particular viscosity of the studied glass. Usually, this viscosity is assumed to be equal to the dynamic viscosity 10^{11} Pa s. All the characteristic temperatures are shown in Table 2. The inclusion of BaO to the SiO_2–Al_2O_3–Na_2O–K_2O–MgO glass–ceramic system significantly increased the T_d, sintering temperature, and sphere formation temperature, while the hemisphere and melting points only marginally increased.

In contrast, BaO strongly reduces T_g, the transition point from solid to liquid state, which can be attributed to the reduction in the viscosity of the glassy phase formed during heating and to the increase in the BaO content in the presence