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Densification of glass powders belonging to the CaO–ZrO_2–SiO_2 system by microwave heating

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Abstract

Densification and microstructural changes of two glassy compositions belonging to the wollastonite and zirconia stability fields in the ternary CaO–ZrO_2–SiO_2 system were studied in a 2.45 GHz multimode microwave cavity. The effect of microwaves is to lower the sintering and devitrification temperature with stronger influence for high zirconia content composition. Correlation was found between dielectric properties and heating rate, showing lower interaction temperature for high zirconia content composition which starts to absorb microwave energy at about 400°C compared to 800°C for the low-zirconia one. Sintering and crystallization processes evolved in complex ways during heat treatment so that the two final glass-ceramic materials exhibit different microstructures, crystalline phases and mechanical properties. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Sintering; Microwave sintering; Glass-ceramics; Microstructure-final; CaO–ZrO_2–SiO_2

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1. Introduction

Recent advances in microwave processing of materials has opened a new area of research in materials science and engineering. A variety of microwave processed materials have been studied.[1] The research areas include the basic theory of the interaction between microwave and materials, microwave sintering, joining, drying, and synthesis, microwave remediation of nuclear and hazardous waste, modeling of microwave processing, system design, dielectric property measurement, and so on. The main interest in microwave processing lies in discovering new ways to utilize the microwave energy as an alternative in materials processing to substantially save time and energy consumption, and to significantly improve specific properties of the products.

Although microwave processing of various ceramic materials has already been thoroughly studied, there are many important materials which are still unexplored, and research on new materials or improvement of existing ones is endless. Microwave processing of numerous ceramic materials has been investigated, but the interest has been focused mostly on crystalline ones. On the other hand, up to now the research on microwave processing of non-crystalline or amorphous inorganic solids, such as glasses gels, and low crystallinity solids has been very limited.

In a previous study [2] authors compared conventional and microwave heating of the understudied systems and showed that the main advantages (higher density and shrinkage of the treated samples) of microwave heating became evident at soaking temperatures lower than 1000°C. Hence, the main objectives of this work are the evaluation and understanding of microwave effect on sintering, crystallization and other related phenomena occurring during microwave processing of two glassy powders belonging to the CaO–ZrO_2–SiO_2 system, which contain different amounts of ZrO_2. Characterization covers various testing techniques concerning dielectric properties at high temperature, density, densification behavior, microstructure and mechanical properties of glass-ceramics products.

2. Experimental procedure

The studied glassy compositions belong to two different stability fields, wollastonite, $CaSiO_3$ and zirconia, ZrO_2, of the ternary CaO–ZrO_2–SiO_2 system [3] corresponding to

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the following compositions (wt%) A-glass, CaO 33, ZrO_2 12, SiO_2 55 and B-glass CaO 32, ZrO_2 16, SiO_2 52.

The carefully mixed raw materials, calcite (54,5%CaO), quartz (100%SiO_2), and zirconium silicate (64%ZrO_2, 36%SiO_2), were melted in platinum crucibles in an electric melting muffle furnace at about 1500°C for 30 min. The melts were quenched in water to obtain amorphous frits.

The frits were ground using an agate mortar and sieved to obtain a powder with a grain size of less than 45 μm. A 5 wt% water solution of polyvinyl alcohol was added to the powders which were then pressed at 35 MPa to obtain small pellets of 15 mm diameter and 5 mm thickness.

The sintering and devitrification behavior of the compositions was studied by performing a series of heat treatments in a microwave oven according to the indications from the dielectric properties measurements performed at high temperature on the glassy powders. The heating rate was performed at 100°C/min from room temperature to the firing temperature (900, 950, 1000, 1050°C) followed by 20 min soaking time and then cooling down to room temperature extracting the samples from the oven.

