Original Paper

Glasses and glass-ceramics of the system $CaO-MgO-Al_2O_3-SiO_2$ obtained from natural sedimentary raw materials

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Common and low-cost natural sedimentary raw materials such as ball clay, dolomite, quartz sand and diatomite were used as the main constituents for the production of glasses and glass-ceramics of the system $CaO-MgO-Al_2O_3-SiO_2$. The crystallization of the glassy batch was promoted by the addition of a nucleation agent (TiO_2). The crystallization sequence was examined by DTA, XRD, SEM, and thermal expansion analyses. Wollastonite and diopside are the main phases detected and the amount and grain size/shape of crystals were found to be strongly dependent on titania additions and on the annealing conditions. The characterization of relevant functional parameters of glass and glass-ceramic samples revealed interesting results.

1. Introduction

The use of common natural and inexpensive raw materials, subproducts, and wastes for the production of glasses and glass-ceramics presents economical and ecological advantages when compared with pure chemical-grade reagents. Technological issues are sometimes problematic and require further studies and adaptations but products with similar characteristics can be obtained [1 to 6]. Clays of different chemical-mineralogical types, natural-occurring calcium and magnesium carbonates, quartz sand and diatomite are normally present in sedimentary rocks and can be used for this purpose [7]. Sludge generated from wastewater treatment of several industrial activities and fly ash are good examples of promising reusable wastes [8 and 9].

A substantial amount of research has been conducted in the past decade to obtain alkaline and alkaline earth silicate glasses. By using controlled conditions, crystalline phases such as diopside, wollastonite, anorthite, and akermanite can be precipitated from the glass, resulting in glass-ceramics with high mechanical and chemical resistance [10 to 15]. Kinetic aspects dictate that optimal glass formulations belong to the $CaO-MgO-Al_2O_3-SiO_2$ quaternary system. The production of such glasses from natural and abundant raw materials (ball clay, dolomite, quartz sand, and diatom-

ite) is now attempted. Amongst these components, diatomite is less common and considered as a subproduct. In the centre of Portugal, huge amounts have been formed on the top of important kaolin and quartz sand reserves. Diatomite is basically constituted by microscopic amorphous silica diatomaceous skeletons, which have a large amount of very small intrinsic pores (equivalent size $\approx$ 100 nm) [16]. As a consequence, this material shows high specific surface area (> 20 m^2/g) and very low apparent density ($\approx$ 0.4 g/cm^3). During the last few years, the amount of exploitation was only 4500 t/a, mostly for filtration applications and as charge of inks and mortar. Its price is seriously penalized by the relatively high iron content.

The selection of the starting parent glass composition should favour the formation of aluminous pyroxenes, by promoting the partial isomorphous substitution of sodium and aluminium ions for calcium and magnesium ions in the diopside structure. These substitutions are easier in continuous solid solutions between diopside-jadeite phases and by the expected high solubility (20 %) of the Ca-Tschermak's in the diopside structure [10]. Nevertheless, an excess of calcium and magnesium relative to the stoichiometric diopside composition might give wollastonite formation.

The formation of glass-ceramics will be also attempted, by following suitable annealing conditions and/ or by adding TiO_2 as nucleating agent. The characteristics of the final products should be compatible with

Table 1. Relevant properties of tested samples, values of Vickers microhardness include the standard deviation (in parenthesis)

properties	G	5G	7G	5GC	7GC
apparent density in g/cm^3	2.75	2.81	2.84	2.86	2.93
thermal expansion coefficient in 10^{-6} K^{-1} (between 20 to 400 °C)	8.83	8.95	9.38	8.31	8.32
dilatometric softening temperature, T_s, in °C	703	719	707	–	–
Vickers microhardness in GPa	6.30 (0.10)	6.44 (0.08)	6.31 (0.12)	5.93 (0.14)	6.44 (0.05)
colour	light green	green-yellow	yellow-red	green, "marble like"	green, "marble like"

those of the materials formed from chemical-grade reagents.

