Highly translucent nanostructured glass-ceramic

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Abstract

Transparent and translucent glass-ceramics (GCs) are found in an increasing number of domestic and high-technology applications. In this paper, we evaluated and optimized the effects of two-stage heat treatments on the resulting crystalline phases and microstructure of a glass of the SiO2-Li2O-P2O5-TiO2-CaO-ZnO-Al2O3 system. The objective was to develop a transparent nanostructured glass-ceramic (GC). After numerous heat treatment trials, we found that a long nucleation period of 72 h at 455 °C followed by a crystal growth treatment at 660 °C for 2 h resulted in a highly translucent GC having homogenously distributed nanocrystals. We thus developed a GC having crystals under 50 nm, with a high crystallized fraction (52%vol Li2SiO3 and 26%vol Li2SiO4), transmittance of approximately 80% in the visible spectrum for 1.2 mm thick specimens, nano hardness of 8.7 ± 0.1 GPa (load of 400 mN), a high elastic modulus of 138 ± 3 GPa as measured by nanoindentation, and good flexural strength (350 ± 40 MPa) as measured by ball-on-3 balls tests. Due to its high content of Li+, this GC has the potential to be chemically strengthened and can be further developed to be used in a number of applications, such as on displays of electronic devices.

1. Introduction

Glass-ceramics (GCs) are inorganic, non-metallic materials prepared by controlled crystallization of glasses via different processing methods. They contain at least one type of functional crystalline phase and a residual glass. The crystallized volume fraction may vary from ppm to almost 100% [1]. GCs can have a number of superior properties, such as high hardness, strength and toughness, high chemical durability, transparency or translucency, thermal stability, and even bioactivity. GCs have found numerous applications in special kitchenware, labware, telescope mirrors, dental prostheses, ballistic protection, immobilization of radioactive waste, substrates of hard discs, biological implants, hosts for luminescent materials and others [2]. For instance, lithium disilicate (LD) GC is one of the most popular materials in the field of restorative dental substances [3]. Due to their high strength and toughness, adequate hardness, combined with high chemical durability and superior aesthetics, which ensures a tooth-like appearance, they are extensively used for dental inlays, onlays, crowns and bridges [4].

Research to improve the mechanical properties of LD GCs has aroused great interest in the past few years. Commercial GCs have a flexural strength of 250–550 MPa and fracture toughness from 1.5 to 3.0 MPa m1/2 [5–7]. Translucency is an important property which affects the esthetic and is critical for dental restorations. Based on the translucency properties of human enamel and dentine, restorative materials should be optimized for successful esthetic rehabilitation [8], for instance, dental restorations require different degrees of translucency for different applications [9].

On the other hand, transparent GCs have been developed from many chemical systems thus far, and depending on the system, can be used for various applications. For example, certain GCs based upon “stuffed” β-quartz solid solution structures in the Li2O–MgO–ZnO–Al2O3–SiO2 system – with titania and/or zirconia as the nucleating agent – can be used for ballistic protection, in broadband optical amplification, tunable and IR lasers and solar collectors [10]. GCs containing LD crystals have been cited as transparent GCs for ballistic protection [11]. Some excellent reviews [12–17] have been written on these transparent GCs, which
will not be discussed here.

Transparency in GCs requires very low light scattering and absorption. The attenuation of light due to scattering (turbidity) depends upon the difference in the refractive index of the numerous phases and the size distribution of the crystals in the residual glass matrix [13,18]. To ensure that GCs transmit visible light, the crystal size of all phases should be much smaller than the wavelength of visible light. Moreover, the optical anisotropy within the crystals and the refractive index difference between crystals and glass matrix should be very small [19].

