Surface and volume crystallization in fluorrichterite based glasses

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1. Introduction

Glass-ceramics are ceramic materials developed through the controlled crystallization (nucleation and crystal growth) of a glass. Given that the main glass-forming systems are based on silicates compositions, the major crystalline phases in glass-ceramics are also silicates [1]. Among crystalline silicates of interest in glass-ceramics, inosilicates or chain silicates are a silicate group whose structure is characterized by the arrangement of silicate tetrahedra in chains. Single chains (Si4O12n−2), double chains (Si6O18n−6) and even complex chains are feasible. Minerals belonging to the inosilicate group include the pyroxenes (single chain) and the amphiboles (double chain) [2].

A general amphibole formula may be written as A0.1B2.5C(Si,Al)3O22(OH,F)2 where the most common cations are: A: Na, K; B: Na, Ca, Mg, Fe2+; C: Mg, Fe3+, Al, Fe3+. Glass-ceramic materials comprising amphibole minerals can enclose one or more of K-fluorrichterite (KNaCaMg3Si2O5F3), fluorcanasite (K2Na4Ca2Si12O26F24) and agrellite (NaCa2Si2O15F2) crystalline phases [3]. The microstructure of fluoro-amphibole glass-ceramics consists of arbitrarily faced needle-shaped crystals, encouraging several crack deflections when cracked. Glass-ceramics in this system are distinguished by high values of flexural strength and fracture toughness, as well as excellent acid and alkali chemical durability [3,4].

Fluorrichterite glass-ceramics have already found commercial applications as high-performance tableware (Pyroceram® and Correlle® brands). However, in spite of their outstanding technological properties, there is a lack of scientific data on fluorrichterite glass-ceramics since the literature on this subject is limited to few papers reported on the preparation of oriented fluorrichterite/diopside glass-ceramics by electrochemically induced nucleation [5]; the effect of crystallization heat treatment on the microstructure and flexural strength of fluorrichterite glass-ceramics [6]; the study of their crystallization behavior [7–9] and of the feasibility of using fluorrichterite glass-ceramics as biomaterials, such as heat-pressed dental ceramics [4,10,11], glass-ceramics with osteoconductive potential [12–15] or glass-ceramics suitable for hard tissue augmentation [16].

However, limited papers report on the progress of crystals at the earliest stage of the devitrification of fluorrichterite. In previous papers, we stated the concurrence of surface and bulk crystallization in the devitrification process of Na-fluorrichterite glasses [17]. Surface crystallization mechanism predominates at the beginning of the crystallization process; however, volume crystallization attains significance with increasing fluorine content in glass composition [18]. The purpose of the present paper is to study the crystal growth in the initial steps of devitrification of glasses belonging to the SiO2-CaO-MgO-Na2O-F system with variable fluorine content.

2. Experimental

A glass with the stoichiometric composition of fluorrichterite, Na2CaMg3Si2O5F2 and from now on labeled as RE glass, was studied in the SiO2-CaO-MgO-Na2-O-F system and synthesized from silica sand with low contents of iron oxide and reagent grade (MgCO3)4Mg(OH)2·5H2O, CaCO3, Na2CO3 and MgF2. In base to RE composition, three additional glass compositions...
with 6, 8 and 10 wt.% of fluorine were formulated. They were labeled as R6, R8, and R10, respectively.

The raw materials mixtures were homogenized in a planetary ball mill (TURBULA, WAB-GROUP, Switzerland) for 15 min. The batches were melted at 1450ºC for 2 h in an electric furnace. Alumina-silica crucibles were used to contain the melts. After homogenization, melts were cooled in two different ways in order to get glasses as bulk or frit form. Thus, bulk glasses were obtained by pouring the melt on a brass mold. In order to minimize residual stress and to avoid glass devitrification, bulk glasses were annealed at a temperature of \( T_g - 100 \)ºC for 2 hours. For each glass composition, \( T_g \) was previously determined from differential scanning calorimetry (DSC) on glass samples with the same chemical composition (18). The \( T_g \) values determined for the RE, R6, R8 and R10 glasses are 565º, 560º, 550º and 535ºC respectively. On the other hand, frit glasses were obtained by pouring the melts into cool water.

