

## Development and characterization of $3\text{CaO}\cdot\text{P}_2\text{O}_5\text{--SiO}_2\text{--MgO}$ glass-ceramics with different crystallization degree

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**Abstract:** The  $\text{CaO}\text{--P}_2\text{O}_5\text{--SiO}_2\text{--MgO}$  system presents several compounds used as biomaterials such as hydroxyapatite (HA), tricalcium phosphate (TCP) and TCP with magnesium substituting partial calcium (TCMP). The  $\beta$ -TCMP phase with whitlockite structure has interesting biological features and mechanical properties, meeting the requirements of a bioactive material for bone restoration. In this work, the production of Mg-doped TCP,  $\beta$ -TCMP, has been investigated by crystallization from a glass composed of 52.75 wt%  $3\text{CaO}\cdot\text{P}_2\text{O}_5$ , 30 wt%  $\text{SiO}_2$  and 17.25 wt% MgO (i.e., 31.7 mol% CaO, 10.6 mol%  $\text{P}_2\text{O}_5$ , 26.6 mol% MgO and 31.1 mol%  $\text{SiO}_2$ ) using heat treatments between 775 °C and 1100 °C for up to 8 h. The devitrification process of the glass has been accompanied by differential scanning calorimetry (DSC), high-resolution X-ray diffraction (HRXRD), relative density and bending strength measurements. The characterization by HRXRD and DSC revealed the occurrence of whitlockite soon after the bulk glass preparation, a transient non-cataloged silicate between 800 °C and 1100 °C, and the formation of diopside in samples treated at 1100 °C as crystalline phases. The overall crystalline fraction varied from 26% to 70% depending on the heat treatments. Furthermore, contraction of the *a*-axis lattice parameter and expansion of the *c*-axis lattice parameter of the whitlockite structure have been observed during the heat treatments, which were attributed to the  $\beta$ -TCMP formation with the partial substitution of  $\text{Ca}^{2+}$  by  $\text{Mg}^{2+}$ . Relative densities near 99% and 97% for the glass and glass-ceramics respectively indicated a discrete reduction as a function of the devitrification treatment. Bending strengths of 70 MPa and 120 MPa were determined for the glass and glass-ceramic material crystallized at 975 °C for 4 h, respectively.

**Keywords:** glass-ceramics; heat treatment; high-resolution X-ray diffraction (HRXRD); bending strength

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## 1 Introduction

Calcium phosphate ceramics are used as artificial bone material, in the form of solid pieces, filling powders and porous films. Currently, calcium phosphate ceramics are widely used in orthopedic and dental applications as repair for bone defects, increasing and maintaining of alveolar bone crests, reallocation of tooth root, auricular implants, consolidation of spine, and coating of metal implants [1]. The advantage of these ceramic materials consists in their chemistry based on calcium and phosphorus, which contribute to the ionic equilibrium between the biological liquids and the ceramic [2]. The use of glass and glass-ceramics as bone implants may be limited by inadequate mechanical properties. Therefore, fracture strength becomes a relevant factor to be evaluated for their use as structural implants, which require the ability to withstand stress without failure.

Calcium phosphate-based ceramics are only available as blocks or granules used in small implants and in non-load bearing areas, or as coatings for metals, because there is a potential risk of failure due to their very slow resorption kinetics and poor mechanical properties. Of all calcium phosphates, tricalcium phosphate (TCP) and hydroxyapatite (HA) have been studied most intensively because of their use in biological applications for their high compatibility with natural bone. HA is considered as the most similar artificial and bioactive material to bone and teeth [3]. However, the natural bone mineral component is mainly non-stoichiometric HA (i.e., Ca:P molar ratio is other than 1.67 and differs in crystallinity and specific surface area), making it more reactive in a biological environment. On the other hand, TCP is known for its resorption by body, because it has a Ca:P molar ratio of lower than 1.67 and therefore greater solubility and resorption capacity *in vivo*, ensuring its bone-conductivity and bioactivity [4].

The TCP with composition of  $\text{Ca}_3(\text{PO}_4)_2$  exhibits a Ca:P molar ratio of 1.5. The TCP exists in four crystal modifications depending on temperature and pressure.  $\beta$ -TCP is stable until 1125 °C, transforming into  $\alpha$ -TCP at higher temperatures. At 1430 °C, the transformation into  $\gamma$ -TCP occurs.  $\gamma$ -TCP and a high-pressure form are difficult to obtain [5]. Of these four polymorphs,  $\beta$ -TCP phase is the most promising for bioceramic implant materials because of its low ratio of dissolution, chemical stability and mechanical strength,

attending the requirements for a material in regenerative medicine [6].

A  $\beta$ -TCP variation is the  $\beta$ -TCMP phase with whitlockite-like structure, corresponding to a solid solution with composition of  $\text{Ca}_{2.589}\text{Mg}_{0.411}(\text{PO}_4)_2$ .  $\beta$ -TCMP is formed by the substitution of  $\text{Ca}^{2+}$  by  $\text{Mg}^{2+}$  ions, preferentially on Ca(5) sites in the  $\beta$ -TCP structure [7]. Hence, the preparation of whitlockite is interesting for applications in both bone and tooth replacements. TCP can be obtained either by solid-state reaction or by sintering calcium-deficient apatites. However, the limits of solid-state reaction are inhomogeneity, non-uniformity in the particle size distribution, and a higher chance of impurities in the final product as well [8,9]. On the other hand,  $\beta$ -TCMP was present in glass-ceramics based on  $3\text{CaO}\cdot\text{P}_2\text{O}_5\text{-SiO}_2\text{-MgO}$  system via crystallization glass bulk [10].