Therefore, the microstructure and size of LD (lithium metasilicate) crystals and the composition of the residual glass matrix can be tailored in GCs to tune their opacity, translucency and transcrancy. Wang et al. [20] investigated the influence of the P₂O₅ nucleating agent on the size of LD crystals in a SiO₂–Li₂O–K₂O–Al₂O₃–ZrO₂–P₂O₅ glass system. For P₂O₅ contents below 2.0 mol%, the maximum size of the LD crystals was 200–400 nm. Zhang et al. [21] studied the effect of heat treatments on the size of the LD crystals in a glass of the following system SiO₂–Li₂O–K₂O–Al₂O₃–ZrO₂. They achieved a GC with a crystal size of 400 nm after treating at 650 °C for 72 h and 830 °C for 3 h. Bai et al. [22] developed a highly translucent LD GC from a Li₂O–SiO₂–Al₂O₃–K₂O–P₂O₅ glass system, with crystal sizes of 100 nm and 200 nm for single-stage and two-stage heat treatments, respectively. Morimoto S. and Emem W. [23] investigated the relationship between the fracture strength and crystal size of transparent/translucent Li₂O–SiO₂ GCs. Their visual scale of transparency varied from transparent, slightly translucent, weakly translucent, weakly translucent. Their GCs had LD crystals of 20–60 nm, and 60–80% crystallinity. The strongest material (~240 MPa measured by three-point bending method) was obtained for a weakly translucent GC having 77% crystallinity and crystals of approximately 60 nm.

The above described studies show that to improve the transcrancy of the LD GCs, or to obtain transparent LD GCs, a finer grained microstructure needs to be achieved.

In this work, we investigated the crystallization behavior, microstructure and optical transmittance of a novel LD GC obtained from a multicomponent glass of the SiO₂–Li₂O–P₂O₅–TiO₂–CaO–ZrO₂–ZnO–SrO–Al₂O₃ system. Our objective was to obtain the finest possible microstructure that could lead to a transparent or, at least, to a highly translucent GC that could be chemically strengthened. The intended application of the transparent or translucent material would be for displays of smartphones and similar devices.

2. Experimental procedure

The parent glass composition was calculated using the software programs Reformix® and Sciglass®. It was formulated to give a glass having a refractive index, thermal expansion coefficient, and density values intermediate between those of the lithium disilicate and lithium metasilicate glasses. The originally designed composition (mol%) was 52.6 SiO₂; 40 Li₂O; 2.5 P₂O₅; 2.3 TiO₂; 1.4 CaO; 0.4 ZrO₂; 0.4 ZnO; 0.2 SrO; 0.2 Al₂O₃. This composition was obtained from the following reagent grade chemicals: lithium carbonate (Li₂CO₃ – Synth, Brazil), high-purity quartz powder (SiO₂ – Vitrovita, Brazil), Phosphorus pentoxide (P₂O₅ – Sigma Aldrich, USA), titanium dioxide (TiO₂ – Sigma Aldrich, USA), calcium carbonate (CaCO₃ – Synth, Brazil), zinc oxide (ZnO – Alfa Aesar, USA), zinc oxide (ZnO – Synth, Brazil), strontium carbonate (SrCO₃ – Sigma Aldrich, USA) and alumina (Al₂O₃ – Alcoa, Brazil).

A well-mixed batch of precursor powders was melted in a platinum crucible at 1250 °C for 4 h in an electrical furnace in air, to obtain 100 g of glass. The melts were poured between two stainless steel plates every 1 h, chased and re-melted three times. Finally, they were cast in a stainless-steel mold, and the resulting glass pieces (cylinders of 12 mm in diameter and 30 mm in length) were annealed at 400 °C for 2 h for stress relief.

A differential scanning calorimetry (DSC) test was performed in small pieces of ~20 mg using a Netzsch DSC 404 equipment to determine the characteristic temperatures of the glass using a heating rate of 10 °C min⁻¹ up to 1200 °C. A sample nucleated at 455 °C by 72 h was also investigated by DSC. Glass transition temperature (Tg), peak temperatures of the crystallization (Tp), and melting temperature (Tm) were identified for both samples. The tangent method was used to obtain Tg [24].

