The role of TiO\textsubscript{2}, ZrO\textsubscript{2}, BaO and SiO\textsubscript{2} on the mechanical properties and crystallization behavior of fluorapatite–mullite glass–ceramics

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Abstract

The effect of TiO\textsubscript{2}, ZrO\textsubscript{2}, BaO and extra addition of silica on the crystallization behavior, microstructure and mechanical properties of an apatite–mullite based glass–ceramic system were investigated by means of X-ray diffractometry (XRD) and scanning electron microscopy (SEM). The precipitated crystalline phases were fluorapatite [Ca\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}F\textsubscript{2}] and mullite [Al\textsubscript{6}Si\textsubscript{2}O\textsubscript{13}], which apart from the extra bearing SiO\textsubscript{2} specimen were rod-like in the other specimens. The rod-like crystalline phases’ lengths were small, i.e. <20 μm, in the TiO\textsubscript{2} and BaO containing glass–ceramics, but small addition of ZrO\textsubscript{2} enhanced the length of crystalline phases to approximately 50 μm. The flexural strength and fracture toughness of the prepared glasses and glass–ceramics were also studied. The results showed that the additive oxides affected both parameters differently. The highest fracture strength and fracture toughness values belonged to the TiO\textsubscript{2} and BaO containing glass–ceramics which contained smaller crystal size. The mechanical properties of the prepared glass–ceramic samples did not differ strongly and/or were even decreased by addition of ZrO\textsubscript{2} and extra amount of SiO\textsubscript{2}.

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1. Introduction

Fluorapatite (Ca\textsubscript{5}(PO\textsubscript{4})\textsubscript{3}F) containing glass–ceramics has attracted attention because of its compatibility with the natural apatite of the human bone and teeth [1,2]. Fluorapatite is a bioactive compound with an apatite-like structure, in which OH groups have been substituted by fluorine ones. Furthermore, its crystalline structure is more stable than hydroxyapatite, which is an important issue where bioactivity receives attention based on crystalline stability [1–3]. Similarity between hardness of fluorapatite-based glass–ceramics and tooth enamel is another advantage that makes them new candidates for substitution of hydroxyapatite in restorative dentistry [1–3].

In most cases, bulk crystallization is the dominant mechanism of crystallization of needle-like fluorapatite in glass specimens. It is said that using P\textsubscript{2}O\textsubscript{5} in the glass SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3}–CaO–CaF\textsubscript{2} system leads to the crystallization of fluorapatite and mullite phases [4–9]. It is also shown that a liquid–liquid phase separation takes place prior to crystallization [4–9]. Phase separation leads to droplet-like areas, which are rich in calcium and phosphorous ions. Following the precipitation of apatite in these droplets, changing the composition of the residual glass phase leads to the precipitation of mullite [4,5,8]. In these specimens fluorapatite is responsible to link to the tooth enamel and bone [3] and mullite induces adequate mechanical properties [10]. The latter phase plays a key role in biocompatible glass–ceramics since they are mostly planned to use in the stress bearing areas [2]. Despite of various studies that were performed on the chemical resistance, flexural strength, biocompatibility and phase separation of the apatite–mullite glass–ceramics [4–10], to our knowledge there are few documents about the performance of minor glass ingredients in points of crystallization behavior and mechanical properties views. The primary purpose of the present study was to gain more insight to the effect of some components like TiO\textsubscript{2}, ZrO\textsubscript{2}, and BaO and also additional amount of silica in the mentioned regards.

2. Materials and methods

The initial glass composition contained 4.5SiO\textsubscript{2}, 3Al\textsubscript{2}O\textsubscript{3}, 1.5P\textsubscript{2}O\textsubscript{5}, 3CaF\textsubscript{2}, and 2 CaO (mole ratio). Reagent grade chemicals Al (OH)\textsubscript{3}, CaF\textsubscript{2}, TiO\textsubscript{2}, ZrO\textsubscript{2}, BaCO\textsubscript{3}, CaCO\textsubscript{3}, phosphoric acid, and SiO\textsubscript{2} were used as the starting materials in this study. The chemical composition of the prepared glasses, which are coded as G, GS, GZ, GB and GT, are shown in Table 1.