The measurements of the dielectric properties at high temperature were obtained by using the resonant cavity technique which employs the determination of the changes in the resonant frequency and Q-factor of the cavity. Detailed description of the apparatus and technique used at Nottingham University are reported elsewhere. [4]

A 900 W, 2.45 GHz commercial microwave oven (Panasonic mod. 6371NN) was used in this study after temperature calibration and measurements reproducibility. [5] Since the interaction between microwaves and materials is strongly dependent on the properties of the materials and since we worked with glasses with intrinsically low dielectric losses at low temperature, a sintering packet was made for an efficient microwave heating. The sintering packet (Fig. 1) consists of a crucible, zirconia cylinder, molybdenum disilicide rods, and thermal insulation Duraboards TM3000. The crucible is also made of the same board. The zirconia cylinder vertically surrounding the samples acts both as a microwave susceptor (microwave-absorbing material) and as a thermal insulator. Being a microwave susceptor, it absorbs and converts microwave energy to heat, thus, preheating the sample to the critical temperature at which the glasses start to absorb microwaves remarkably. In this study, temperature was measured by a platinum-shielded S-type (Pt-Pt10Rh) thermocouple, properly grounded to the metallic wall of the microwave cavity. This avoids the interference of microwaves with the electromotive force of the thermocouple that makes the temperature readings random or erroneous, before the temperature rises to such a level that microwaves are efficiently absorbed by the workpiece. Since the samples are under a constant and relatively rapid rotation mode, and the thermocouple is stationary, it is not practical to allow the tip of the thermocouple in contact with the samples. To solve this problem, a small piece of alumina or of the material being processed, is attached with the shielded tip of thermocouple, so that the temperature measured by the thermocouple is the temperature of the material and not that of the air in the vicinity of the specimen. Furthermore, since the tip of the thermocouple is very close to the surface of the sample, the measured temperature can be assumed very close to that of the specimen.

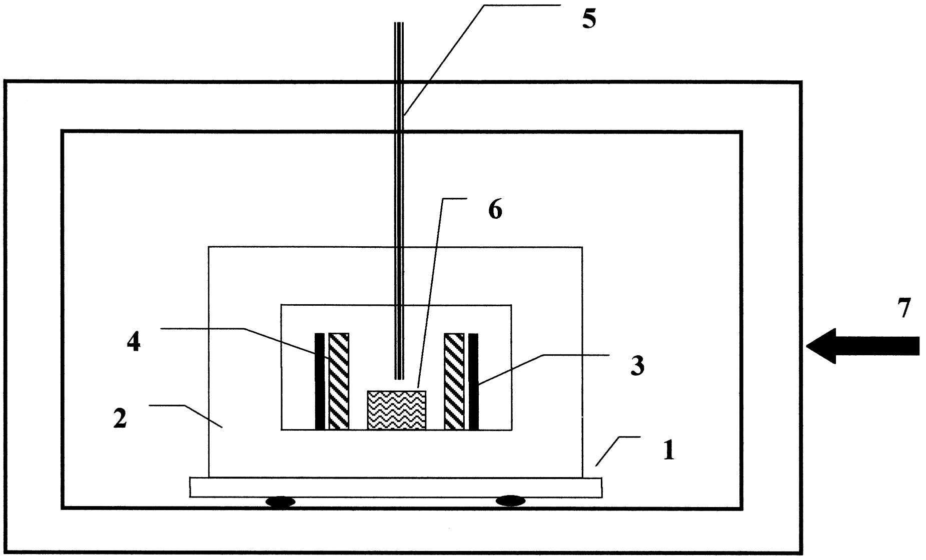


Fig. 1. Schematic design of microwave oven: 1 Turntable, 2 Fibermax Insulator, 3 $MoSi_2$ rods, 4 Zirconia Cylinder, 5 Thermocouple, 6 Sample, 7 Microwave port.

The density of the sintered materials was measured by using the Archimede's method. Further measurements of linear shrinkage were performed.

Small pieces of the crystallized materials were mounted in epoxy resin and superficially polished down to 0.3 μm alumina paste. Successively the resin surface was coated with a thin film of Au/Pd in order to observe the morphology and the densification degree of the samples by scanning electron microscopy, (SEM) (Philips XL 40) equipped with X-ray energy dispersion spectrometer (EDS) (EDAX 9900). To detect and identify the crystalline phases formed during the heat treatments, X-ray diffraction (XRD), was performed. Patterns were collected using a powder diffractometer (Philips PW3710) with Ni-filtered Cu $K\hat{\alpha}$ radiation in the 2Θ range from 10 to 50°. For each samples, room temperature Vickers microhardness measurements (Matsusawa DMH-2) were made using 50 g load with a 15 s dwell time.