Glass samples were heat-treated in a tubular electrical furnace, with a variation of ±1 °C. The selected heat treatments were: nucleation at the glass transition temperature (Tg = 455 °C) for 30 min and crystal growth for 30 min at different temperatures. Considering the DSC curve, the following crystal growth temperatures were used: 560 °C, 580 °C, 660 °C, 700 °C, 725 °C and 750 °C. To obtain nanometric crystals, the nucleation time was extrapolated to 72 h at 455 °C and samples were submitted to crystal growth for 2 h at 560 °C, 600 °C, 660 °C and 700 °C.

After heat treatment, the samples were ground with SiC abrasive papers of different granulometries down to a 1200 grit, and then polished using a suspension of CeO₂ in water. Scanning electron microscopy (SEM, Tescan Mira 3 – FEG) was used to observe the microstructure of polished transversal sections (after etching by a 5 vol% HF solution for 10 s). Sample surfaces were previously recovered with a thin layer of gold.

X-ray diffraction (XRD) analysis was used to investigate the development of crystalline phases upon heat treatment. XRD data were collected on bulk samples by means of a diffractometer (Bruker D2 Phaser, Karlsruhe, Germany) using Cu Kα radiation. The samples were scanned at scattering angles, 2θ, from 10° to 40°, with a step size of 0.02° and a collection time of 1 s. The crystalline phases were identified using Joint Committee for Powder Diffraction Studies (JCPDS) standard diffraction patterns. The amount of the crystal phases (crystallized volume fraction) was estimated according to the procedure used by Daganano et al. [25]. The Crystallinity Index, CI%, was calculated by evaluating the crystalline area, AC, and the total area, AT (AT = amorphous + crystalline), combined in Equation (2.1):

\[ CI\% = \left(\frac{AC}{AT}\right) \times 100\% \]  

Data management and analysis was performed using the software Origin 8.5.

Considering the most translucent GC, its crystalline volume fraction was determined by XRD and Rietveld refinement of the crystal structures. Alumina powder was mixed to a powdered sample in a 1:1 proportion by weight. The diffractogram was recorded using Cu Kα radiation and was measured in the 0–θ geometry at room temperature using a Rigaku Ultima IV diffractometer in the Bragg-Brentano geometry. The 20 range was scanned from 10° to 80°, with a step size of 0.02° in the 20 scale, 10 s for each step. The volume fraction of the crystalline phases and alumina were determined by Rietveld refinement of the XRD patterns where the amorphous glass contribution was considered as part of the background. Rietveld refinement of the crystal structures was performed using the TOPAS-Academic software [26]. Using the known amount of alumina added to the powdered GC and its estimated volume fraction obtained by Rietveld refinement, a simple rule of mixture allowed for the calculation of the volume fractions of each crystalline phase and the residual glass phase in the GC. The densities of the alumina and the crystallized phases used in the calculation of the crystallized volume fraction were the values obtained from the Rietveld refinement. The glass density was measured experimentally.

The hardness (H) and elastic modulus (E) of the parent glass and GC were measured using instrumented indentation with an UNAT Nanoindenter (ASMEC) with a Berkovich diamond tip. The maximum applied load was 400 mN. A matrix of 25 indentations was made in each sample, and the values of H and E were calculated using the Quasi Continuous Stiffness Measurements (QCSM) [27]. The computed values of H and E are the averages of all indentations.

The indentation fracture toughness (Kc) measured by Vickers
indentation was calculated using the Niihara’s model [28], according to the following equations:

\[
\frac{K_C\phi}{H^{1/2}} \left(\frac{H}{E\phi}\right)^{1/2} = 0.035 \left(\frac{E}{H}\right)^{1/2} \quad 0.25 \leq \frac{1}{a} \leq 2.5
\]

(2.2)

\[
\frac{K_C\phi}{H^{1/2}} \left(\frac{H}{E\phi}\right)^{1/2} = 0.129 \left(\frac{E}{H}\right)^{1/2} \quad \frac{c}{a} \geq 2.5
\]

(2.3)

where \(a\) is the half-diagonal indent impression, \(c\) is the radial crack length, \(l = c-a\), and \(\phi\) is a constant equal to 3. In some cases, the crack dimensions satisfied both conditions, \(l/a < 2.5\) and \(c/a > 2.5\), as in our case. Therefore, \(K_C\) was calculated as the average of the two equations. Six Vickers indents were made using a Leica VMHT MOT microindenter with an applied load of 5 N and 15 s of dwell time at room temperature. The air humidity was 68%. The indent impressions were measured by an optical microscope and the reported \(K_C\) values were the average of all indentations.