The thoroughly mixed batches were melted in an alumina crucible at 1550 °C in an electric furnace for 2 h. Then the molten glasses were cast into a pre-heated steel mold. The resulted glass specimens were cooled naturally to room temperature. Glass transition temperatures and crystallization behavior were investigated using differential thermal analysis (Shimadzu DTG 60 AH). To study the crystallization behavior of the different glasses, the glasses were heat treated from 780 °C to 1200 °C at a heating rate of 10 °C/min for 3 h and then furnace cooled to room temperature. The crystallinity of the specimens was identified by
X-ray diffractometry (Jeol JDX-8030 and Siemens-D500). The microstructure of the samples was examined using a scanning electron microscope (Philips – XL 30 and Cambridge – S 360). The samples were etched by 10 wt.% HF solution prior to SEM analysis. The 3-point bending strength of specimens were determined using rectangular bars (3 × 4 × 25 mm) and a universal testing machine (SANTAM-20), at a cross-head speed of 0.1 mm/min. Flexural strength values for glass and glass–ceramics samples were calculated using the following relationship [11]:

\[ FS = 3 PL/2WD^2 \]

where FS is flexural strength (MPa); P is failure load (N); L is specimen length (mm); W is specimen width (mm) and D is specimen height (mm). Before testing, prepared flexural strength samples were annealed at 500 °C for 2 h. Fractography of the broken surfaces was performed by scanning electron microscopy method. Single-edge-notched beam method (SENB) was used to measure the fracture toughness of glass–ceramic samples. The glass–ceramic specimens were notched with a 0.1 mm diamond saw disk in a low speed Buehler cutting machine and then fractured in a three-point bending test. The notch depth, c, was measured with an optical microscope. The fracture toughness (Kic) value was calculated according to the following formula [11]:

\[ K_{ic} = \frac{F}{Wt^{3/2}} \times f(c/t) \]

\[ f(c/t) = 2.9 \left( \frac{c}{t} \right)^{1/2} - 4.6 \left( \frac{c}{t} \right) + 21.8 \left( \frac{c}{t} \right)^{1/2} - 37.6 \left( \frac{c}{t} \right)^{3/2} + 38.7 \left( \frac{c}{t} \right)^{5/2} \]

where \( K_{ic} \) is the fracture toughness (MPa); F is the critical load (N); W is specimen width (m); t is specimen thickness (m) and \( f(c/t) \) is the stress intensity shape factor. The data were analyzed using one-way analysis of variance (ANOVA) and the means were compared by Tukey’s test (5% significance level).

3. Results

Fig. 1 depicts the DTA traces of various glasses. The crystallization peak temperatures (\( T_{p1} \) and \( T_{p2} \)) of different glasses have been summarized in Table 2. Accordingly, there are two distinct crystallization peaks in every one. Besides, the glass transitions (\( T_g \)) and the crystallization peak temperatures have changed with the addition of the mentioned oxides. Based on these results, while SiO2 and ZrO2 increase the crystallization peak temperatures and their \( T_g \), TiO2 and BaO show contradictory trends. Figs. 2, 3 and 4 show the X-ray diffraction patterns of the glasses after heat treatment at different temperatures. As it can be seen in Fig. 2a, fluorapatite appears after heat treatment at 780 °C only in the glasses GT and GB, probably due to the lower viscosity of these two glasses at this temperature. Fig. 2b shows that this phase appears with lower intensities in G, GZ and GS at 870 °C. Although the present authors were not able to detect a liquid–liquid phase separation, crystallization of the fluorapatite as the first crystalline phase in the \( P ^ {5+} \) and \( Ca ^ {2+} \) rich areas of a liquid–liquid phase separated glass, has been reported previously for the same glass system [4–6]. Comparing Figs. 2b and 3 reveal that while mullite precipitates at 870 °C in GT and GB glasses it is crystallized in GZ and G glasses at 970 °C. Fig. 4a shows that GS glass composition needs higher temperature for crystallization of mullite. According to this figure, it is not possible to judge about the precipitation of mullite in GS after heat treatment of this glass at 1100 °C.