In recent years, the chemical modification of  $\beta$ -TCP through ionic substitutions has received much attention, considering that major components of biological tissues are composed of a calcium phosphate mineral phase containing a variety of other elements [11].  $\text{Mg}^{2+}$  is considered the most important ion used in calcium substitution in the crystal structure of  $\beta$ -TCP, leading to a change in the biological and chemical behavior of these materials. Incorporation of  $\text{Mg}^{2+}$  ions suppresses the  $\beta \rightarrow \alpha$  TCP phase transition and the bone metabolism improves, reducing cardiovascular diseases by promoting catalytic reactions and controlling biological functions [8]. Banerjee *et al.* [12] demonstrated better cell attachment and proliferation for doped  $\beta$ -TCP in an *in vitro* cell-material interaction study and in an *in vivo* study as well. The authors reported that bone forms more quickly in doped samples than in control samples.

As reported by Schroeder *et al.* [13],  $\beta$ -TCP crystallizes in the rhombohedral space group  $R3c$  (161) with unit cell parameters of  $a=b=10.439 \text{ \AA}$  and  $c=37.375 \text{ \AA}$  (hexagonal setting). Whitlockite ( $\beta$ -TCMP) is very similar to the  $\beta$ -TCP structure with unit cell parameters of  $a=b=10.337 \text{ \AA}$  and  $c=37.068 \text{ \AA}$ . Enderle *et al.* [14] examined  $\beta$ -TCP powders with Mg additions obtained by a solid-state reaction, using X-ray powder diffraction combined with the Rietveld method. A maximum of about 16 mol%  $\text{Mg}^{2+}$  substitution on Ca(4) and Ca(5) sites in the  $\beta$ -TCP structure was found. Exceeding 15 mol%  $\text{Mg}^{2+}$  will result in either un-reacted magnesium chloride (Mg adsorbs on the calcium phosphate surface) or even the precipitation of Mg-rich phases, such as stanfieldite.

The present work investigated an alternative route to the conventional powder processing method to prepare  $\beta$ -TCMP by crystallization from a bulk glass based on the  $3\text{CaO}\cdot\text{P}_2\text{O}_5\text{-SiO}_2\text{-MgO}$  system. Furthermore, the resulting mechanical properties such as hardness and fracture toughness were related to the degree of crystallization.

## 2 Experimental procedure

### 2.1 Synthesis of glasses and glass-ceramics

High-purity powders of  $\text{CaCO}_3$  (SYNTH),  $\text{MgO}$  (SYNTH),  $\text{SiO}_2$  (Fluka) and  $\text{Ca}(\text{H}_2\text{PO}_4)_2\cdot\text{H}_2\text{O}$  (SYNTH) were used as starting materials, and the glass with composition of 52.75 wt%  $3\text{CaO}\cdot\text{P}_2\text{O}_5$ , 30 wt%  $\text{SiO}_2$  and 17.25 wt%  $\text{MgO}$  was prepared. This glass composition has already been studied and combines good bioactivity with considerable mechanical strength [15,16]. The powders were mixed by ball milling for 4 h using isopropilic alcohol as vehicle. After milling, the powder mixture was dried at  $90^\circ\text{C}$  for 24 h and passed through a sieve 230 Mesh with openings of  $64\ \mu\text{m}$  for deagglomeration.

The melting of the glass was done in a platinum crucible at  $1600^\circ\text{C}$  for 4 h. The liquid glass was poured into a metallic mould, casting bars of  $15\ \text{mm} \times 15\ \text{mm} \times 50\ \text{mm}$ . Immediately after casting, the specimens were annealed at  $700^\circ\text{C}$  for 2 h and then cooled down to room temperature at a rate of  $3^\circ\text{C}/\text{min}$ .

Samples were further treated at different temperatures for 0.25 h, 2 h, 4 h and 8 h, and also cooled down at a rate of  $3^\circ\text{C}/\text{min}$  in order to induce crystallization of the bioglass. Sample designation of the heat-treated materials is summarized in Table 1.

**Table 1 Sample designation of glass-ceramics obtained by heat treatment**

Heat treatment ( $^\circ\text{C}$ )	Time (h)			
	0.25	2	4	8
775	V775-1	—	V775-4	V775-8
800	V800-1	V800-2	V800-4	V800-8
850	V850-1	V850-2	V850-4	V850-8
900	V900-1	V900-2	V900-4	V900-8
975	V975-1	V975-2	V975-4	V975-8
1000	—	—	V1000-4	—
1050	—	—	V1050-4	—
1100	—	—	V1100-4	—

Additional heat treatments were made at  $700^\circ\text{C}$  for 4 h (V700-4) and  $950^\circ\text{C}$  for 4 h (V950-4).

### 2.2 Characterizations

The non-isothermal crystallization kinetics was studied using differential scanning calorimetry (DSC, Model 404, NETZSCH, Germany). Glass powders of different particle size and monolithic pieces were treated in a platinum crucible at  $10^\circ\text{C}/\text{min}$  from room temperature until  $1200^\circ\text{C}$ .

The densities of the V700-4, V775-4, V900-4, V975-4 and V1100-4 bulk samples were determined by the immersion method proposed by Archimedes. Real densities of the samples were evaluated by a helium picnometer model AccuPyc 1330-Micrometrics using crushed samples with particle size smaller than  $63\ \mu\text{m}$ .