The fracture strength was measured using a ball-on-three-balls (B3B) apparatus [29,30] using three 4 mm (radius) alumina balls under the samples and a fourth ball centralized on their upper surface. The jig was made of stainless steel. The tests were carried out using a universal testing machine (AGS-S kN, Shimadzu) with a displacement rate of 1 mm min\(^{-1}\) at 80% relative humidity. The samples had a disk format with 12 mm in diameter and 1.2 ± 0.1 mm thickness. All samples received a final polishing in a CeO\(_2\) water solution. The glass samples were annealed at 430 °C for 2 h and the GC samples were annealed at 510 °C for 2 h and all the samples were furnace cooled to room temperature at a rate of 2 °C min\(^{-1}\) for stress relief from the polishing process. Immediately before the tests, the samples were gently polished using a CeO\(_2\) water solution.

The biaxial fracture strength, \(\sigma\), was calculated by Ref. [30,31]:

\[
\sigma = f(R, R_c, t, \nu) \frac{P}{F}
\]

(2.4)

where \(f\) is a dimensionless factor, which depends on the sample radius (\(R\)), ball radius (\(R_c\)), sample thickness (\(t\)), and sample Poisson’s ratio (\(\nu\)), and \(P\) is the failure load. A minimum of 6 samples was tested for each condition.

UV VIS-NIR optical transmittance spectra were recorded in the wavelength range of (300–800) nm using a scan speed of 60 nm/min and a double-beam spectrophotometer (PerkinElmer, Lambda 900). All the samples were measured with a thickness of 1.20 mm after gridding in SiC papers with different granulometries and polishing in a CeO\(_2\) solution.

3. Results

The DSC curves of the parent glass and a sample nucleated for 72 h at 455 °C are shown in Fig. 1. The characteristic temperatures of these pieces are presented in Table 1. \(T_d\) does not change after the nucleation treatment. Five crystallization peaks are identified for both samples. The three other crystallization peaks (\(T_{P1}, T_{P2}\), and \(T_{P3}\)) of the nucleated sample also shift to lower temperatures when compared to the crystallization peaks of the parent glass. In summary, after nucleation, all the crystallization peaks move to lower temperatures, as shown in Table 1. On the other hand, no differences in the liquidus temperatures (\(T_{L1}, T_{L2}\) and \(T_{L3}\)) were observed for the parent glass and nucleated sample.

Fig. 2 shows XRD patterns of GCs nucleated at 455 °C for 30 min and treated at different temperatures for crystal growth. The GC, treated at 560 °C for 30 min, presents low intensity XRD peaks, indicating a small crystallized fraction. Moreover, the baseline is defined by a broad hump between 20 and 40 (2\(\theta\)), characteristic of the amorphous structure. This temperature is close to the first DSC crystallization peak of the glass (\(T_{P1}\)), and the formation of two crystalline phases are observed: lithium disilicate (\(\text{Li}_2\text{Si}_2\text{O}_5\)) and lithium metasilicate (\(\text{Li}_2\text{SiO}_4\)). Samples heat treated up to 700 °C present the same two crystalline phases, however the relative intensity of \(\text{Li}_2\text{Si}_2\text{O}_5\) peaks gradually increase with the crystal growth temperature, whereas the baseline hump becomes flatter. At 725 °C and 750 °C, \(\text{Li}_2\text{SiO}_3\), \(\text{Li}_2\text{Si}_5\text{O}_{10}\) and \(\text{Li}_2\text{PO}_4\) are observed.

