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Preparation of foamed glasses from CRT TV glass by means of hydrothermal hot-pressing technique

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Abstract

The feasibility to prepare foamed glass specimens by using waste TV monitor (panel) glass as starting material under hydrothermal hot-pressing (HHP) conditions, followed by a conventional heating of the compact, was investigated. Hydrothermally hot pressed glass compacts were preliminarily prepared at a constant temperature of 200 °C, with a loading pressure of 20 MPa and two different water contents (5 and 10 wt%), for reaction intervals between 0.5 and 2 h, employing a glass particle size <38 μm. After the powder densification stage, firing of the compacted disk glass was conducted over a temperature range of 650–850 °C for 1 h. Microstructural observations conducted by SEM showed the formation of a new glass phase which incorporates water, this phase was formed during the glass densification stage at 200 °C for 2 h, with a water content of 10 wt%. The lowest apparent density achieved on these glass compacts heated at 700 °C for 1 h was 0.36 g/cm^3. This value is similar to that of other foamed glasses that have close cell network and low thermal conductivity (0.0021 W/cm/°C).

Keywords: Porous materials; Hydrothermal hot-pressing; CRT glass; Waste materials; Glasses

1. Introduction

In general, the Cathode Ray Tube (CRT) represents nearly two thirds of the total television or computer monitor weight, where 85 wt% of the CRT weight corresponds to glass. The development of novel materials by recycling this type of glasses has recently been the research subject of some investigations.[1,2] Some of the most recent studies have been directed towards for preparing novel glass-ceramic materials with a very high level of controlled morphology of its microstructural constituents.[1] One of the emerging routes for future processing of CRT glass is being orientated towards the production of foamed glasses. At present, the route proposed for foaming monitor glasses involves the addition of SiC and TiN which act as reducing agents at high temperature. These compounds lead to the formation of gas (CO_2 and N_2) at high treatment temperatures (800–900 °C) and simultaneously the foaming of a softened glass phase is also promoted.[3]

The present authors have recently reported an alternative route for preparing porous glasses, which involves the previous preparation of a precursor glass compact by treating glass particles in the presence of aqueous solvents, by means of the hydrothermal hot-pressing technique (hereafter referred to as HHP). Subsequently, the exposure of the glass compacts at temperatures in the range of 650–750 °C in air, resulted in a remarkable foaming of the glass. This process was applied to common glass used for the preparation of glass containers (bottle glass). In this particular case, it was found that the formation of pores proceeds by decomposition of a new glass phase formed during the hydrothermal hot pressing compaction, which incorporates water molecules in its structure. The decomposition of this phase at high temperature results in gradual water evaporation. Simultaneously, the formation of a pyroplastic mass of softened glass promoted a bulk expansion of the glass compact. The maximum compressive strength for the close cell porous glass was 14 MPa and its apparent density

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was 0.40 g/cm^3; the thermal conductivity of this porous specimen was 0.21 W/(m K).[4] These porous materials are likely to have a good performance as thermal insulators because their thermal conductivities lie within the values corresponding to thermal insulating materials such as wood or fiber glass wool.[5] Furthermore, based on the increasing interest for developing glass porous materials with stable and controlled pore size, particularly for thermal and acoustic insulation proposes, from engineering, economic and environmental points of view, the production of glass foams is an interesting route for the use of waste glasses.[6–8] Therefore, in the present work we intended to study the effect of some parameters such temperature, time and water content on the densification of CRT powder glass during HHP treatments. Additionally, the feasibility for preparing foamed glass was investigated by heat treatments of HHP'ed CRT TV glass compacts in air.

2. Experimental procedures

2.1. Hydrothermal hot pressing of TV panel glass

The as received CRT TV panel glass was employed for preparing HHP glass compacts. The panel glass was milled for 12 h and then sieved to obtain a small glass particle size, less than 38 μm. The chemical composition determined by using inductively coupled plasma atomic emission spectrometry (ICP-AES) showed that the glass consisted basically of SiO_2 (50.05 wt%), BaO (24.14 wt%), Na_2O (9.5 wt%), K_2O (8.90 wt%) and Al_2O_3 (2.21 wt%), and other oxides in minor amount. Initial experiments were conducted to evaluate the densification behavior of the CRT panel glass powder. A small CRT glass powder sample (5 g) was well kneaded with either 5 or 10 wt% of deionized water, which was used as solvent for the hydrothermal reaction. The mixture was then placed into the cylindrical chamber of the autoclave for HHP, and the vessel was heated at a constant rate (5 °C/min) up to the desired treating temperature of 200 °C. The temperature and loading uniaxial pressure (20 MPa) were kept constant during a reaction interval of 0.5, 1 or 2 h.