### 2.3 Phase analysis

The heat-treated samples were analyzed by high resolution X-ray diffraction (HRXRD), using a diffractometer with multiple axes (Huber, Germany). The samples were crushed and sieved until particle size smaller than  $32\ \mu\text{m}$ . The measurements were realized in a setup of two coupled concentric circles ( $\omega$ - $2\theta$ ), with a monochromatic X-ray beam of  $10\ \text{keV}$  ( $\lambda = 1.2398\ \text{\AA}$ ). The powders were put in a cylindrical support of  $10\ \text{mm}$  in diameter and  $2\ \text{mm}$  in depth and maintained rotating in order to promote randomness of orientation of the crystallographic planes. The diffracted beam was collected by a germanium crystal (200) and a scintillation detector. The powders were analyzed under diffraction angles ranging from  $7^\circ$  to  $50^\circ$ , with a step width of  $0.01^\circ$  and 1 s exposure time per position.

The amount of the crystalline phase contained in the glass-ceramic samples was determined by an adoption of the methods used by Krimm and Tobolsky [17], where the percentage of crystallinity  $I_c$  is calculated by the ratio of the crystalline area  $A_c$  present in the diffractogram of the glass-ceramics to the total area  $A_t$  ( $A_t = \text{amorphous} + \text{crystalline}$ ) present in these diffractograms, using the following equation:

$$I_c = (A_c / A_t) \times 100\% \quad (1)$$

After determining the degree of crystallinity, the amount of the whitlockite phase has been estimated, using an internal standard. This technique consists of relating the peak intensities of a crystal phase with the peaks of the internal standard material, added in a known proportion. For this analysis, the sample materials and metallic tin as internal standard were mixed in certain proportions, as shown in Table 2,

and analyzed by X-ray diffraction using Cu K $\alpha$  radiation, in the  $2\theta$  range of  $8^\circ$  to  $62^\circ$ , with a step width of  $0.05^\circ$  and 3 s exposure time per position.

**Table 2 Sample to metallic tin mass ratio (internal standard)**

Sample	$m_{\text{glass}}$ (g)	$m_{\text{tin}}$ (g)	$m_{\text{glass}}/m_{\text{tin}}$
V775-4	0.875	1.595	0.55
V850-4	0.446	0.849	0.53
V950-4	0.349	0.701	0.50
V975-4	0.704	1.320	0.53
V1100-4	0.704	1.329	0.53

The relationship of the peak intensity of the whitlockite phase and the internal standard was determined by the area of the (200) plane of whitlockite and the area of the (211) plane of tin (Fig. 1).

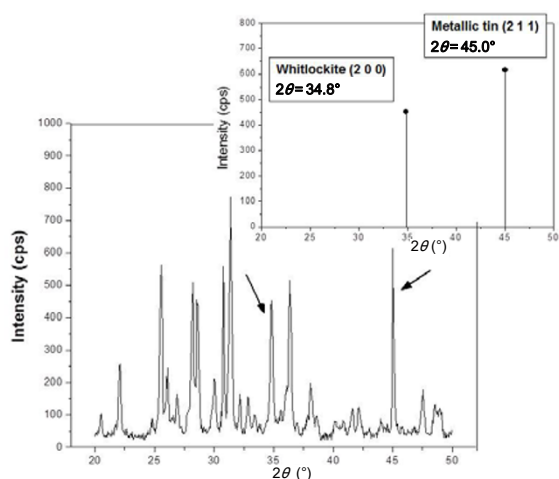


Fig. 1 Quantification of the whitlockite phase in the glass-ceramic materials using Sn as internal standard.

The crystal structure of the samples was analyzed by X-ray diffraction and refined by the Rietveld analysis. This analysis permits to evaluate the influence of the thermal treatment on the structure of whitlockite by the variations of the lattice parameters and the volume of the unit cell in functions of the treatment temperature.

## 2.4 Mechanical properties

The strength of the glass and glass-ceramics heat treated at  $700^\circ\text{C}$ ,  $775^\circ\text{C}$ ,  $900^\circ\text{C}$ ,  $975^\circ\text{C}$  and  $1100^\circ\text{C}$  for 4 h was determined by four-point bending tests, using a MTS 810 (50 N) universal testing machine. Batches of six samples were grinded and polished, obtaining bars of  $2.0\text{ mm} \times 1.5\text{ mm} \times 25.0\text{ mm}$

according to ASTM C 1161-02c. The tests were conducted using a four-point bending device with outer and inner spans of 20 mm and 10 mm, respectively, and a velocity of the crosshead displacement of 0.2 mm/min. The bending strength of the samples was calculated by

$$\sigma_f = \frac{3}{2} F_A \frac{I_1 - I_2}{bh^2} \quad (2)$$

where  $\sigma_f$  is the bending strength (MPa);  $F_A$  the rupture load (N);  $b$  the width of the sample (mm);  $h$  the height of the sample (mm);  $I_1$  the outer span distance (mm) and  $I_2$  the inner span distance (mm).

## 3 Results and discussion

### 3.1 Thermal analysis

The results of DSC (Fig. 2) for a monolithic sample and powder samples of size ranges of  $125\text{--}75\ \mu\text{m}$  and  $38\text{--}22\ \mu\text{m}$  respectively indicate that the heat-treated glass exhibits a step near to  $715^\circ\text{C}$ , which is attributed to the glass transition temperature  $T_g$ . Two exothermal peaks are also detected at  $T_{p1} = 830^\circ\text{C}$  and at  $T_{p2}$  varying between  $915^\circ\text{C}$  and  $975^\circ\text{C}$  depending on the particle size.