Fig. 3 shows the visual aspect of the glass and GCs nucleated at 455 °C for 30 min and further treated at different temperatures for crystal growth for 30 min. The GCs treated up to 700 °C are translucent, as shown in Fig. 3 b-e. On the other hand, heat treatment at temperatures higher than 700 °C results in opaque samples, as can be seen in Fig. 3 f-g, and this higher opacity can be associated with the crystallization of the \(\text{Li}_2\text{PO}_4\) phase as shown in Fig. 2.

Fig. 4 shows SEM micrographs of sample surfaces chemically etched in HF 1% for 10 s, of the GCs nucleated at 455 °C for 30 min and further treated for crystal growth for 30 min at different temperatures. All samples present a nanocrystalline microstructure, with crystals under 60 nm. The samples treated at the two lowest temperatures, 660 °C and 700 °C, Fig. 4 a and b, respectively, show a higher amount of residual glass, which was removed by the acid attack and appears as pores. The size of these pores, or residual glass portions, are around 140 nm, which corresponds to almost three times the typical size of the crystals. The GC treated at 750 °C presents a small amount of residual glass and the pore sizes are smaller (110 nm).

Fig. 5 shows optical transmittance in the ultraviolet, visible and infrared as a function of the wavelength of the glass and GCs nucleated at 455 °C for 30 min and further treated for crystal growth for 30 min at different temperatures. Pristine glass showed very high transparence all over the spectrum from the ultraviolet to the infrared, with the UV absorption edge cut-off at 340 nm. At least up to 700 °C, the cut-off does not change significantly, remaining in the ultraviolet region. However, the GC heat treated at 725 °C showed an important redshift of the cut off to the visible region (620 nm), which moved to the infrared region for the sample heat treated at 750 °C. Moreover, the transmittance values at 555 nm can be used to compare the different specimens. Since the human eye is most sensitive to 555 nm, this wavelength is used by the International Commission on Illumination (CIE) [32] and Japanese Industrial Standard (JIS) [33]. The most translucent GC was heat treated at 560 °C for 30 min; presenting a transmittance of 66% at 555 nm. The transmittance continuously decreases with the temperature of heat treatment reaching 56% for the GC heat treated at 700 °C. The transmittance for GCs heat treated at 725 °C and 750 °C are below 2% at 555 nm, as these samples are optically opaque.

To enhance nucleation, other samples were heat treated for a much longer time period at 455 °C, i.e., for 72 h and submitted to different treatments for crystal growth for 2 h to reach the highest possible crystallized fraction, keeping the crystal size in a nanoscale range. As
shown by Fig. 6, samples treated at 560 °C and 660 °C for 2 h after nucleation, present only a few crystallization peaks in the XRD patterns and a large amorphous halo indicating a significant amount of residual glass. The CI% of these samples are 18% and 26%, respectively, as characterized regarding its mechanical properties, microstructure and crystalline fraction, as this sample presented a high CI%, only two crystalline phases, a visually transparent aspect and high optical transmittance in visible range.

Fig. 10 shows the XRD pattern of the powdered GC mixed with α-alumina for phase quantification. The crystalline phases identified are alumina (Al₂O₃), lithium metasilicate (Li₂SiO₃), lithium dicalcium silicate (Li₂Ca₂SiO₅). The crystallized volume fractions determined by Rietveld refinement are: 52 ± 3% Li₂SiO₃ and 26 ± 2% Li₂SiO₃ and 22 ± 6% of residual glass.

The hardness (H) and elastic modulus (E) of this GC were determined by instrumented indentation as a function of the contact depth, as shown in Fig. 11. The GC displayed a higher H and E than the parent glass. At the deepest contact depth, the hardness are 7.0 ± 0.1 GPa and 8.8 ± 0.1 GPa for the glass and GC, respectively. The elastic moduli are 92 ± 1 GPa and 139 ± 2 GPa, respectively. The indentation fracture toughness (K₁c) of the glass-ceramic calculated using Niihara’s model is 1.0 ± 0.1 MPa m¹/², slightly higher than the K₁c of the glass, which is 0.8 ± 0.1 MPa m¹/². Using the B3B technique, we found that the parent glass and the GC (460 °C 72 h + 660 °C 2 h) have fracture strengths of 161 ± 36 MPa and 350 ± 40 MPa, respectively.