2. Experimental procedure

Abundant natural Portuguese raw materials of sedimentary origin were used as the major starting materials for the parent glass formation: a) ball clay (BM-8, Barracão – Leiria) whose average chemical composition (in wt%) is 53.32 SiO_2, 28.71 Al_2O_3, 2.27 Fe_2O_3, 0.80 TiO_2, 0.23 CaO, 0.11 MgO, 0.09 Na_2O, 1.85 K_2O, 11.88 L.O.I.; b) as-received diatomite (Sociedade Anglo-Portuguesa de Diatomites, Óbidos that is previously calcined at 600 °C to burn out the organic matter and has the following average composition (in wt%): 87.62 SiO_2, 2.22 Al_2O_3, 4.55 Fe_2O_3, 1.60 CaO, 4.01 K_2O; c) 98.5 % pure dolomite (Barracão – Leiria); d) 98 % SiO_2-containing quartz sand (Mibal, Barqueiros – Barcelos). Reactive-grade Na_2CO_3 and TiO_2 were used as fluxing and nucleation agents, respectively. The chemical composition (in wt%) of the starting glass (named G) was calculated from the average chemical composition of raw materials: 54.14 SiO_2, 6.35 Al_2O_3, 1.46 Fe_2O_3, 0.13 TiO_2, 19.73 CaO, 13.41 MgO, 3.47 Na_2O, 1.28 K_2O. It was prepared from the following batch (in wt%): 12.3 ball clay, 47.8 dolomite, 17.6 quartz sand, 17.9 diatomite, 4.4 Na_2CO_3.

Quartz sand, dolomite and ball clay were separately dry ball milled. This previous step was not used for diatomite, due to its fragile character and fineness. The complete mixture was melted in corundum crucibles by electrical means at 1420 °C/1 h. The refined glass melt was poured out into a stainless steel mould and was subsequently annealed at 650 °C/1 h. In order to promote an effective crystallization, TiO_2 nucleation agent was added (5 and 7 wt% in excess to the glassy batch). Modified glass compositions are named 5G and 7G. Due to the refractoriness of titania, the melting temperature was increased to 1450 °C. Glass samples were then submitted to a typical double-stage annealing treatment, according to the thermal expansion and DTA results. Corresponding formed glass-ceramics are named GC, 5GC, and 7GC.

Differential thermal analysis (DTA) was performed in a Setaram Labsys™ apparatus (France) up to 1000 °C, at a heating rate of 10 K/min. Thermal expansion behaviour of the as cast and devitrified glasses was studied by dilatometric analysis performed up to 1000 °C at a heating rate of 10 K/min (Linseis L75, Germany). Crystalline phases were identified by XRD in the 2θ range of 5 to 80 ° using a Cu-tube diffractometer (Rigaku Denk Co., Japan). Microstructural details were obtained by scanning electron microscopy (SEM) (Hitachi S4100, Japan) on previously polished and etched (by dipping for 2 min in a 5 vol.% HF solution) glass-ceramic samples. Apparent density of glass and glass-ceramic samples was determined by the Archimedes method (Hg immersion). Vickers microhardness of the glass and glass-ceramic samples was estimated from five indentations made on different regions of each sample (load of 9.8 N). A Shimadzu-M microhardness indenter (Japan) was used and photos of indentation zones were made by an optical microscope (Zeiss, Jenaphot 2000, Jena (Germany)).

3. Results and discussion

Glassy melts of all compositions exhibit suitable viscosity and flow characteristics and pour out without difficulties. The addition of titania tends to change the colour from green to yellow and red hues. Gloss and transparency are maintained. The relevant properties are shown in table 1.

Figure 1 shows thermal expansion curves of all samples. Characteristic glass transition temperature (T_g) and dilatometric softening point (T_s) of the G sample are at about 650 and 703 °C, respectively. The same points tend to slightly increase on TiO_2-doped samples ($T_g \approx$ 670 to 690 °C; T_s = 719 °C and 707 °C for 5G and 7G, respectively).