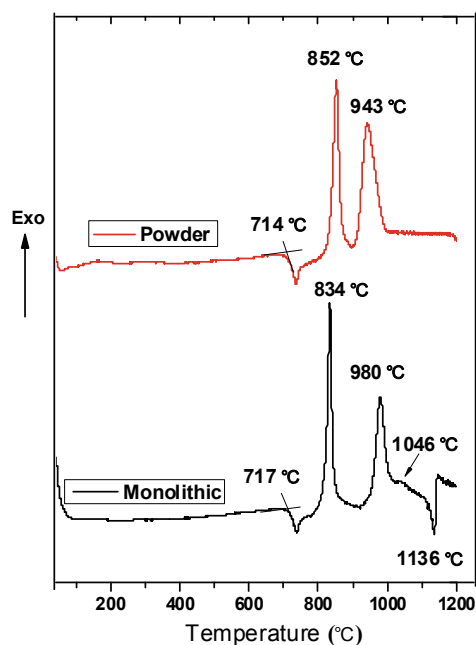


Fig. 2 Thermal analysis of  $3\text{CaO}\cdot\text{P}_2\text{O}_5\text{--SiO}_2\text{--MgO}$  glass.

Another exothermal reaction at  $1040^\circ\text{C}$  has been observed in the bulk sample, but of small intensity,

suggesting a phase transformation of the material. This phase transformation may be confirmed later by the analysis of the crystal phases present. At last during cooling of the glass an exothermal peak at  $T \approx 1115$  °C has been observed.

Previous studies [15,16] suggested that the first peak corresponds to the formation of the TCP with partial substitution of Mg by Ca (whitlockite) of composition  $3(\text{Ca},\text{Mg})\text{O}\cdot\text{P}_2\text{O}_5$ , and the second corresponds to the precipitation of enstatite with partial substitution of Ca by Mg,  $(\text{Mg},\text{Ca})\text{O}\cdot\text{SiO}_2$ . Later results of the phase analysis by X-ray diffraction (Fig. 3) confirm the crystallization of the primary phase whitlockite, but enstatite has not been found. It is only known that the second exothermal peak is due to the formation of a metastable silicate that recrystallizes at temperatures above 1050 °C, as indicated by the third exothermal peak, into the stable phase diopside,  $\text{CaMgSi}_2\text{O}_6$ .

Furthermore, it is possible to affirm that the whitlockite phase presents internal crystallization, because no variation of the transformation temperature with the particle size of the materials occurs. On the other hand, the crystallization of the silicate, indicated by the second exothermal peak, varies with the particle size of the material. With increasing surface (decreasing particle size), the crystallization temperature decreases, indicating that the crystallization of the diopside phase occurs

preferentially at the surface. This crystallization behavior has been studied by Ray *et al.* [18] in the thermal analysis of glasses.

### 3.2 Crystallization behavior

The crystallization process of the materials can be accompanied by analyzing Fig. 3, showing a decrease of the glassy phase and the formation of the whitlockite phase, the transient silicate and the diopside.

Sample V700-4 exhibits an amorphous, glassy structure, because no diffraction peak is observed but only a diffuse high background characteristic of materials without long-range atomic order. In sample V775-4, the formation of whitlockite can be verified besides the amorphous phase. The samples V800-4, V900-4 and V975-4 exhibit quite similar diffractograms, with whitlockite and the transient silicate as crystal phases, only differing in their crystallization degree which tends to increase with increasing heat-treatment temperature. In sample V1100-4, diopside instead of the transient silicate has been detected, suggesting a phase transformation has occurred.

All glass-ceramics studied in this work present the whitlockite phase (PDF#87-1582) with Ca substituting Mg,  $(\text{Ca},\text{Mg})\text{O}\cdot\text{P}_2\text{O}_5$ . It is believed that the formation of whitlockite is induced by the phase separation