On the whole, it can be concluded that fluorapatite and mullite arise respectively from the first and the second DTA exothermic peaks. Heat treatment of glasses GB, GZ, GS and G at higher temperatures led to increasing of the mullite intensity. However, the glass GT showed a different behavior in this regard above 970 °C (Fig. 4b). It seems that the solubility of mullite crystals in the residual glass phase is responsible for this effect.

The microstructures of the glasses after heat treatment at various temperatures were investigated. Fig. 5a and b demonstrate the SEM micrographs of glass G after heat treatment at 970 °C and 1100 °C for 3 h, respectively. Fig. 5a shows that heat treatment at 970 °C leads to precipitation of the rod-like crystals of apatite and mullite, with maximum length of about 5 μm. The morphology of crystals changes at 1100 °C (Fig. 5b). It can be seen that the crystalline particles have been dissolved in the glassy phase with the increasing of the heat treatment temperature to 1100 °C.

<table>
<thead>
<tr>
<th>Table 1</th>
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<tr>
<td>The chemical composition of different glasses (parts weight).</td>
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<tr>
<td>Glasses</td>
</tr>
<tr>
<td>SiO2</td>
</tr>
<tr>
<td>Al2O3</td>
</tr>
<tr>
<td>CaO</td>
</tr>
<tr>
<td>CaF2</td>
</tr>
<tr>
<td>P2O5</td>
</tr>
<tr>
<td>TiO2</td>
</tr>
<tr>
<td>BaO</td>
</tr>
<tr>
<td>ZrO2</td>
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</tbody>
</table>

<table>
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<tr>
<th>Table 2</th>
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<tbody>
<tr>
<td>Peak crystallization temperatures of different glasses.</td>
</tr>
<tr>
<td>Glass composition</td>
</tr>
<tr>
<td>GT</td>
</tr>
<tr>
<td>GB</td>
</tr>
<tr>
<td>GZ</td>
</tr>
<tr>
<td>GS</td>
</tr>
<tr>
<td>G</td>
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</table>
The SEM micrographs of the heat-treated glass GS at 970 °C and 1100 °C are shown in Fig. 6a and b, respectively. Accordingly, the spherical morphology of apatite and mullite crystals is independent of the heat treatment temperature. The microstructures of the glass–ceramics GZ and GB heat treated at 970 °C and 1100 °C are shown in Figs. 7 and 8, respectively. Based on these figures, the length of rod-like crystalline phases is between 5 and 10 μm after heat treatment at 970 °C. The crystalline particles kept their morphology even when the specimens were heated at 1100 °C (Fig. 8a and b). Furthermore, the approximate lengths of crystalline phases increase to about 20 and 50 μm in GB and GZ glass–ceramics, respectively. Fig. 9a represents the SEM micrograph of glass GT after heat treatment at 780 °C for 3 h. Based on the EDX and XRD results, spherical crystalline phases are primary fluorapatite particles. As Fig. 9b shows, the spherical particles modify to the rod-like ones, with a maximum length of about 5 μm, after heat treatment at 970 °C for 3 h. The rod-like particles that according to EDX analysis could be attributed to both fluorapatite and mullite crystals ultimately start to dissolve in residual glass phase at 1100 °C.