DTA results (figure 2) denote two shallow exothermic peaks at 910 and 950 °C for the G glass, which might indicate that surfacial crystallization is dominant [17]. The addition of titania changes the intensity and position of both peaks. 5G sample shows a higher first peak
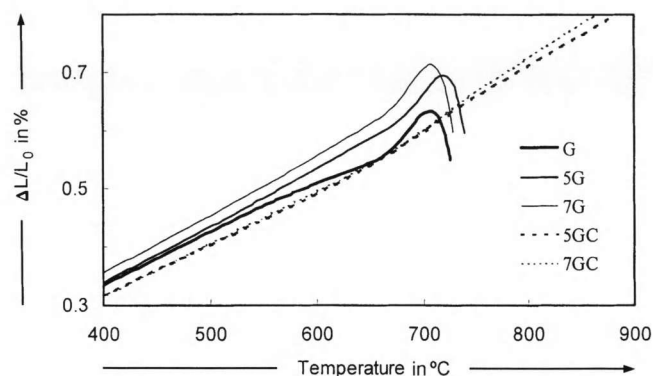
Figure 1. Thermal expansion curves of the glasses and glass-ceramics; G: starting glass, 5G and 7G: glass samples with 5 and 7 wt% TiO$_2$, 5GC and 7GC: glass-ceramic samples with 5 and 7 wt% TiO$_2$, respectively.
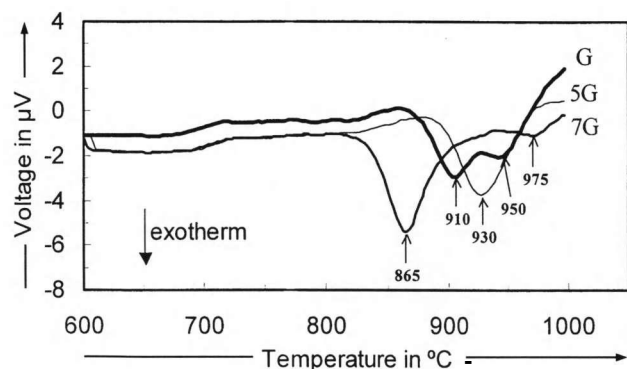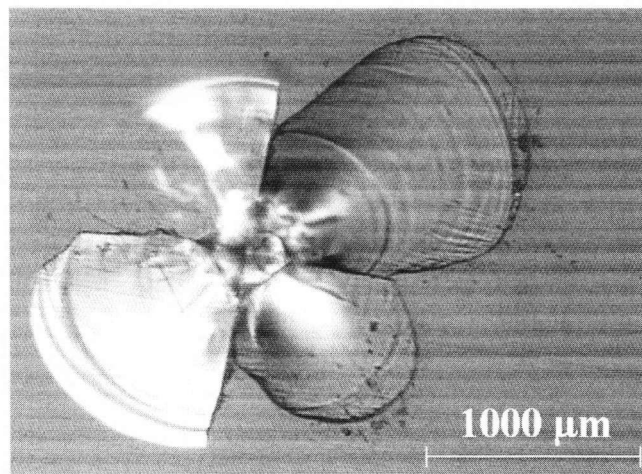

Figure 2. DTA curves of different glass compositions, G, 5G and 7G; explanation for these designations see caption for figure 1.

a)

b)

Figures 3a and b. Views of the indentation zone of a) 5G glass and b) 5GC glass-ceramic samples.

and a simultaneous shift to 930 °C, while the second peak smoothes out. The first peak is even more intense for 7G sample and is located at a lower temperature (about 865 °C) than in the previous case. The second exothermic peak is placed at about 975 °C and is much less intense.

Taking into account both thermal analyses, we might assume that the nucleating temperature is set at 700 °C and all samples were held for 1 h at this temperature during the annealing process. A second unequal holding stage was implemented in order to promote different crystallization levels: 900 °C/2 h, 950 °C/2 h, and 1000 °C/5 h. Finally, cooling to room temperature was carried out during about 1.5 h.