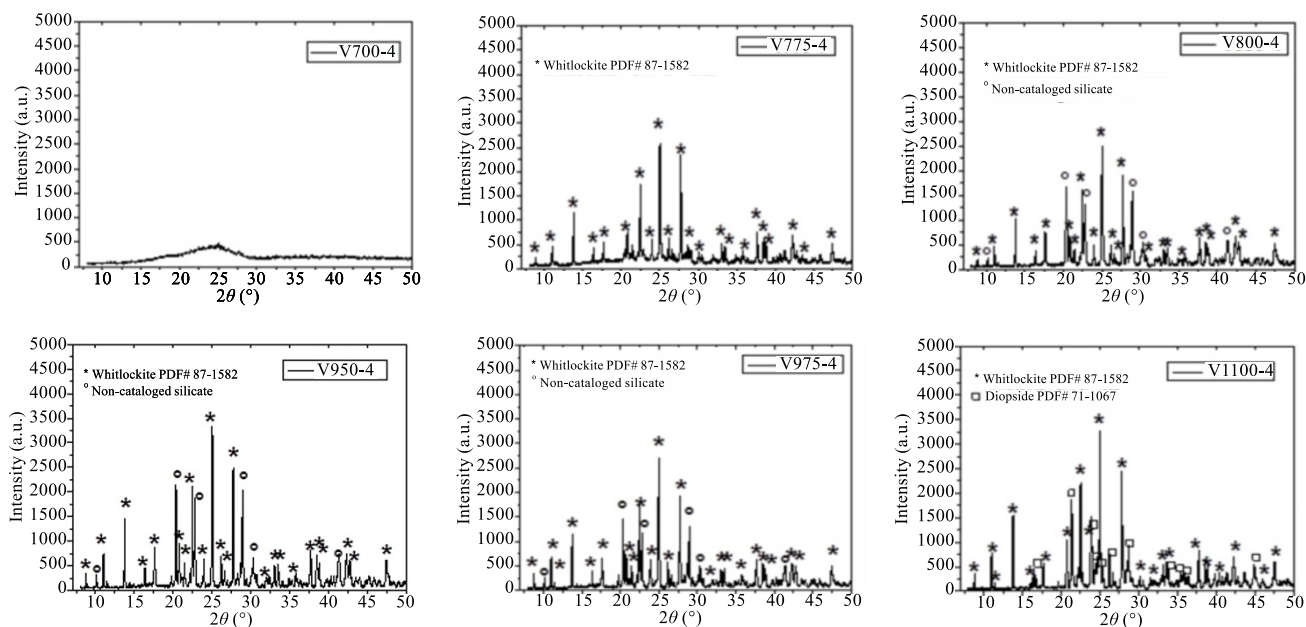


Fig. 3 Crystal phases present in glass-ceramics of the system  $3\text{CaO}\cdot\text{P}_2\text{O}_5\text{-SiO}_2\text{-MgO}$  after heat treatments at different temperatures.

already existent in the glass in form of silica droplets [19]. This phase is TCP with partial substitution of Ca by Mg with composition of  $\text{Ca}_{2.5725}\text{Mg}_{0.4275}(\text{PO}_4)_2$ , also known as  $\beta$ -TCMP.

A second phase starts to crystallize at 800 °C. In a previous study [20], it has been suggested that this phase is enstatite,  $(\text{Mg,Ca})\text{O}\cdot\text{SiO}_2$ , but it has been verified that some of the main peaks do not correspond to this phase. Furthermore, after carefully comparing the X-ray diffraction results with the JCPDS data base, no compatible phase has been identified. Therefore, the authors believed that the “transient silicate” is a metastable phase, originated from the residual glassy matrix after crystallization of whitlockite. This phase disappears in samples treated at 1100 °C (Fig. 3). Metastable phases are quite commonly observed during the crystallization of a glass by thermal treatment [21].

A third crystalline phase, diopside (PDF#71-1067),  $\text{CaMgSi}_2\text{O}_6$ , has been found only in the sample V1100-4. This phase is considered to be the result of a transformation of the transient silicate. When glass-ceramics with metastable phases are heated up to temperatures high enough that solid-state reactions may occur, transformations into stable phases take place, in this case, diopside. The results of the DSC analysis enforce this supposition as indicated by the third exothermal peak at 1046 °C, suggesting a phase transformation characterized by smaller enthalpy.

For a comparative analysis in regard to the crystallization temperatures of the phases, the diffractograms are plotted in the same figure (Fig. 4). For this a  $2\theta$  range between 17° and 27° is chosen, because the most intense peak referring to whitlockite

is observed at approximately 25°.

In general, the main crystallographic changes of the structure of the material occur between 700 °C and 775 °C as shown in Figs. 3 and 4, and between 975 °C and 1100 °C, due to the start of the crystallization process and the transformation into diopside, respectively.

As the phase transformations and the increasing crystallinity interfere directly in the bioactivity and mechanical properties, an estimate of the amount of whitlockite present in the glass-ceramics has been made using an internal standard. In the quantitative X-ray diffraction analysis using an internal standard, the peak intensities are related to the volumetric proportion of the phases present. In the glass-ceramics analyzed in this work, an amorphous phase, whitlockite, a transient silicate (between 800 °C and 975 °C) and diopside (above 1050 °C), have been identified. However, the peak intensities of whitlockite and tin (the internal reference material) cannot be related directly with their respective volume amounts, because the X-ray absorption of each phase is different. To solve this problem, it would be necessary to analyze mixtures containing known proportions of whitlockite and tin, which is not possible. On the other hand, the ratio of the peak intensities of each phase is associated to the volume proportion of whitlockite and tin in each sample, which makes it possible to determine the relative variation of whitlockite by comparison of different samples.

For this comparison, equal proportions between the mass of the sample and tin are necessary. A correction factor,  $CF$ , has been calculated in order that the ratio between the mass of whitlockite and tin always equals 1:1 (arbitrary value) and this is multiplied with the peak intensity of tin. In this way, it may be concluded, for example, that an increasing proportion of whitlockite in the samples indicates a decrease of the amount of glass or the silicate phase and vice versa.

The integrated peak intensities of whitlockite and tin, as well as the correction factor  $CF$  used are listed in Table 3. The term  $x_w$  relates the peak intensities of whitlockite and tin with the sample mass and the internal standard using the correction factor, and represents a numerical value associated to the whitlockite volumetric fraction of different samples. The analysis of this numerical value permits to establish the interaction of crystal phases in function of the temperature of the heat treatment.

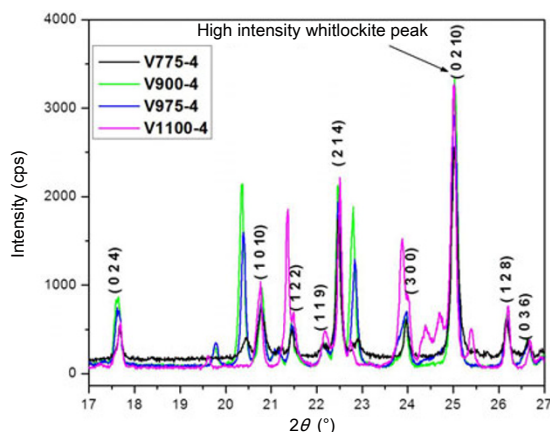


Fig. 4 Comparison of the diffractograms obtained after different heat treatments.