Flexural strength values of the glasses and glass–ceramics heat treated at 1100 °C for 3 h are given in Table 3. The glasses GZ and GS have significantly the highest and lowest flexural strength values, respectively \((p < 0.05)\). After heat treatment, the glass–ceramic GS shows the less flexural strength and glass–ceramics GB and GT represent the highest values \((p < 0.05)\). On the other hand, the glass–ceramic GZ, which indicates intense X-ray diffraction patterns of mullite, shows a moderate flexural strength. Fig. 10a shows the fracture surface of this specimen heat-treated at 1100 °C for 3 h. It can be seen that a crack has been extended around crystalline particles. Fig. 10b represents the fracture surface of the same composition heat treated at 1100 °C for 15 min and then rapidly cooled to room temperature. This figure shows that surface crystallization occurred in the specimen. This phenomenon can reduce the mechanical strength [12,13]. The measured fracture toughness values for glass–ceramics are also summarized in the Table 3. The observed trend in fracture toughness of glass–ceramic samples is similar to their flexural strength values. Glass–ceramic GS presents statistically the lowest fracture toughness \((0.6 \text{ MPa m}^{0.5})\) value, while glass–ceramics GB \((2.1 \text{ MPa m}^{0.5})\) and GT \((1.8 \text{ MPa m}^{0.5})\) show the highest \(K_{IC}\) value \((p < 0.05)\).

4. Discussion

As it was expected, addition of silica and zirconia \((\text{SiO}_2\) and \(\text{ZrO}_2\)) led to the increasing of the glass transition and crystallization temperatures of the GS and GZ compositions. Conversely, barium oxide and titanium oxide reduced the mentioned characteristics of the glasses GB and GT. This behavior is attributed to rising of the glass viscosity with increasing of \(\text{SiO}_2\) and \(\text{ZrO}_2\), through reduction of non-bridging oxygen and/or high ionic field strength of these two oxides [14–18]. A contradictory explanation can be recommended for the effect of barium and titanium oxides, i.e. they increase the numbers of non-bridging oxygen in the glasses and hereby decrease the viscosity of the glasses [18–23].
To investigate the crystallization procedure and development of the crystalline phases in the prepared glasses, the samples were heat treated at different temperatures for 3 h. Based on the XRD results, apatite and mullite were precipitated in the glasses after the mentioned heat treatment and there was not any footprint of other crystalline compounds, such as TiO₂ and ZrO₂, in the XRD patterns, meaning that they did not act as a nucleation agent in the glasses. Furthermore, based on the DTA peak crystallization temperatures and the dilatometric softening point temperature of the glasses, it seems that GS has a higher viscosity than GZ. This makes the condition difficult kinetically for the precipitation of the crystalline phases in the GS glass composition and leads to reduction of their XRD peak intensities of the crystalline phases. Consequently, crystallization of glasses GB and GT to fluorapatite and mullite at respectively lower temperatures of 780 °C and 870 °C should not be extraordinary.

The SEM micrographs of the samples support the above-mentioned results. While apatite and mullite precipitate in the GS as spherical particles in the adopted heat treatment temperature interval, they precipitate in the other glasses as rod-like particles. This difference could be related to the high viscosity of the former glass, due to its higher SiO₂ content [24–26]. Spherical fluorapatite particles can also be seen in GT at lower temperatures. Based on the SEM figures, the size of rod shaped crystals in the glass–ceramics GB and GZ is significantly larger than that of G and GT and their aspect ratio has been increased with BaO and ZrO₂ addition. The mean lengths of crystals were approximately 20 and 50 μm in glass–ceramics GB and GZ, respectively.