3. Results and discussion

Fig. 2 shows tan δ versus temperature plot for both A and B-glass glassy powders. The two patterns are qualitatively quite similar, showing a sharp dielectric loss increase at temperatures $> 800°C$ for A-glass and $< 400°C$ for B-glass. The ZrO_2 content and the ionic mobility of the modifier ion (Ca^{2+}) can be considered mainly responsible for the interaction between the microwave field and the material. Very likely the B-glass absorbs microwave energy at a lower temperature because it contains more a suscepting additive, ZrO_2, than the A-glass; whilst at higher temperatures the glass viscosity decreases, more rapidly in A-glass, this way enhancing ion mobility. The Ca^{2+} ion is more mobile with respect to the Si^{4+} and Zr^{4+} ions and A-glass shows a higher amount of CaO. At temperatures higher than 1100°C it becomes evident the existence of some modifications in the glassy samples, mainly crystallization, which affects the tan δ curve in both compositions.

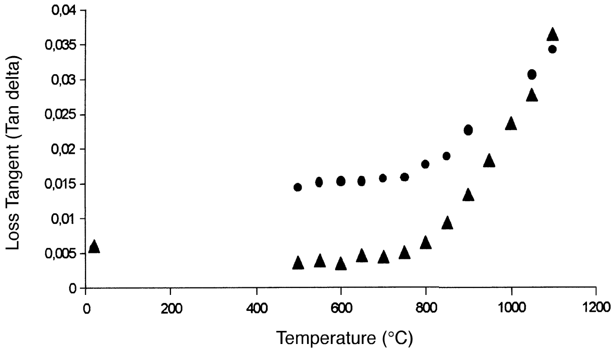


Fig. 2. Tan δ vs temperature of glasses at 2.21 GHz: (▲) A-glass; (●) B-glass.

From the above mentioned observations, it is possible to suppose that B-glass composition will present an early densification process with respect to A-glass, when subjected to microwave irradiation. Such hypothesis was confirmed in Fig. 3, where B-glass presents a remarkable linear shrinkage with respect to A-glass at lower temperature. At higher temperature B-glass presents a negligible expansion while in A-glass no evident change is observable. These results agree with the apparent density data obtained from Archimede's method (Table 1). For sintering temperature of about 950°C both samples are strongly densified, whilst at higher temperature a small density reversion phenomenon—i.e. density decreasing value with increasing sintering temperature—was observed.

In Fig. 4 the crystallization evolution of the samples at different temperatures is reported. A-glass at the lowest temperature, 900°C, is completely amorphous, as confirmed by the presence of a single broad band typical of glassy materials. Increasing the temperature, the sample devitrifies forming wollastonite, $CaSiO_3$ (ICDD file no. 10489), as single crystalline phase presents in this composition for all the temperatures. As regarding B-glass a very different crystal evolution was observed: already at 900°C the XRD pattern reveals the presence of a crystalline phase, identified as calcium zirconium silicate of stoichiometry $2CaO{\cdot}4SiO_2{\cdot}ZrO_2$ (ICDD file no. 39194), which remains the main crystalline phase up to 1050°C. At about 1000°C a secondary crystalline phase, wollastonite, appears.

Microstructural evolution has been studied using electron microscopy following either morphological changes or densification behavior with increasing temperature.

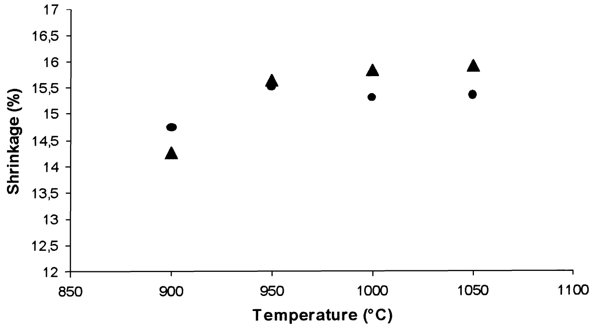


Fig. 3. Linear shrinkage of the samples during heat treatments: (▲) A-glass; (●) B-glass.