**Table 3 Estimation of the amount of whitlockite in some glass-ceramics using Sn as internal standard**

Sample	Integrated intensity whitlockite $I_w$	Integrated intensity tin $I_E$	$CF = m_{\text{sample}}/m_{\text{tin}}$	$x_w = I_w / (CF \times I_E)$
V775-4	41.7	36.9	0.55	2.06
V850-4	181.4	54.3	0.53	6.30
V950-4	176.3	71.4	0.50	4.94
V975-4	133.3	102.6	0.53	2.45
V1100-4	84.1	62.8	0.53	2.53

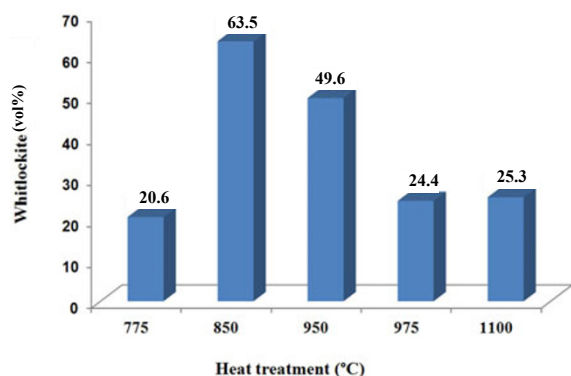


Fig. 5 Relative volume percentage of whitlockite in the glass-ceramics treated at different temperatures.

Figure 5 shows the volume proportions of the whitlockite phase in the samples V775-4, V850-4, V950-4, V975-4 and V1100-4.

Based on the X-ray diffractograms shown in Figs. 3 and 4, the results of the quantitative analysis of whitlockite listed in Table 3 and illustrated in Fig. 5, it can be concluded that in the sample V775-4, whitlockite formation has started but still in a low proportion in regard to the glass phase. In the sample V850-4, the amount of whitlockite has increased to approximately 63 vol%. The heat treatments at 950 °C and 975 °C result in a decrease of the whitlockite fraction of the crystallized portion, probably due to the formation of the transient silicate. In the sample V1100-4, the proportion of whitlockite remains almost the same as in the sample V975-4.

The X-ray diffractograms of glass-ceramic powders obtained by heat treatments of 0.25 h, 2 h, 4 h and 8 h show that time does not significantly influence the formation of new phases during crystallization, except for samples treated at 800 °C, where it has been possible to observe the crystallization of the silicate increases with the time of heat treatment (Fig. 6).

In order to evaluate the effect of the heat-treatment time on the crystallization, the crystallinity has been

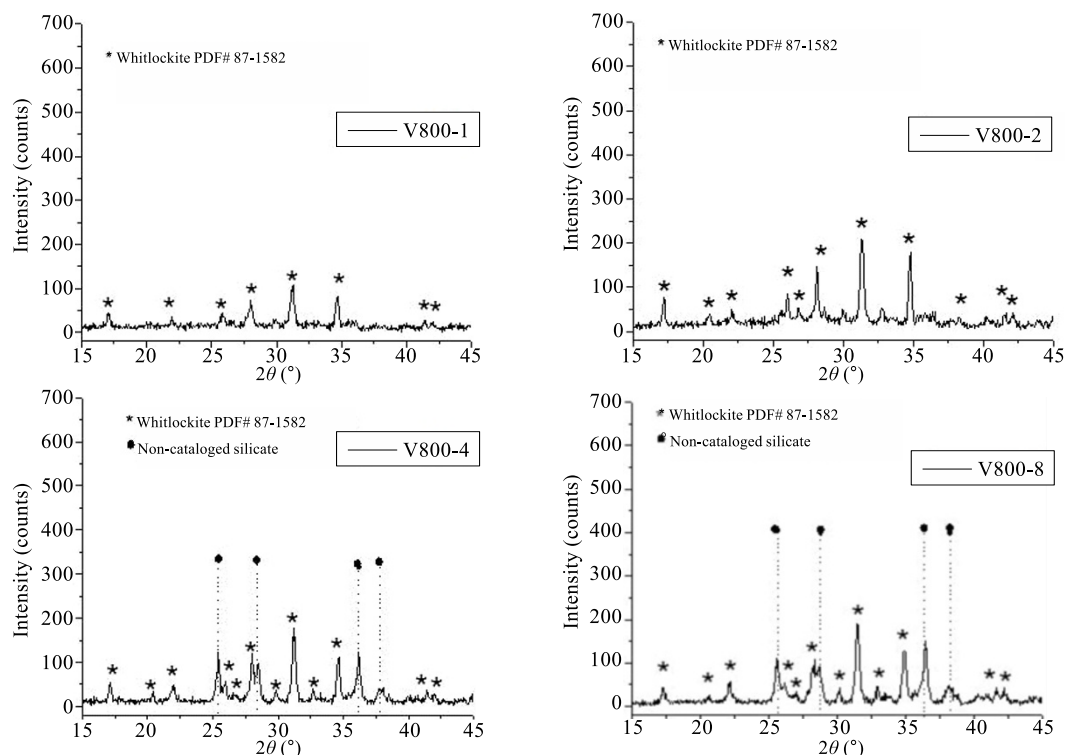


Fig. 6 Effect of the time of heat treatment on the formation of the “transient silicate” at 800 °C for 0.25 h (V800-1), 2 h (V800-2), 4 h (V800-4) and 8 h (V800-8).

estimated and compared. Therefore, the method used by Krimm and Tobolsky [17] has been taken as basis (Eq. (1)), and the percentages of crystal phases obtained during the treatments at varying temperatures are shown in Fig. 7.