The chemical analysis of the resulting glasses was determined by X-ray fluorescence (XRF)(BRUCKER S8 Tiger spectrometer, USA) The analysis was performed on pressed pellets of powder glass samples (<63 µm). The crystallization mechanism study was conducted by both DSC and field emission scanning electron microscopy (FESEM). DSC study (SETARAM Labsys Thermal Analyzer, France) was carried out on samples with two different particle sizes, i.e., fine (< 63 µm powder) and coarse (~ 3 × 3 × 4 mm fragment). The samples were heated under flowing air from room temperature to 1400ºC at a heating rate of 50ºC·min\(^{-1}\). Samples of 40 mg were placed in platinum crucibles and calcined Al\(_2\)O\(_3\) was used as the reference material. All the DSC curves were normalized with respect to the sample weight.

For corroborating the preferential crystallization mechanism (surface or volume), the beginning of crystal growth was promoting by subjecting fragment samples of parent glasses to thermal treatments at the temperature interval 800–1100ºC for 5 min. For each composition, the pair (temperature, time) that results in the minimum crystal development that can be detected by XRD were selected. To carry out the crystallization treatments, the glass fragments were placed in the furnace, previously heated at the treatment temperature. After 5 min, the samples were taken out of the furnace and air-cooled. The microstructure of the subsequent glass-ceramic materials was examined by FESEM (HITACHI S-4800P microscope, Japan) using an acceleration voltage of 20 kV. Samples were polished to a 1 µm finish using diamond pastes after initially grinding with SiC powder. The samples were subsequently etched for 10 s in a solution of 5% HF, ultrasonically washed with distilled water and ethyl alcohol, dried and coated with Au-Pd (Balzers SCD 050 sputter, Lienchestein). Semi-quantitative analysis of the different phases was performed by energy-dispersive X-ray spectroscopy (EDS) with a Link eXL detector provided by a beryllium (Be) window.

The amorphous character of the as-melted glasses and the mineralogical analysis of the crystalline phases devitrified after thermal treatment was accomplished using X-ray diffraction (XRD) (BRUKER D8 Advance equipment with Ni-filtered Cu K\( \alpha \) radiation, USA) at 30 mA and 40 kV. Data were recorded in the 5–60º 2\( \theta \) range (step size 0.019732º and 0.5 s counting time for each step).

3. Results

After batch melting and homogenization, both cooling approaches (bulk or frit form) lead to glasses with homogeneous appearance and free of macroscopic defects, such as bubbles or crystalline inclusions. The X-ray diffraction study shows that, regardless of the cooling method followed in their manufacture, the resulting materials are entirely amorphous since their diffractograms exhibit a shapeless halo in the range 2\( \theta \) = 20–40º, which is indicative of glassy materials. In all cases, the lack of diffraction peaks reveals the absence of crystalline phases formation during cooling. As an example, Figure 1 shows the XRD pattern of R10 glass prepared in bulk form by pouring the melt on a mold.

![Figure 1](image-url)
Table 1 shows the chemical composition of the investigated glasses determined by X-ray fluorescence. In the course of the melting process, the molten glass is enriched in silica and alumina due to corrosion of the melt against the walls of the silica-alumina refractory crucibles used in the melting of raw materials mixtures [19]. Simultaneously, the fluorine percentage is reduced to a greater extent due to its volatilization as SiF₄ [20].

The thermal behavior of glasses was evaluated by DSC in samples with two different particle sizes, i.e., fine and coarse. As an example, Figure 2 shows the DSC curves recorded from powder and fragment samples of R10 glass prepared in bulk form. Independently of both cooling step (pouring on mold or on cool water) and particle size (fine or coarse) of glass sample, the DSC curves show one exothermic peak indicating that subsequent heat treatments could lead to the glass devitrification. The thermal stability of the glasses can be evaluated from the relative positions of the characteristic temperatures, viz. Tₐ (glass transition temperature), Tₙ and Tₚ (onset and peak crystallization temperatures, respectively), and Tₘ (melting temperature) [18,21].