The crystallization process is very slow in the G starting composition. There was no evidence of bulk development of crystals at 950 °C, and a heterogeneous product made of coarse crystalline aggregates (of diopside and wollastonite) and large voids was formed only at 1000 °C.

The addition of TiO$_2$ tends to improve the crystallization process, probably due to the promotion of phase separation [17 to 21]. According to Zhunina et al. [10] the nucleation effect of TiO$_2$ in glasses of the

CaO−MgO−Al$_2$O$_3$−SiO$_2$ system is due to the formation of highly dispersed particles of TiO$_2$- rich immiscible liquid, which act as mechanical centres or seeds for the crystallization of monoclinic pyroxenes. Obviously, this process tends to be more effective as the titania content increases (i.e., in 7G sample). Crystallization also starts at the surface and is clearly denoted by the crusty appearance at 900 °C. Volumetric crystal growth is observed at 950 °C and complete bulk crystallization is achieved at 1000 °C. Compared with the GC sample, a holocrystalline structure is obtained for titania-doped glass-ceramics. Green-yellowish and yellow-reddish colours of 5G and 7G parent glasses transform into green "marble-like" colour in the resulting 5GC and 7GC samples. These materials possess large grains, while GC samples are made of finer crystals.

Crystallization tends to increase the apparent density and to decrease the thermal expansion of glasses (see table 1). No significant differences of Vickers hardness values between the corresponding parent and crystallized glasses are observed. Nevertheless, observations of the indentation zone (figures 3a and b) show that glass-ceramics exhibit high resistance to failure by crack
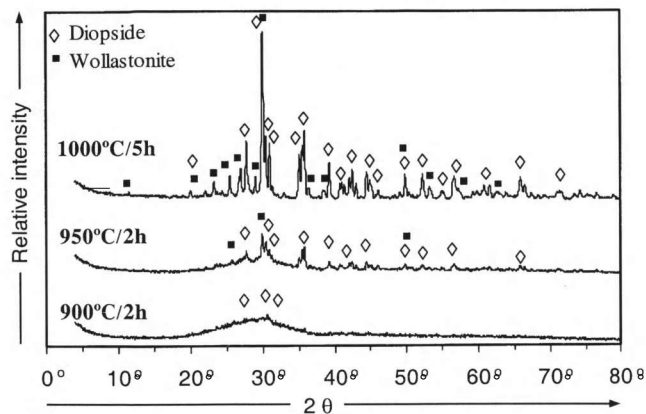
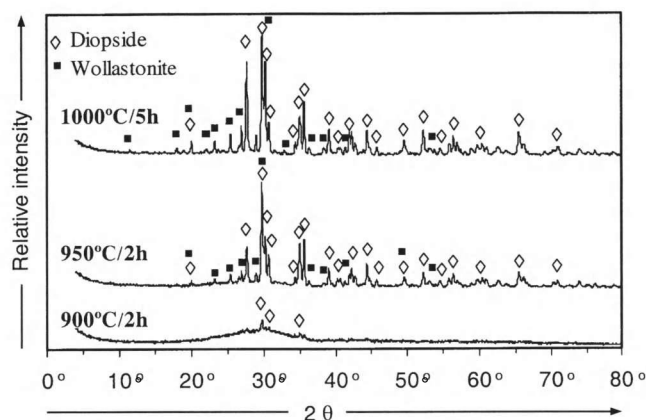Figure 4. X-ray diffraction patterns of 5GC samples annealed at 900, 950 and 1000 °C.
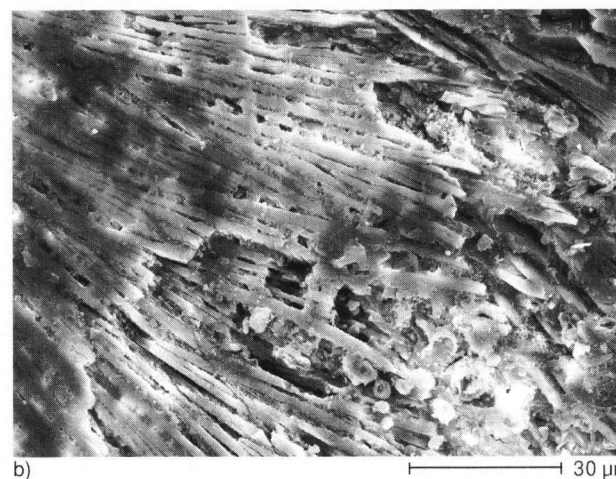