In general, crystallinity increases with increasing duration of the heat treatment. Treatments of 8 h results in the highest crystallinity, because more time is given for that the structural rearrangement of atoms may occur. The highest gain in crystallinity can be observed in samples treated at 775 °C for 4 h and 8 h with an increase of 150%. For samples treated at 800 °C, only small variations for treatments between 0.25 h and 2 h and between 4 h and 8 h can be noted, but crystallinity changes 50% in the interval between 2 h and 4 h. In this case, the increase is attributed to the formation of the transient silicate.

### 3.3 Structural analysis of whitlockite

The variations of the lattice parameters of the whitlockite structure in functions of the heat-treatment temperature are presented in Fig. 8.

In functions of the heat-treatment temperature, it has been possible to calculate the volume change of the unit cell of the whitlockite structure, related to the incorporation of  $Mg^{2+}$  ions into the structure. As reported by Schroeder *et al.* [13], the  $\beta$ -TCP phase has rhomboedric geometry, space group  $R3c$  (161), and lattice parameters of  $a=b=10.439$  Å and  $c=37.375$  Å. The structure of whitlockite,  $\beta$ -TCMP, is quite similar to the  $\beta$ -TCP structure, but of smaller lattice parameters of  $a=b=10.337$  Å and  $c=37.068$  Å, in agreement with the results of the glass-ceramics prepared in this work. This result is the consequence of the substitution of  $Ca^{2+}$  ions by smaller  $Mg^{2+}$  ions ( $r_{Mg^{2+}}=0.75$  Å and  $r_{Ca^{2+}}=1.05$  Å), reducing the

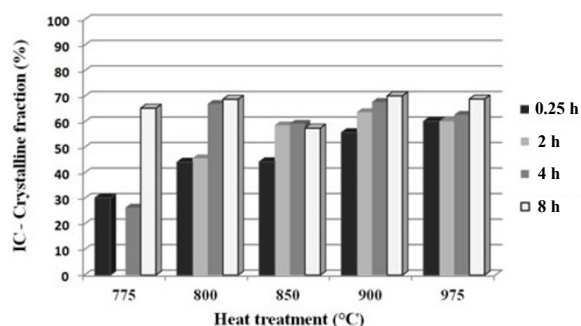


Fig. 7 Effect of the duration of heat treatments at different temperatures on the crystallinity of the materials.

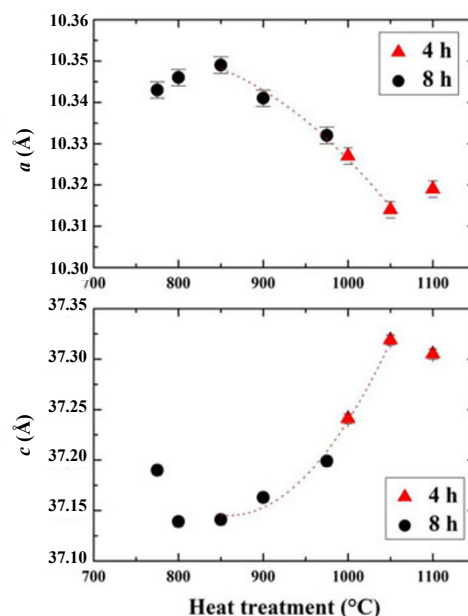


Fig. 8 Variations of the lattice parameters  $a$  and  $c$  of whitlockite due to the heat treatments.

interatomic spacings.

Due to the substitution of  $Ca^{2+}$  by  $Mg^{2+}$  ions in the structure of  $\beta$ -TCP, the lattice parameter  $a$  diminishes from 10.349 Å to 10.332 Å. Studies conducted by Enderle *et al.* [14] and Kannan *et al.* [8] related an expansion of the parameter  $c$  of the  $\beta$ -TCP phase for substitutions of higher than 10 mol% Ca. They attributed this behavior to the observation that until 10 mol%, the  $Mg^{2+}$  ions are allocated in Ca(5) sites resulting in shrinkage along the  $c$  axis, and after this site has been completely occupied, the Ca(4) sites start to be occupied and the lattice parameter  $c$  increases up to the maximum substitution. The solubility limit is 14.25 mol% of  $Mg^{2+}$  ions in the Ca(4) and Ca(5) sites of the  $\beta$ -TCP structure. In this way, it is believed that

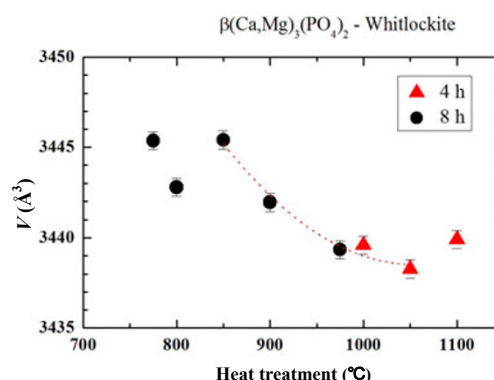


Fig. 9 Variation of the unit cell volume of whitlockite in function of the heat-treatment temperature.



the percentage of  $Mg^{2+}$  ions present in the structure of whitlockite or  $\beta$ -TCMP of the glass-ceramics varies between 10 mol% and 14.25 mol%.