2.2. Heat treatment of the HHP compacts

The expansion of the HHP glass compacts was conducted by a conventional heating in air. Heat treatments were carried out at constant heating rate of 5 °C/min up to the desired temperature in the range of 650–850 °C, and the specimens were held for 1 h at each temperature. After the heating treatment, the expanded specimens were cooled down to room temperature inside the furnace.

2.3. Characterization

The reactivity of the glass particles with water was revealed on polished compact surfaces by scanning electron microscopy (SEM, S-530, Hitachi, Tokyo, Japan), equipped with an energy dispersive X-ray (EDX) equipment. Powder X-ray diffraction analyses were also employed to determine the crystalline phases formed in the expanded specimens using an X-ray diffractometer (Rigaku, Rotaflex) with graphite-monochromatized Cu Kα radiation at 40 kV and 100 mA. The bulk density was measured considering the diameter and thickness of the hydrothermally hot pressed CRT glass specimens, while the apparent density of the foamed glass specimens was determined by Archimedes' principle using a helium pycnometer (Multipycnometer Quantachrome). Prior to the density measurements, the calibration of the pycnometer was conducted by using a standard stainless steel sphere with a volume of 56.5592 cm^3, which was located inside the measuring cell (volume 135 cm^3). The foamed specimens were previously weighted and the volume was measured three times at a helium pressure of 0.117 MPa. The HHP'ed compacts and the expanded specimens were cut and ground to investigate aspects related to the inner microstructure by scanning electron microscopy observations.

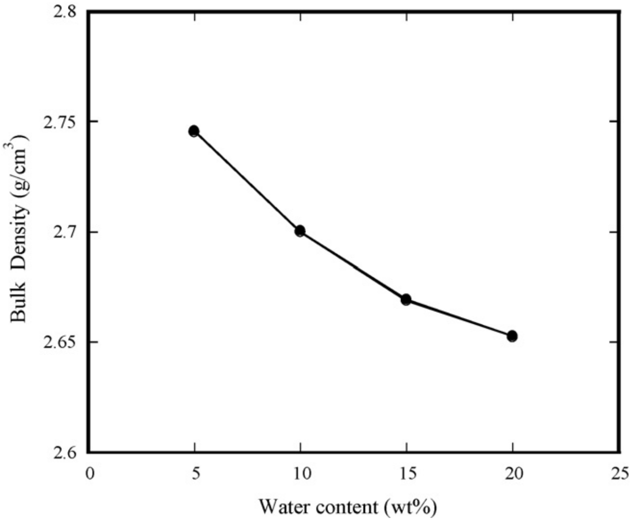

Fig. 1. Variation of the bulk density of the hydrothermally hot pressed compacts prepared at 200 °C for 2 h with different water contents.

3. Results and discussion

3.1. Densification and microstructural evaluation of hydrothermal hot pressed CRT waste glass compacts

In Fig. 1 is shown the typical behavior of the bulk density of hydrothermally densified CRT glass specimens as a function of the water content, the CRT glass compacts were prepared with a glass particle size smaller than 38 μm, at a temperature of 200 °C for 2 h, with a loading pressure of 20 MPa. A slight decrease on the bulk density was obtained by increasing the water content, with a maximum value of 2.74 g/cm^3 achieved for the compact prepared with only 5 wt% of water. The bulk density values determined for the CRT compacts were similar to those reported elsewhere for bottle glass compacts prepared under the same hydrothermal hot pressing conditions.[9] In general, it is well known that during the densification of inorganic powders, i.e. glass powders, under hydrothermal hot-pressing conditions, the solvent (water) added to the powder sample is located at the