Table 1
Density (g/cm^3) data of materials after densification

Temperature (°C)	A-glass	B-glass
900	2.699	2.866
950	2.894	2.909
1000	2.886	2.902
1050	2.887	2.900

The microstructural differences between A and B glass-ceramic materials treated at 900°C are presented in Fig. 5. Fig. 5(a) shows grains with an interconnected morphology indicating the first stage of sintering, during which neck formation occurs. [6] B-glass [Fig. 5(b)] presents a more compacted microstructure with close porosity (pore size of about 5 μm) indicating the final sintering stage. These results are strictly related to those obtained by high temperature dielectrics properties measurements, according to which the zirconia richer composition by reaching the critical temperature at about 400°C, heats up internally sooner than A-glass, hence showing an advanced sintering stage. Not only could internal heating be an explanation for faster sintering, but for the presence of closed porosity. According to some authors [7] in fact, closed pores are considered sites of enhanced material transport and, therefore, more efficiently removed than open ones.

At around 950°C, also A-glass-ceramic reaches the final stage of sintering presenting a round shaped porosity with values of only a few points percentage (Fig. 6). Some microstructure was observed in the 1000°C treated samples, while at 1050°C a slight increase in porosity is observed, A-glass-ceramic being more porous (pore size 20 μm) (Fig. 7) compared to B-glass-ceramics. This sintering behavior is a clear indication that the concurrent phenomenon of crystallization is the dominating one at 1050°C in both glass–ceramic compositions. Due to the migration of some of the elements contained into the residual glassy phase towards crystals during crystallization, the amorphous phase content decreases thus causing a possible lowering in the values of some of the tested properties.

Closer observations of the crystallization process was performed at higher magnifications (2500X) using high contrast BSE images (Fig. 8). At 900°C B-glass-ceramic already shows the formation of acicular crystals, more or less 1 μm long, arranged in a star shape [Fig. 8(a)]. These crystals, brighter in colour than the remaining glass, are richer in zirconia and are positioned on the surface of the remaining glassy grains.

It is possible to explain the formation of these crystals by diffusion of zirconia from the glass to the grain surface/

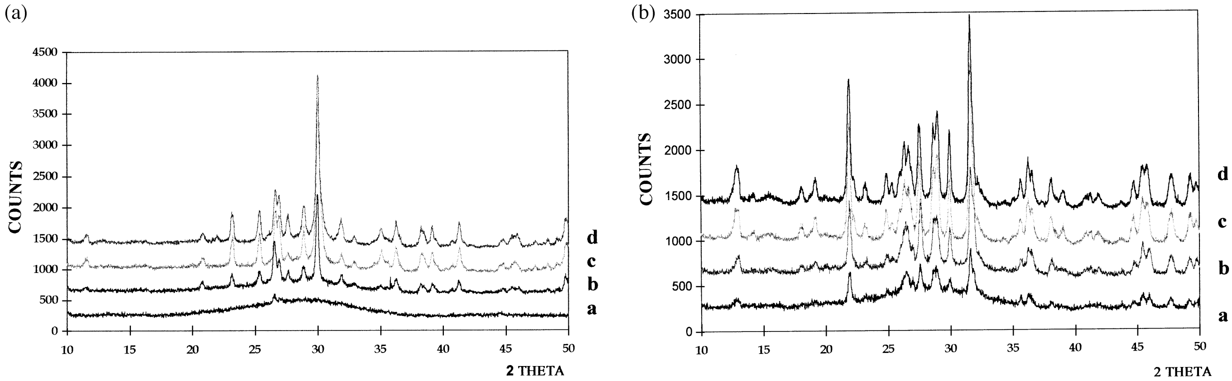
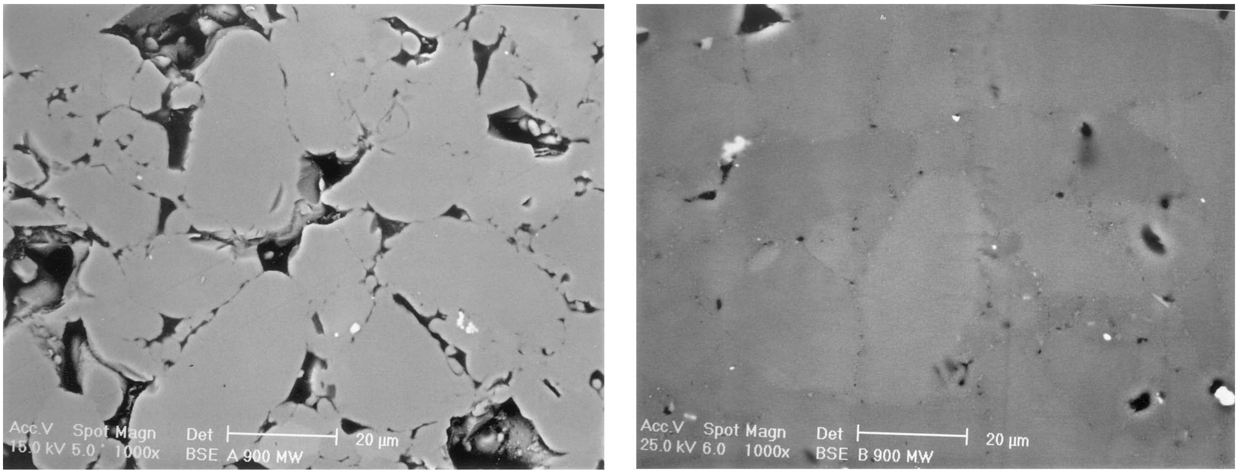