4. Discussion

To develop and control GC microstructures, it is vital that the precursor glass presents internal, volume nucleation. For stoichiometric compositions, the reduced glass transition temperature, Tgr = Tg/Tm (temperature in K) is an empirical parameter that indicates the tendency of oxide glasses to nucleate homogeneously in the volume, [34–38]. In our case, as the current composition is not stoichiometric, we replaced the melting point by the Tl₃, hence the current glass composition shows Tgr = 0.55 (Tgr < 0.6), suggesting that this glass can indeed potentially nucleate internally (Table 1).

The glass stability against crystallization calculated using the Hruby (K₁c = (Tₓ−Tₘ)/(Tₚ−Tₘ) [39] and the Rodrigues (Kₐ= (Tₚ−Tₘ)²/Tₓ) [40] parameters gives values of 0.2 and 13, respectively. Both parameters indicates a poor stability for the developed glass composition when compared to other silicate glasses [40,41], e.g. the K₁c is similar to values for glasses of the reluctant Li₂O-B₂O₃ system [42]. This result indicates that only millimeter thick glassy samples can be made with this composition.

P₂O₅ acts as a nucleating agent in glasses of the Li₂O-SiO₂ system. It has been shown that it induces the liquid-liquid phase separation and the formation of lithium phosphate crystals, which increases the internal crystal nucleation rate [43,44]. Despite the presence of five exothermic peaks in the DSC curve of the glass (see Fig. 1), in samples nucleated at Tgr for 30 min, only two crystalline phases were observed in the GCs heat treated up to 700 °C (Li₂SiO₃ and Li₂S2O₅, see Fig. 2) and for samples heat treated at 725 °C and 750 °C, the three observed phases were Li₂SiO₃, Li₂S2O₅ and Li₂PO₄. Even the GC heat treated at a temperature corresponding to the first DSC crystallization peak (T bp = 566 °C) presents Li₂S2O₅ and Li₂SiO₃ concomitantly, and Li₂SiO₃ remains as the
main crystalline phase for GCs heat treated from 660 °C up to 750 °C. In commercial lithium silicate dental GCs, Li$_2$SiO$_3$ and Li$_2$Si$_2$O$_5$ are typically formed [45]. The crystallization of these phases is typical for GCs of the following composition range in wt.%: 64–73 SiO$_2$, 13–17 Li$_2$O, 0.5–5 Al$_2$O$_3$, 2–5 K$_2$O, 2–5 nucleating agent (preferably P$_2$O$_5$) and additives - up to 4 ZrO$_2$ and small amounts of ZnO and La$_2$O$_3$. Nucleation is catalyzed by nano-scaled Li$_3$PO$_4$ phases, acting by epitaxy of both Li$_2$SiO$_3$ and Li$_2$Si$_2$O$_5$ crystals. After nucleation, lithium disilicate grows as agglomerated nanocrystals. By contrast, lithium metasilicate grows rapidly and decomposes at 780–820 °C, showing a drastic increase in the

Fig. 4. SEM micrographs of the glass-ceramics nucleated at 455 °C for 30 min and treated for crystal growth for 30 min at different temperatures: a) translucent samples: 660 °C; b) 700 °C; opaque samples: c) 725 °C; d) 750 °C. They were etched in HF 1% for 10 s. The average crystal and pore size are indicated for each sample, the numbers in brackets are the standard deviation.

Fig. 5. Optical transmittance in the ultraviolet and visible as a function of wavelength of the glass and glass-ceramics nucleated at 455 °C for 30 min and further treated for crystal growth for 30 min at: 560 °C; 580 °C; 660 °C; 700 °C; 725 °C; 750 °C. All samples were 1.2 mm thick.