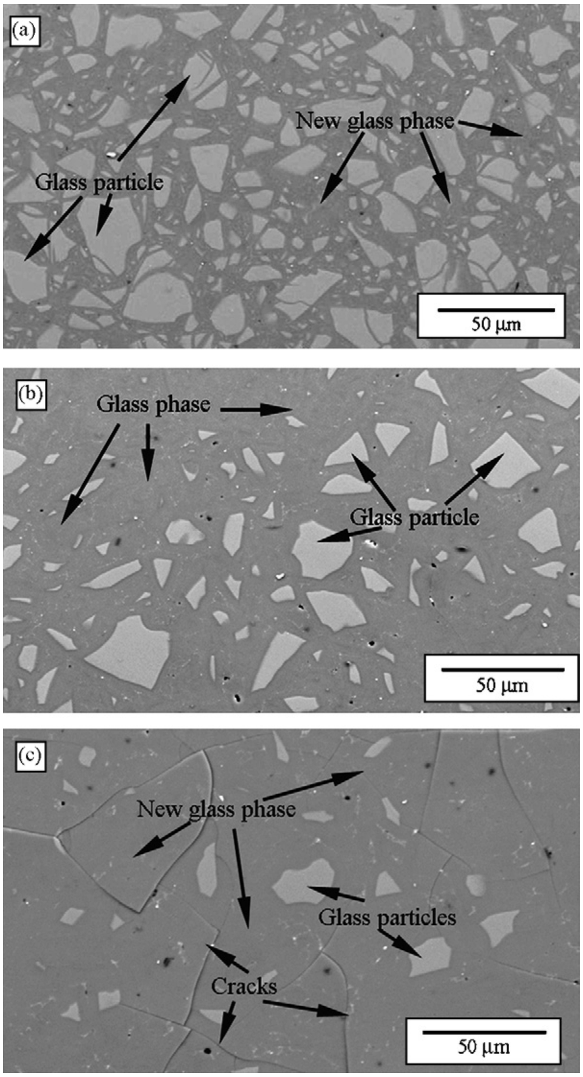

Fig. 2. SEM micrographs of the CRT glass compacts prepared at 200 °C, with a particle size <38 μm and a loading pressure of 20 MPa for 2 h, with water contents of: (a) 5 wt%, (b) 10 wt% and (c) 20 wt%.

interstices between the glass particles; the increase of temperature promotes a chemical reaction between the hydrothermal solvent (water) and the glass particles, which results in the formation of a glass viscous flow. This viscous flow of glass is achieved due to the continuous application of pressure, resulting in the elimination of residual porosity inside the glass compact. From the above mentioned results, we expect that even with an addition of a small amount of water, such as 5 wt%, it is possible to achieve a sufficient dissolution of the CRT glass particles in order to produce a glass viscous flow that promotes the glass particle densification.

The typical microstructure of the hydrothermally hot-pressed CRT compacts prepared with a loading pressure of 20 MPa for 2 h at a temperature of 200 °C, with the addition of different water contents, is shown in Fig. 2. In general, the microstructure of the glass compacts is constituted by two major phases: the remaining original glass particles (white particles) and a continuous phase (grey area) that covers the glass particles, which corresponds to the new glass phase.[10] The increase in the water content promotes a reduction in the residual porosity of the compacts, as well as a further diminution in the size and amount of the original particles. Another particular feature of the CRT glass compacts was revealed in the specimen prepared with 20 wt% of water; this specimen exhibited the formation of a great number of microcracks, which were mainly developed in the new glass phase. This phenomenon might be associated with the incorporation of water inside the structure of the new glass phase, which might result in the generation of residual stresses that decrease the strength of the glass.

Additional X-ray energy dispersive area analyses were conducted on both the remaining original CRT glass particles and the new glass phase (Fig. 3a). The EDX spectrum corresponding to the new glass phase formed in the glass compacts prepared with different water contents (5–20 wt%), revealed that no significant variation on the constituents and their amount took place during the HHP treatments. Thus, the composition of the new phase that promotes the densification of the glass compacts is irrespective of the water content employed for the hydrothermal treatment. In addition, no marked differences between the chemical constituents of the remaining CRT glass particles and those of the continuous new glass phase (Fig. 3a) were detected. Although, chemical compositional differences were not found by EDX analyses between the raw CRT glass particles and the HHP treated compacts. Structural analyses conducted by means of FT-IR spectroscopy, however, revealed that a considerable amount of water is incorporated in the network structure of the CRT glass compacts. In particular, the FT-IR spectrum showed a broad absorption band at 3450 cm^{-1} which corresponds to the presence of water molecules (Fig. 3b). This band gradually broadens by increasing amount of water employed for the hydrothermal treatment. In general, it is well known that the chemical reactivity between glass and water under hydrothermal and supercritical conditions is further accelerated by the high mobility of ionic species and molecules which promote a high rate of ion exchange ($\mathrm{M}^{n+}/\mathrm{H_3O^+}$) in the glass phase.[11] Hence, based on these results, we suggest that the solidification of the CRT glass particles might proceed even with the addition of a small amount of water, above 5 wt%. This water content reacts completely with the small glass particles. However, when a large amount of water was added to the glass powder, the gradual incorporation of water molecules into the structure of the new glass phase might produce a softening of the latter during the HHP treatment.