Fig. 4. XRD patterns of A-glass (a) and B-glass (b) samples treated at: (a) 900, (b) 950; (c) 1000 and (d) 1050°C.



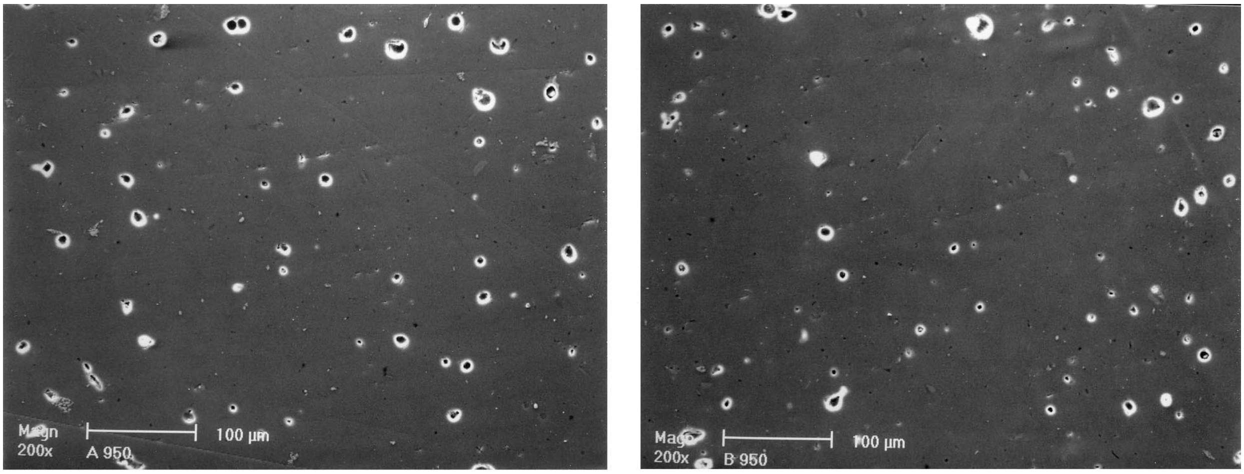
(a) (b)

Fig. 5. SEM micrographs of materials sinterized at 900°C: (a) A-glass; (b) B-glass (1000X).

interface, [8] also considering the observations of some authors on microwave sintering: high temperature zones formation, occurring during microwave sintering, is responsible for the zirconia migration and the formation of the surface/interface of all grains in the sintered compact. The existence of "hot-spots" is caused by heterogeneous density distribution in the sample pellets. Obviously also the theory of heterogeneous crystallization of glass concurs to explain the observed phenomena. [9] The crystalline evolution is very different from the A-glass-ceramic samples to the B-glass-ceramic ones even if experimental conditions are exactly alike (powder size distribution, heat treatment, etc.), and this can hence be attributed mainly to composition differences.