Fig. 6. XRD patterns of glass-ceramics nucleated at 455 °C ($T_g$) for 72 h and heat treated at different temperatures for crystal growth for 2 h. x: Li$_2$SiO$_3$ JCPDS 72–102; Squares: Li$_2$Si$_2$O$_5$ JCPDS 74–2145; black circles: SiO$_2$ JCPDS 86–2331; black squares: Li$_3$PO$_4$ JCPDS 74–358.

Table 2

<table>
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<th>Heat-treatment</th>
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<th>CI%</th>
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<td>455 °C 72 h-700 °C 2 h</td>
<td>Li$_2$SiO$_3$; Li$_2$Si$_2$O$_5$; Li$_3$PO$_4$</td>
<td>60</td>
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mass fraction of lithium disilicate [46]. In our work, it was not possible to separate the formation of lithium metasilicate and lithium disilicate in different temperature ranges. The SiO$_2$/Li$_2$O ratio in our glass composition is 1.3, which is closer to stoichiometric Li$_2$SiO$_3$ than Li$_2$SiO$_5$. Nevertheless, Li$_2$SiO$_5$ remains as the main crystalline phase in our glass-ceramics. This behavior can be attributed to the relatively high amount of P$_2$O$_5$ in the composition (2.5 mol%). As reported by Wang et al. [20], this oxide induces the formation of lithium disilicate as the main crystal phase, and lithium metasilicate and lithium phosphate as minority phases.

The DSC trace changes significantly, after 72 h of nucleation at 455 $^\circ$C, with a reduction of the first and second peak intensities and crystallization peaks, which move to low temperatures, as shown by Fig. 1 and Table 1. The GC heat treated for 2 h, near T$_p$ (557 $^\circ$C), at 560 $^\circ$C and 600 $^\circ$C, present low crystallization fractions (see Table 2 and Fig. 6), and were no longer considered for further characterization.

The GC nucleated by 72 h at 455 $^\circ$C and heat treated at 660 $^\circ$C for 2 h presented high intensity XRD peaks, two crystal phases: Li$_2$SiO$_3$ and Li$_2$Si$_2$O$_5$ (Fig. 6), crystallinity index of 60% (Table 2) combined with high transparency (Fig. 7) and high transmittance (Fig. 8). For these reasons, the mechanical properties of this GC were characterized. Results have shown that the two-stage heat treatments and prolonging the nucleation holding time were decisive to obtain more homogeneous crystal distributions and reduce the loss of optical transmittance by light scattering.

Phase composition and microstructure determine the mechanical properties of GCs [3,5]. A pore-free microstructure, high volume fraction of crystalline phases, and appropriate chemistry and morphology of the precipitated crystals are favorable conditions to improve mechanical properties. In this study, the GC nucleated by 72 h at 455 $^\circ$C and heat treated at 660 $^\circ$C for 2 h, presents a pore free microstructure, with ~50 nm nanocrystals homogeneously distributed in a glassy matrix (Fig. 9),
which resulted in a hardness of 8.8 ± 0.1 GPa and elastic modulus of 139 ± 2 GPa. The increase in GC elastic modulus was 1.5 times compared to the E value of parent glass (92 ± 1 GPa). The biaxial strength (B3B) of the GC is 2.2 times higher than that of the parent glass. These improved properties are justified by the high crystallized fraction of this GC (Fig. 10). As demonstrated by Serbena et al. [47], the mechanical properties of a stoichiometric lithium disilicate GC increases strongly with the crystallized volume fraction. They reported hardness of 8.3 ± 0.6 GPa and elastic modulus of 133 ± 5 GPa for the fully crystallized GC.