Thus, the reduced glass transition temperature Tₐ (Tₐ = Tₐ/Tₘ) is indicative of the crystallization mechanism [22]. A value of Tₐ < 0.58 indicates that crystals developed after thermal treatment will be homogeneously and randomly disseminated all over the whole glass body (volume crystallization) whereas when Tₐ > 0.60 crystals mainly develop at the glass surface and subsequently grow into the glass volume [23,24]. On the other hand, ΔTₚ is described as the difference between Tₚ in fine glass sample and Tₚ in coarse glass sample, ΔTₚ = Tₚ(fine) – Tₚ(coarse) [25]. The values of this parameter definitely help us to predict whether the crystallization process will start in surface or inside the glass particles. Thus, when ΔTₚ > 0 crystals will start growing preferably in the internal volume of the glass particles. On the contrary, when ΔTₚ < 0, the first crystals will be formed on the glass particle surfaces.

Table 2 collects the Tₐ and ΔTₚ values determined from DSC characteristic temperatures. The differences observed in the ΔTₚ values between glasses prepared in frit or bulk form are associated with the different degree of packing of the molecules during the cooling of the melt. If the cooling is very fast (frit) the packing is lower and consequently, frit glasses will show lower Tₐ, Tₘ and especially Tₚ values than bulk glasses. Consequently, glasses prepared in frit or bulk form will also show different ΔTₚ values. Tₐ values suggest that the crystallization mechanism is weakly affected by the fluorine content in glass composition and surface crystallization mechanism is slightly prevalent since Tₐ > 0.60 for all glasses in the series. However, Tₐ values are close to 0.58–0.60 range, which demarcates the edge between surface and volume crystallization.
mechanism. On the contrary, fluorine exerts high influence in the spatial position at which crystals develop in the early stage of glass devitrification. Indeed, $\Delta T_p$ in RE glass with lower fluorine content (2.12 wt.%), is highly negative denoting that first crystals grow on the surface of glass grains but $\Delta T_p$ is close to zero in R10 glass (4.39 wt.% fluorine), which imply that crystals are developed in the glass internal volume. Consequently, the estimation of the $\Delta T_p$ and $T_{gr}$ indicates that the devitrification of these richterite-based glasses mostly involves a surface crystallization mechanism. However, the increment offluorine content in the parent glass composition leads to a variation in the place of the first developed crystals, from surface sites to the internal volume of the glass particles.

For corroborating the preferential crystallization mechanism (surface or volume), the beginning of crystal growth was promoting by subjecting fragment samples of parent glasses prepared in bulk form (quenched) to thermal treatments at the temperature interval 800–1000°C for 5 min and the microstructure of resulting glass-ceramic materials were observed by FESEM. Figure 3 shows a general view of the microstructure of thermally treated glasses and Table 3 collects the dimensional parameters evaluated from the FESEM observations. In Figure 3(a,b) it is clear that devitrification in RE glass initiates through a surface mechanism which in the early stage gives rise to the development of crystals at the surface of glass particle forming a crystalline shell that grows inwards. The thickness ($\bar{e}$) of the crystallization shell varies in the 60–135 µm interval showing an average value of $\bar{e}$ = 120 µm, which indicates that it develops at an average rate of 24 µm/min.

In R6 (Figure 3(c,d)) and R8 glasses (Figure 3(e,f)), crystallization also begins at the glass particle surface but simultaneously, the development of spherulitic crystals in the bulk volume of glasses takes place. The thickness of the crystallization shell decreases as the fluorine content in glass composition increases. Therefore, in R6 thickness is in the 65–90 µm interval with $\bar{e}$ = 80 µm while in R8 it varies in the 46–86 µm range with $\bar{e}$ = 60 µm. Consequently, the shell crystallization range also decreases with fluorine content, showing average values of 16 µm/min and 12 µm/min in R6 and R8 glasses, respectively. Concerning spherulites, the main differentiation in their growth is relating to crystal density (number of crystals per surface unit), which significantly intensifies from an average value of 1.5 crystals/mm² in R6 to 37 crystals/mm² in R8. The observed increase in spherulites number is accompanied by a slight reduction in crystal size, from an average value of 90 µm (R6 glass) to 70 µm (R8 glass).