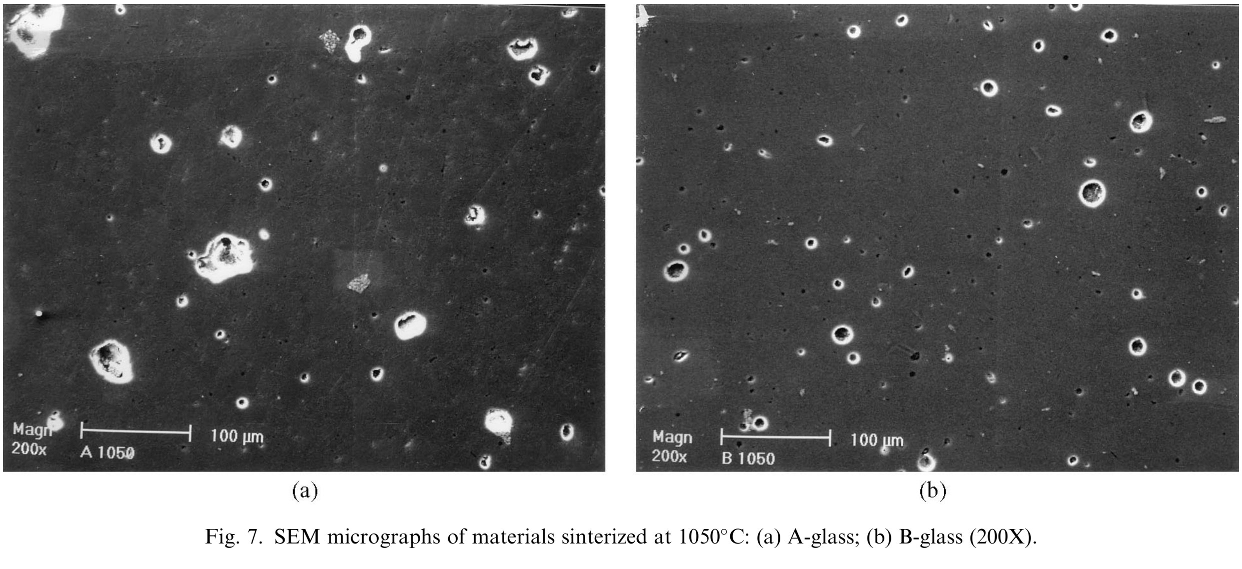
As far as the microstructure at 1000°C is concerned it was possible to observe a complete crystallization for B-glass-ceramic [Fig. 8(b)]. The outer perimeter of the initial grain is still visible, evidenced by the star-like small white acicular crystals rich in ZrO_2. A second crystalline phase, wollastonite (as confirmed from EDS and XRD analyses) with needle-like crystals of approximately 10 µm is separated from the glass, which is almost absent. The formation of the wollastonite crystals indicates a surface-to-inside direction of grain growth with glass depletion in the center of the grains leading to a mechanically weak structure. A-glass-ceramic microstructure [Fig. 8(c)] shows small dendritic crystals of wollastonite of about 5 µm in length, confirming XRD results, evenly distributed in a residual glassy matrix.

Microhardness values are higher for B-glass samples with respect to A-glass samples for all thermal treatments (Table 2). This result is due to the higher zirconia content in B-glass, that improves the mechanical properties. [10]



(a) (b)

Fig. 6. SEM micrographs of materials sinterized at 950°C: (a) A-glass; (b) B-glass (200X).



(a) (b)

Fig. 7. SEM micrographs of materials sinterized at 1050°C: (a) A-glass; (b) B-glass (200X).