The translucency of GCs is largely dependent on light scattering [48]. Light scattering depends on the crystalline content, crystal size and refractive index difference between the crystal phases and glass matrix [19]. In our work, the crystalline content increased with crystal growth temperature (second heat treatment). The average crystal size is under 60 nm, Fig. 5, but samples heat treated at 725 °C become opaque, Fig. 3, probably due to the extra Li$_2$PO$_4$ crystals formed in these samples (Figs. 2 and 12), which can lead to an extra scattering component, once its refractive index is approximately 1.59 [49]. The crystallized fraction (vol%) determined by Rietveld refinement is shown in Fig. 12. The high crystallized fraction (~75 vol%) and the presence of Li$_2$PO$_4$ (~8 vol%) is responsible for the lower transmittance of the samples heat treated at 725 °C and 750 °C. Morimoto S. and Emem W. [23] obtained transparent LD GCs having crystal size up to 24 nm and percent crystallinity up to 67%. With larger grain size and higher crystallinity, they became slightly translucent, having crystal size in the range 27–36 nm, whereas according to the authors, the GCs having crystal size from 40 nm to 60 nm were "weakly" translucent and presented other crystalline phases: LS and alfa-quartz. However, considering the developed GC in this work was nucleated for 72 h at 455 °C and 750 °C became slightly translucent, having crystal size in the range 27–36 nm, whereas according to the authors, the GCs having crystal size from 40 nm to 60 nm were "weakly" translucent and presented other crystalline phases: LS and alfa-quartz. However, considering the developed GC in this work was nucleated for 72 h at 455 °C and developed at 660 °C for 2 h, it was possible to obtain high transparency and high transmittance even for a crystal size of approximately 50 nm. The strongest material of Morimoto S. and Emem W. [23] (240 MPa, measured by three-point bending) was a weakly translucent GC having a crystal size of 60 nm and 77% crystallinity. This result cannot be compared directly with the fracture strength of our GC (350 ± 40 MPa) because the technique used (B3B) was different.

The LD crystals have an average refractive index of 1.55 [8]; which is approximately 1.57 for lithium metasilicate [50]. The refractive index of the residual glass estimated by the Sciglass® software is approximately 1.60. Therefore, the difference in the refractive index between the residual glass and the crystalline phases (Li$_2$SiO$_3$) is approximately 0.05, and considering the secondary phase (Li$_2$SiO$_3$), it is only 0.03. This value is significantly low (difference below 0.1) to yield low scattering [17,51] and justifies the high transmittance observed in the visible spectrum, as observed in Fig. 8. The similarity between the refractive indices of the amorphous and crystalline phases, the presence of nano-crystals and absence of porosity, ensure sufficient light transmission.

In this work, we developed a new lithium disilicate-metasilicate GC having crystals under 50 nm, with high crystallized fraction (78%), transmittance of 80% (1.2 mm) in the visible spectrum, hardness of 8.8 ± 0.1 GPa, high elastic modulus (139 ± 2 GPa) and flexural strength (350 ± 40 MPa in a B3B test). Preliminary tests indicated that it can be chemically strengthened. We are planning to carry out further research work on this topic.

5. Conclusions

We analyzed the effects of two-stage heat treatments on a specially designed SiO$_2$-Li$_2$O-P$_2$O$_5$-TiO$_2$-CaO-ZnO-Al$_2$O$_3$ glass. We characterized the crystallized phases, microstructures transluency and mechanical properties of the resulting glass-ceramics. Our results show that a very long nucleation time was decisive to obtain sufficiently small crystal sizes to minimize light scattering. In the end, we successfully developed a highly translucent nanostructured glass-ceramic having crystals under 50 nm, high crystallized fraction (52 %vol. Li$_2$SiO$_3$ and Fig. 12. Crystallized fraction (vol. %) as a function of crystal growth temperature, for samples nucleated at 455 °C for 30 min and heat treated at 700 °C, 725 °C and 750 °C for 30 min for crystal growth. The glass volume fraction is not included in the calculations.

26 vol% Li$_2$SiO$_3$), transmittance of 80% in the visible spectrum for 1.2 mm tick samples, hardness of 8.7 ± 0.1 GPa, high elastic modulus (138 ± 3 GPa) and flexural strength (350 ± 40 MPa in a B3B test). This GC contains a high amount of Li, and preliminary tests indicated that it has great potential to be chemically strengthened and be further developed for, e.g., electronic device displays.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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