On the other hand, the reaction interval does not seem to have a significant effect on the solidification of the CRT glass particles, because the bulk density of the compacts was almost constant for the specimens prepared for various reaction intervals (0.5–2 h). The average bulk density determined for the specimens treated at different reaction intervals was 2.58 $\mathrm{g/cm^3}$. This value is nearly similar to those determined on the glass compacts prepared with various water contents (Fig. 1). Furthermore, the microstructure analysis by SEM of the specimens treated at different reaction intervals shows a marked increase in the reactivity of the glass particles with water, which accel-

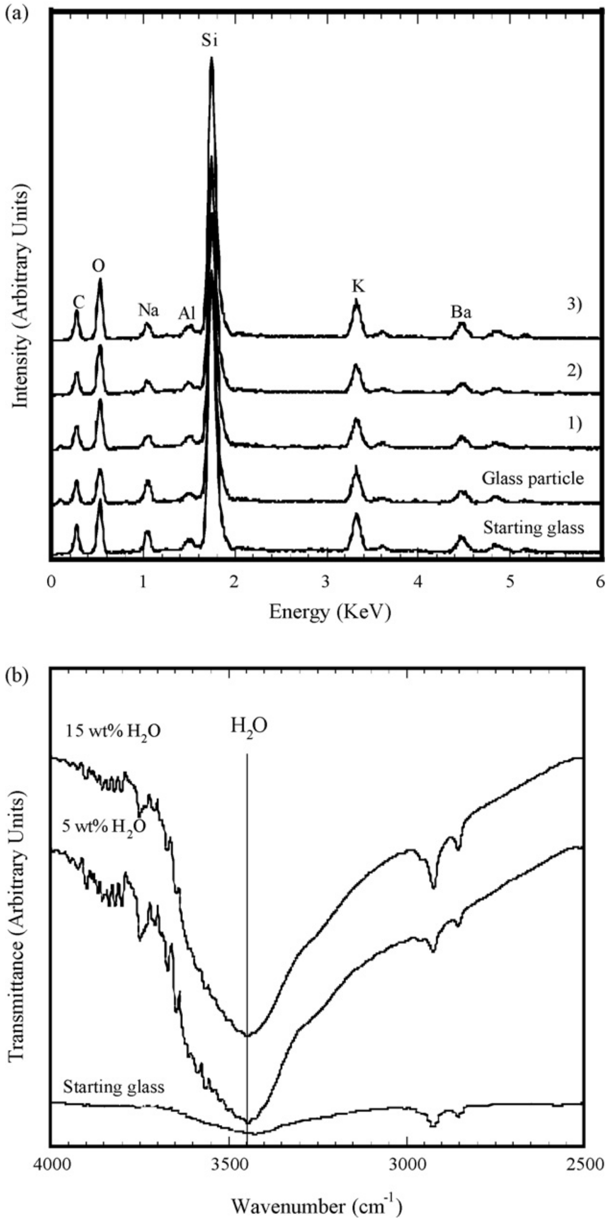

Fig. 3. (a) EDX spectra of the original CRT glass particles and of the new glass phase obtained for CRT glass compacts prepared at 200 °C for 2 h, with water contents of: (1) 5 wt%, (2) 10 wt% and (3) 20 wt%. (b) Infrared spectra of the original waste glass powder and the compacts prepared by HHP at 200 °C, for 1 h, loading pressure of 20 MPa, with two different contents of water.

erates the formation of the new glass phase. However, it is clear that at short reaction intervals the reactivity of the glass particles is limited, therefore, particles with a large size remained in the glass compacts, in comparison with the size of the particles remaining in the specimens treated for intermediate (60 min) and long (120 min) reaction intervals, although there is not great difference between the size of the remaining glass particles for the specimens treated for the latter two reaction intervals, as is seen in Fig. 4. These results showed that the reactivity of the CRT glass under HHP conditions is similar to that reported elsewhere for other different waste glasses solidified by the same processing technique.[4]