Various parameters such as the morphology, the size of crystalline particles, and their amounts control the mechanical strength of a particular glass–ceramic [10–13]. The nature of the phases is another crucial factor that has relatively significant impact on the mechanical strength of the glass–ceramic bodies [10–13]. The presence of more than one crystalline phase in any glass–ceramic system can lead to a complex mechanical behavior [8,10]. Mismatch between densities,
elastic modulus and thermal expansion coefficients of the glass and crystal phases could also lead to the internal stresses in the glass–ceramic structures and modify their mechanical strength [8,10]. In the glass series, the glass GZ shows the highest flexural strength. High field strength of zirconium ion can be accounted as a reason for this result [14–18]. However, glass GZ does not earn the first rank in this regard between the glass–ceramic series heat treated at 1100 °C. To gain a better understanding of effective parameters influencing the flexural strength of glass–ceramic GZ, the fracture surface of these glass–ceramic heat treated at 1100 °C for different times were investigated by means of SEM. According to SEM result (Fig. 8a), the glass–ceramic GZ has the largest crystalline particles compared to other glass–ceramics. These large crystalline particles can weaken the specimen via formation of micro-cracks in the crystal–glass interfaces owing to their thermal expansion and elastic modulus mismatches (Fig. 10a) [10,13]. Based on Fig. 10b, which shows the cross-section of the glass after heat treatment for 10 min, these large crystalline particles originate from the surface crystallization mechanism, which occurred in the glass GZ.

It is known that needle-like crystalline phases improve the mechanical properties more considerably rather than the spherical ones [10,26]. Therefore, it will be reasonable to conclude that spherical fluorapatite and mullite crystalline phases play key role in reduction of the flexural strength values of the glass–ceramic GS when compared to GT and GB. It is also noticeable to say that the most strengthening of the glasses, which has been happened in GB, is attributed to its fine and high content of crystalline particles [10–13], originated from a bulk crystallization mechanism occurred in it.
The differences of $K_{IC}$ values of the prepared glass–ceramics originate from their microstructures. The critical stress intensity factor is denoted by the Griffith–Irwin equation:

$$K_{IC} = Y \sigma f c^{1/2}$$

where $\sigma_f$ is the stress at fracture, $c$ is the depth of an equivalent flaw and $Y$ is a geometrical factor that accounts for the location and geometry of the critical flaw and type of loading [13,27–29]. It seems that the higher values of the flexural strength of glass–ceramics GB and GT are responsible for their higher fracture toughness.

Table 3
Mean flexural strength and fracture toughness values of glass–ceramic samples.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>G</th>
<th>GS</th>
<th>GZ</th>
<th>GB</th>
<th>GT</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Point bending strength (MPa) of glasses</td>
<td>124 ± 35*</td>
<td>152 ± 25</td>
<td>187 ± 13</td>
<td>130 ± 27*</td>
<td>112 ± 20</td>
</tr>
<tr>
<td>3-Point bending strength (MPa) of glass–ceramics</td>
<td>173 ± 22*</td>
<td>180 ± 38*</td>
<td>213 ± 38</td>
<td>247 ± 29</td>
<td>235 ± 27</td>
</tr>
<tr>
<td>Fracture toughness (MPa m$^{0.5}$) of glass–ceramics</td>
<td>1.3 ± 0.06*</td>
<td>0.6 ± 0.2</td>
<td>1.4 ± 0.3*</td>
<td>2.3 ± 0.03</td>
<td>1.8 ± 0.02</td>
</tr>
</tbody>
</table>

*, • and * denotes that there is no significant difference between values marked with similar symbols ($p<0.05$).
5. Conclusions

Addition of TiO₂, BaO, ZrO₂ and extra amounts of silica to the base glass led to some changes in the crystallization temperatures and morphology of the crystalline phases. While TiO₂ and BaO were effective in decreasing the crystallization temperature of the fluorapatite and mullite crystalline phases, ZrO₂ and the extra amounts of SiO₂ increased the crystallization temperature. Except for extra silica bearing specimen that showed spherical morphology for both apatite and mullite phases, apatite and mullite precipitated in the other prepared glass–ceramics as rod-like crystals. Mechanical properties results showed that the highest strengthening and toughening of the glasses occurred in the BaO containing glass as it was crystallized more extensively rather than the others. On the other hand, the least improvement in bending strength of crystallized specimens belonged to the ZrO₂ bearing one, as crystallization happened in it by the surface crystallization mechanism and so it had the largest crystalline particles.

References