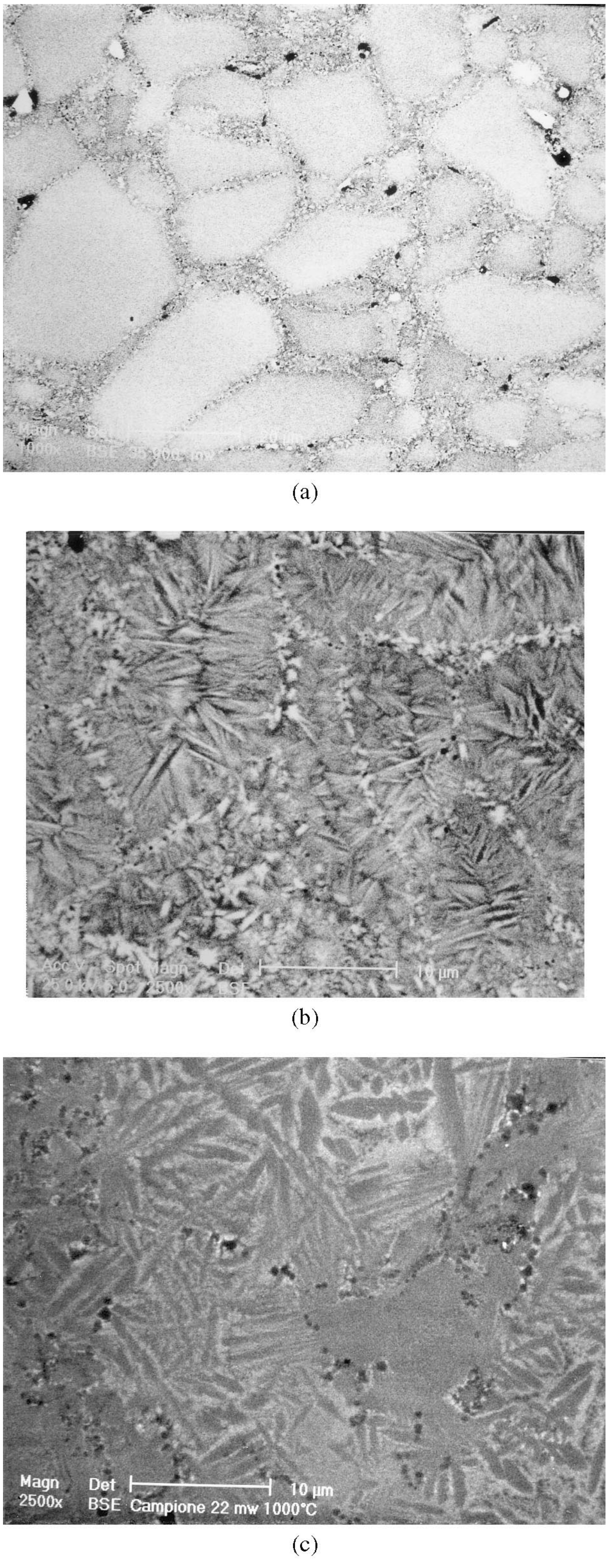


Fig. 8. SEM micrographs of sinterized materials: (a) B-glass at 900°C (1000X); (b) B-glass at 1000°C and (c) A-glass at 1000°C (2500X).

Comparing these results with those obtained for densification, a correlation between low VHN (6.62 GPa) values and excessive crystallization appears evident.

Table 2
Vickers microhardness values (GPa) of different samples

Temperature (°C)	A-glass	B-glass
900	6.25 ± 0.15	7.05 ± 0.16
950	7.05 ± 0.21	7.41 ± 0.16
1000	7.74 ± 0.18	7.77 ± 0.19
1050	6.82 ± 0.23	6.62 ± 0.21

4. Conclusion

During microwave heating, B-glass densifies at lower temperatures (900°C) than A-glass, the latter at this temperature presenting open porosity indicating an early stage of sintering. At this same temperature B-glass already shows small crystals of $2CaO{\cdot}4SiO_2{\cdot}ZrO_2$ grown on the glassy grain surface. On increasing the temperature both samples densify further. While for B-glass the main phase is $2CaO{\cdot}4SiO_2{\cdot}ZrO_2$ and the secondary one is wollastonite, $CaSiO_3$, the crystalline phase separated from the A-glass is only wollastonite, within a dendritic habitus. On increasing the temperature an excessive crystallization occurred for both compositions.

The linear shrinkage, density and microhardness results have a good correlation with sintering behavior: maximum values are reached at about 900–950°C for B-glass and 950–1000°C for A-glass, while at higher temperatures a worsening of all physical parameters is seen due to the crystallization process. This effect is caused by the proportional relationship between volume fraction of crystalline phases, glass composition and crystals nature and the mechanical properties, so that, if observed from this point of view, glass-ceramic materials can be considered as brittle-crystals composite.

This study pointed out the effect of composition on microwave treated glasses, both during densification and crystallization, drawing to the conclusion that the presence of a suscepting oxide speeds up the heating cycles.

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