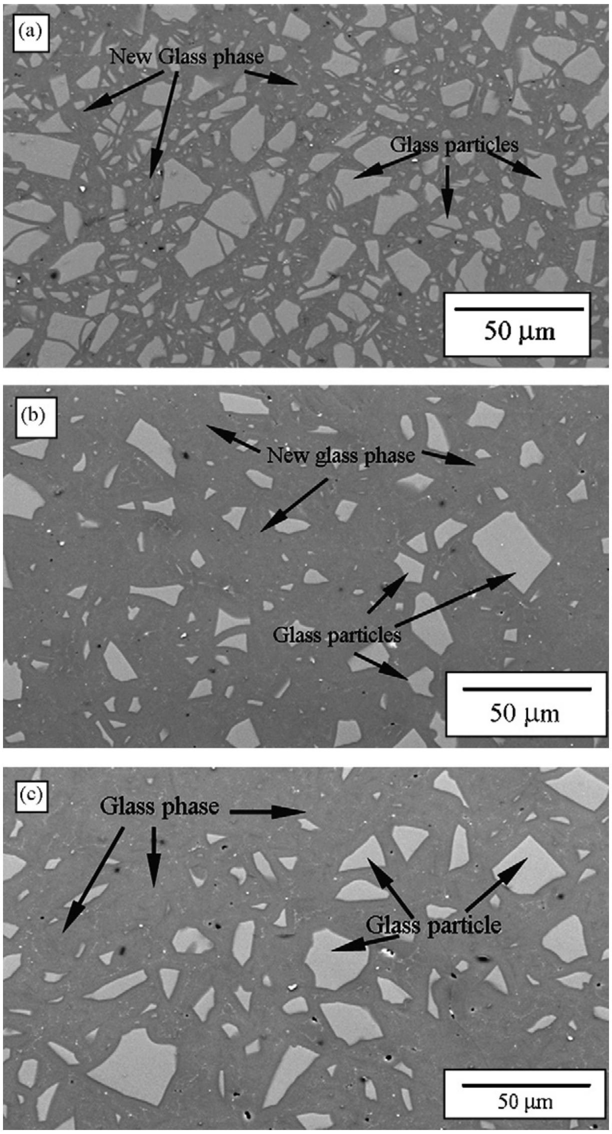

Fig. 4. SEM micrographs of glass compacts obtained at 200 °C with 10 wt% of water and 20 MPa; the compacts were prepared at reaction intervals of: (a) 30 min, (b) 60 min and (c) 120 min.

3.2. Effect of the experimental parameters, water content and foaming temperature, on the expansion process of the HHP'ed CRT glass compacts

Initial attempts were conducted to establish the appropriate temperature range in order to conduct the foaming of the CRT compacts. In a preliminary evaluation, the weight loss of the HHP'ed compacts during heating in air was measured over the temperature range of 50–800 °C. It was found that a marked decrease in the glass compact weight started at a temperature as low as 650 °C. At temperatures between 650 and 750 °C, the HHP'ed glass compacts with homogeneous incorporation of water molecules in the structure of the new glass phase, remarkably increased their volume size without disruption of the original disk shape. However, at temperatures above 800 °C, a significant deformation of the shape of the foamed specimens was appreciated.