The contraction of the whitlockite structure may be better understood by the analysis of the unit cell volume, as shown in Fig. 9. Initially, the sample V775-8 presents a unit cell volume of about  $3445 \text{ \AA}^3$ , and with increasing temperature of the heat treatment, the volume decreases to about  $3438 \text{ \AA}^3$  for the sample V1050-4, corresponding to a volume reduction of less than 1%. Whitlockite (PDF#87-1582) presents a unit cell volume of  $3439.05 \text{ \AA}^3$ , in agreement with the standard used in this work, indicating that the measurements and the refinements done using the high-definition X-ray diffractograms are in good agreement with the literature [14].

The results of density, relative density and bending strength are presented in Table 4.

**Table 4 Density, relative density and bending strength of the samples**

Sample	$\rho_{\text{real}}$ (g/cm <sup>3</sup> )	$\rho_{\text{apparent}}$ (g/cm <sup>3</sup> )	Relative density (%)	Bending strength (MPa)
V700-4	$2.933 \pm 0.003$	$2.87 \pm 0.01$	$98.8 \pm 0.3$	$71 \pm 4$
V775-4	$2.913 \pm 0.003$	$2.86 \pm 0.09$	$98.3 \pm 0.3$	$105 \pm 7$
V900-4	$3.012 \pm 0.002$	$2.94 \pm 0.01$	$97.6 \pm 0.3$	$116 \pm 10$
V975-4	$3.043 \pm 0.002$	$2.96 \pm 0.01$	$97.3 \pm 0.3$	$119 \pm 12$
V1100-4	$3.079 \pm 0.002$	$2.97 \pm 0.12$	$96.3 \pm 2.5$	$69 \pm 4$

The real density of the samples increases as a function of the heat-treatment temperature because of the crystallization of phases. The sample V700-4 (nucleated glass) exhibits a density of  $2.933 \text{ g/cm}^3$ , while sample V975-4 with some residual glass phase, whitlockite and the “transient silicate” as crystal phases shows an increase of 3.5% in real density. The V1100-4 sample, with residual glass phase, whitlockite and diopside, shows a further density increase of almost 5%. The crystalline phases, whitlockite and diopside, with theoretical densities of  $3.7 \text{ g/cm}^3$  and  $3.28 \text{ g/cm}^3$ , respectively, cooperate directly with the increased density of the samples.

This behavior is well accepted, because with increasing crystallinity of the material, a volume decrease is expected due to the restructuring approach of atoms from the amorphous glass matrix. However, the relative density of these samples decreases with increasing heat-treatment temperature. This behavior can be related to the formation of voids in the structure due to the rearrangement of atoms by the

crystallization process. Recent studies [22,23] showed the formation of internal porosity in the diopside–albanite glass-ceramic system, associated to diopside crystallization, called “induced crystallization porosity”. Porosity is generally of the closed and intragranular type, and found in the center of the samples.

The bending strength values range between 70 MPa and 120 MPa for the glass and glass-ceramics, respectively. It is possible to note an increase of about 70% in bending strength of the samples thermally treated at  $975 \text{ }^\circ\text{C}$ , compared with the untreated glass sample. This improvement in strength is due to the higher atomic ordering found in materials with a high crystallinity (crystalline phase  $\approx 65\%$ ), which lowers the defect energy and thus decreases the tendency to fracture. Possibly, the “silicate transient” phase may be contributing to the improvement of the flexural strength of the material, since a higher content of this phase is found in the sample V975-4. In contrast, at temperature of  $1100 \text{ }^\circ\text{C}$ , a lower modulus of rupture is found, which can be related to the lower relative density of 98.5%.

## 4 Conclusions

Time and temperature of the thermal treatments influence the crystallization behavior of whitlockite in the glass-ceramics system of  $3\text{CaO}\cdot\text{P}_2\text{O}_5\text{--SiO}_2\text{--MgO}$ . Increasing the duration of the heat treatment results in higher degrees of crystallinity, while higher temperatures result in different crystal phases. For all glass-ceramics studied, the major crystal phase formed has been whitlockite or  $\beta$ -TCMP,  $3(\text{Ca,Mg})\cdot\text{P}_2\text{O}_5$ . Furthermore, a metastable silicate phase has been found in samples treated in the temperature range between  $800 \text{ }^\circ\text{C}$  and  $1000 \text{ }^\circ\text{C}$ . Close to  $1050 \text{ }^\circ\text{C}$ , this phase transforms into the stable phase diopside,  $\text{CaMgSi}_2\text{O}_6$ . By variation of the heat treatments, it has been possible to obtain glass-ceramics with a degree of crystallinity superior to 20% and a maximum volume percentage of 60% of whitlockite in the crystallized part of the material, after a treatment at  $850 \text{ }^\circ\text{C}$  for 4 h. The substitution of  $\text{Ca}^{2+}$  by  $\text{Mg}^{2+}$  ions in the whitlockite structure has been confirmed by Rietveld analysis with the variations of the lattice parameters of the  $\beta$ -TCP structure, suggesting the incorporation of up to 14 mol% of  $\text{Mg}^{2+}$  ions. Furthermore, the

crystallization of phases from the glass leads to a decrease of the relative density. However, a high whitlockite-phase content in the glass-ceramics leads to increasing bending strength, approximately 120 MPa for samples heat treated at 975 °C for 4 h.

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