Figure 5. X-ray diffraction patterns of 7GC samples annealed at 900, 950 and 1000 °C.

Figures 6a and b. SEM observations of a) 5GC and b) 7GC samples annealed at 1000 °C.

development (qualitative higher toughness). In the corresponding parent glasses the cracks flow quickly from the vertices of the indentation marks, and large scums tend to be formed between the cracks (figure 3a). In contrast glass-ceramics show very small and confined cracks and absence of scums (figure 3b).

X-ray diffraction (XRD) patterns show the gradual transformation from a typical glassy-amorphous structure (at 900 °C) into highly ordered arrangements of the corresponding glass-ceramics (figures 4 and 5). Moreover, the crystallization effect of titania for similar annealing treatments is clearly demonstrated. For example, the formation of diopside solid solutions is anticipated in TiO_2-doped compositions (major peaks are still visible at 900 °C). Wollastonite only starts to precipitate at 950 °C, and its formation seems to be also favoured by the presence of titania. Titania-based compounds were never observed by XRD, as expected from the relatively low added amounts. The crystallinity degree of 7GC samples is higher than that of 5GC, as confirmed by XRD and SEM observations (figures 6a and b). These micrographs also show the dominance of a surfacial crystallization mechanism, as denoted by typical crystal morphology. Wollastonite-type coarse acicular crystals [11] are visible and tend to spread out through the whole

volume of the material. Other types of crystals, mostly spherical or ellipsoidal and very small (less than 1 µm), are also present and seem to belong to pyroxene solid solutions. Estimated chemical composition (EDS) of the acicular crystals is somewhat different from the stoichiometric wollastonite. The amount of Al_2O_3 and MgO is significantly higher, due to the presence of pyroxene elements in the wollastonite structure [21 and 22]. The composition of the tiny crystals confirms the formation of an Na_2O-rich aluminous pyroxene. As another consequence, the lattice parameters of pyroxene solid solutions formed on 7GC samples annealed at 1000 °C ($a = 9.81$, $b = 8.79$, $c = 5.52$) are somewhat different from those of the pure diopside phase ($a = 9.73$, $b = 8.91$, $c = 5.25$) [21].

4. Conclusions

The formation of vitreous phases from common and cheap natural raw materials at current temperatures (1420 to 1450 °C) was found to be easy. Glasses exhibit suitable working properties. Annealing at temperatures between 900 and 1000 °C led to surfacial crystallization.

The use of TiO_2 as nucleating agent improves the crystallization process, whilst not causing a change in the crystallization mechanism. After crustification at 900 °C, crystals tend to grow in volume (at 950 °C) and a holocrystalline "marble-like" material was obtained at 1000 °C (7GC sample). Current glass-ceramic samples are made of large crystals, showing different sizes and shapes. When large acicular wollastonite crystals spread out to the interior of the glass, very fine diopside crystals tend to be intercalated with wollastonite particles. As a consequence, chemical composition and lattice parameters are different from the pure phases.

Competitive prices and suitable properties, now under full exploitation, make these glasses and glass-ceramics attractive candidates for several common applications (e.g. facade walls or glassy tiles). The use of nucleating agents that give fine-grained bulk-crystallized glasses should also be attempted.

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5. References

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