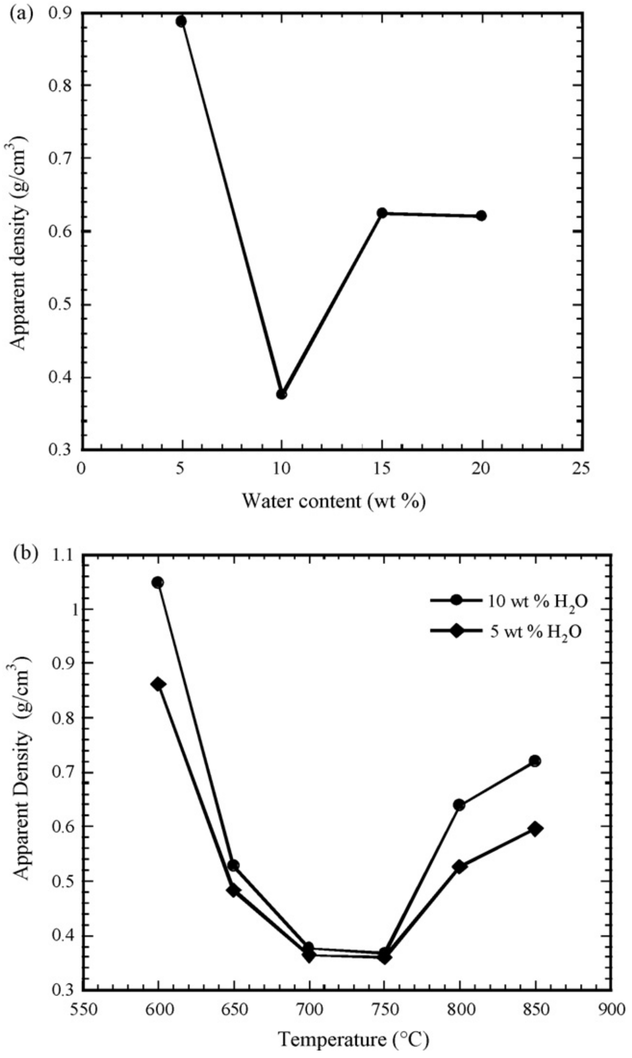

Fig. 5. (a) Variation of apparent density against the water content used for preparing the HHP'ed glass compacts, these samples were expanded at 700 °C in air; (b) apparent density of glass specimens foamed at different temperatures which were prepared with 5 and 10 wt% of water. All the HHP'ed glass compacts were prepared at standard conditions of 200 °C for 2 h with a loading pressure of 20 MPa, respectively.

The effect of the water content used for preparing the HHP'ed glass compacts on the foaming process of the glass is shown in Fig. 5a. This figure shows the variation of the apparent density of the CRT glass compacts prepared with different water contents after heat treatments conducted at 700 °C for 1 h in air. In general, the apparent density of the foamed specimens was reduced by increasing the amount of water used for the previous HHP step. A minimum apparent density value of 0.38 g/cm^3 was obtained for the HHP'ed sample prepared with 10 wt% of water. In contrast, when the glass compacts were prepared with a larger amount of water (>10 wt%), a slight increase in the apparent density of the foamed specimens occurred. The apparent density determined for the foamed compacts prepared with 15 or 20 wt% of water was almost constant (0.62 g/cm^3). Fig. 5b shows the variation of the apparent density of the foamed specimens as a function of the heating temperature for the CRT glass compacts prepared with 5 and 10 wt% of water. It is clear that the variation of the apparent density of the foamed glass specimens is irrespective of the water content used for preparing the HHP'ed glass compacts at temperatures between 650 and 750 °C. During the heat treatment, the glass compacts exhibited a remarkable expansion which resulted in the lowest average apparent density value (0.36 g/cm^3) achieved on the specimens treated at 750 °C (Fig. 5b). Above this temperature, the apparent density of the foamed glass compacts tends to increase gradually. The strongest influence on the apparent density of the foamed glass may be associated with the water content as well as with the chemical composition, because due to the presence of a large amount of alkaline ions, namely Na^+ and K^+, the transition temperature of the glassy phase is reduced.

The marked increase on the apparent density determined for the foamed specimens prepared with large water contents (15 or 20 wt%) and heating temperatures above 800 °C, might be associated with two factors: (a) amount of water incorporated into the new glass structure and (b) presence of a large amount of alkaline and alkaline-earth metals in the raw composition of the glass. We surmise, based on the present results that a combination of both factors might cause a collapse of the inner porosity, which leads to an increase in the apparent density of the glass compact. Indeed, regarding the amount of water diffused within the glass structural network, it is well known that even during conventional hydrothermal treatments with water vapor, water rapidly diffuses into the structural glass network; subsequently, the decomposition of this glass leads to the release of water molecules, resulting in a marked expansion of the glass at a relatively low temperature (700 °C).[12] Another point that deserves emphasis is that related with the viscosity of the glass. In particular, the diffusion of water molecules into the glass structural network leads to a steady variation of the glass viscosity during the foaming step.[13] In addition, a decrease in the transition (T_g) and softening temperatures of the glass phase is promoted by the large content of alkaline ions (Na^+ and K^+) together with the water diffused in the CRT glass network, which also resulted in the reduction of the glass viscosity during the heat treatment. Moreover, the increase in the apparent density of the foamed glasses with large water contents and high heating temperatures might be attributed to a marked coalescence of the inner porosity; under these conditions, a higher increase in the gas pressure inside the pores, due to a higher release of water vapor, breaks down more easily the surrounding glass walls, which accelerates the coalescence of the pores.

Details of the typical inner microstructure and morphology of the porous glass specimens are shown in the SEM micrographs of Fig. 6. The CRT glass compacts were prepared under HHP conditions of 200 °C for 2 h with different water contents. The typical microstructure revealed in the foamed sample is constituted by a homogeneously distributed cellular hollow network. Furthermore, the formation of small semispherical pores was revealed in the specimen prepared with 5 wt% of water, after a heat treatment carried out at a temperature of 700 °C. The pores were well delimited by a thin wall and the average pore size obtained was 115 μm. In contrast, a significant increase in the pore size was determined for the glass compact prepared with 10 wt% of water. During the foaming process,

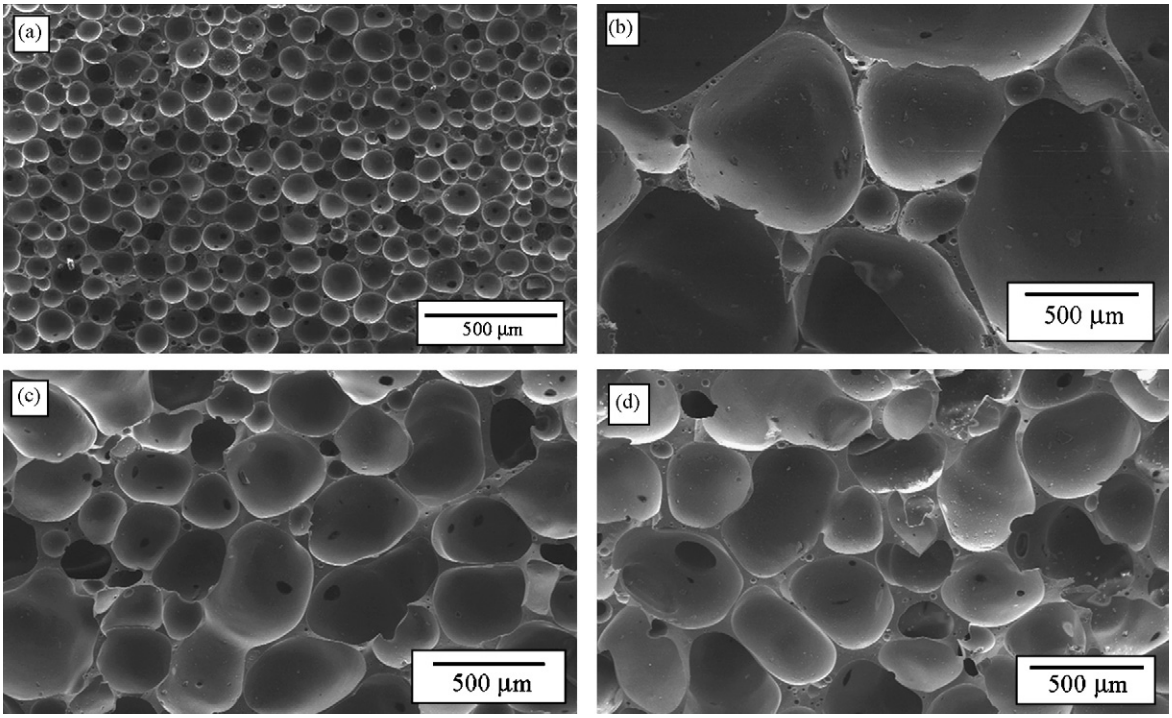

Fig. 6. SEM images of a fracture surface of the foamed glass obtained at 700 °C for 1 h; these samples correspond to HHP'ed glass compacts prepared at a temperature of 200 °C for 2 h, with 20 MPa and a water content of: (a) 5 wt%, (b) 10 wt%, (c) 15 wt% and (d) 20 wt%.

the pores underwent a significant deformation which produced irregular pores. The average size of the large pores obtained in this sample was of 1 mm. This behavior agrees with the results obtained for the apparent density, because the minimum density value (0.36 g/cm^3) corresponded to the CRT glass compact prepared at 200 °C, 10 wt% of water and 20 MPa. Moreover, a slight decrease in the pore size (500 μm), as well as a damage in the pore walls, were observed after the heat treatment of HHP'ed specimens prepared with large water contents (15 and 20 wt%) (Fig. 6c and d). We surmise that the decrease in the glass viscosity was related to the pore wall fracture and the pore shape disruption observed. This particular phenomenon was marked in the HHP glass compacts prepared with water contents larger than 10 wt%. In these cases, the release of a large amount of water from the glass structural network might produce an over pressure inside the water vapor bubbles formed in the softened glass. Hence, this steady state achieved during the glass foaming process caused a collapse of the porosity as well as an increase in the apparent density of the porous CRT glass specimens (Fig. 5).

3.3. *Structural features of the expanded glass specimens*

The X-ray diffraction analysis conducted on the expanded specimens showed that some structural changes occurred in the glass phase during the heat treatments (foaming step) carried out at different temperatures. Fig. 7 shows the typical X-ray diffraction patterns obtained for the CRT glass compacts prepared under HHP conditions at 200 °C for 2 h, with 10 wt% water, after being treated at 700 °C for 1 h in air. In general, these results revealed that the amorphous HHP'ed CRT glass underwent a devitrification process during the heat treatment. After the treatment, a small amount of crystalline phases were identified in the diffraction pattern, but a large amount of the original glassy material remained without major changes. A similar trend was observed for glass compacts prepared either with small (5 wt%) or large (15 or 20 wt%) water amounts. The main crystalline phases found after the foaming process were quartz (SiO_2), barium silicate ($BaSiO_3$), potassium silicate (K_2SiO_3) and barium–potassium silicate ($K_2Ba_3Si_8O_{20}$).

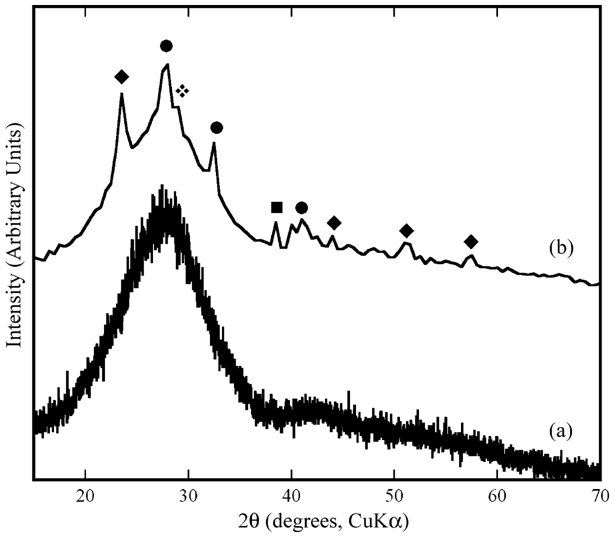

Fig. 7. X-ray diffraction patterns of: (a) HHP compact and (b) glass foamed at 700 °C for 1 h in air. Crystalline phases: (●) quartz (SiO_2), (♦) barium–potassium silicate ($K_2Ba_3Si_8O_{20}$), (❖) barium silicate ($BaSiO_3$) and (■) potassium silicate (K_2SiO_3).

4. Conclusions

In accordance with the current results, it was found that the addition of a small amount of water (10 wt%) influences the expansion process of glass compacts prepared under HHP conditions and subsequently heated in air. An increment in the water amount allows increasing the reactivity of glass particles with water during the hydrothermal hot pressing process. We assumed that the Na^+ Ba^{+2} and K^+ ions had an active participation in the softening of the glass particles in order to produce a new glass phase. The glass compact incorporating 10 wt% of water exhibits the lowest apparent density ($0.36\ g/cm^3$) after a foaming treatment conducted at 700 °C for 1 h in air. In particular, this specimen had the most remarkable expansion which produced irregular pores having an average size of 1 mm. These results revealed that the CRT glass is susceptible to be used for the production of close cell porous material with high potential as a thermal insulator, when compared with other different waste glasses such as bottle glass. The collapse of the close cell pore network and the partial glass devitrification seem to be influenced by the amount of water originally incorporated into the glass structure; this water reduced the glass viscosity during the foaming process. A preferential crystallization of three major phases, quartz (SiO_2), barium silicate ($BaSiO_3$), potassium silicate (K_2SiO_3) and barium–potassium silicate ($K_2Ba_3Si_8O_2$) was determined during the foaming of the HHP'ed CRT glasses.

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