In R10 glass (Figure 3(g,h)) the crystallization process follows a similar trend but some differences in both crystalline shell and spherulites are observed. In this case, the shell thickness decreases down to an average value of $\bar{e}$ = 45 µm, which implies a growth rate of 9 µm/min. Regarding spherulites development, crystal density in the bulk volume highly increases until reaching a value of 2.730 crystals/mm² and simultaneously, crystal size is reducing down to an average diameter of 14 µm. Therefore, the microstructural analysis showed in Figure 3 corroborates that in the studied richterite-based glasses crystallization begins at glass surface but volume crystallization plays an important role as the fluorine content in glasses compositions increases.

Figure 3(a,b) evidences the lack of spherulites development in the interior of RE glass particle heat-treated at 1000°C for 5 min. However, the DSC curve recorded from a coarse sample of RE glass prepared in bulk form shows an exothermic peak indicating a crystallization process in the internal volume that at 1000°C should be in progress. For clarifying the development of spherulites in RE glass, fragment samples were heat treated in the 1000–1100°C temperature interval for 5 min. X-ray diffractograms and microstructure of the resulting materials are shown in Figures 4 and 5 respectively and Table 4 collects the EDS carried out in different areas marked in Figure 5.

Figure 4 supports that thermal treatment of RE glass at 1000°C for 5 min leads to a mainly amorphous material with slight diffraction peaks, which match with F-richterite (JPCDS file No. 25–0080) phase. The crystallization shell developed after thermal treatment of RE glasses at 1000°C for 5 min (Figure 5(a)) is comprised of tiny crystal showing a dendritic growth. EDS analyses indicate that the chemical composition of shell crystals is close to F-richterite (57.35 SiO₂, 24.03 MgO, 6.69 CaO, 7.40 Na₂O, 4.53 F₂, wt.%), although both a light increasing of SiO₂, MgO y Na₂O and a decrease in Al₂O₃ y CaO content is detected. These dissimilarities are likely due to isomorphic substitution of (Mg²⁺ + Si⁴⁺) for (Al³⁺ + Al³⁺) and of (Na⁺ + Si⁴⁺) for (Al³⁺ + Ca²⁺), very common in amphiboles [26]. The detailed observation of the residual glassy phase in the

<table>
<thead>
<tr>
<th>Glass</th>
<th>Cooling</th>
<th>Particle size</th>
<th>$\Delta T_p$</th>
<th>$T_{gr}$</th>
<th>$T_{pg}$</th>
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</thead>
<tbody>
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<td>RE</td>
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<td>Powder</td>
<td>915</td>
<td>1123</td>
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<td></td>
<td></td>
<td>Fragment</td>
<td>933</td>
<td>1352</td>
<td>1463</td>
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<td>Powder</td>
<td>928</td>
<td>1173</td>
<td>1458</td>
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<tr>
<td></td>
<td></td>
<td>Fragment</td>
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<td>1238</td>
<td>1473</td>
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<td>Frit</td>
<td>Powder</td>
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<td>1153</td>
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<tr>
<td></td>
<td></td>
<td>Fragment</td>
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<td>1334</td>
<td>1463</td>
</tr>
<tr>
<td>R8</td>
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<td>Powder</td>
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<td>1119</td>
<td>1445</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fragment</td>
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<td>1140</td>
<td>1456</td>
</tr>
<tr>
<td></td>
<td>Frit</td>
<td>Powder</td>
<td>923</td>
<td>1143</td>
<td>1441</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fragment</td>
<td>934</td>
<td>1220</td>
<td>1462</td>
</tr>
<tr>
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<td>Bulk</td>
<td>Powder</td>
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<td>1095</td>
<td>1440</td>
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<tr>
<td></td>
<td></td>
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<td>913</td>
<td>1098</td>
<td>1478</td>
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<tr>
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<td>Frit</td>
<td>Powder</td>
<td>908</td>
<td>1085</td>
<td>1458</td>
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<td></td>
<td></td>
<td>Fragment</td>
<td>913</td>
<td>1079</td>
<td>1473</td>
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</tbody>
</table>
material resulting from the thermal treatment of RE glass at 1000°C for 5 min (Figure 5(b)) makes clear the occurrence of tiny spherical agglomerates with an average diameter of ~ 65 nm, which should correspond to crystalline germs of bulk crystallization. The thermal treatment of RE glass at 1050°C for 5 min...
Figure 4. XRD patterns for coarse samples of RE glass prepared in bulk form after heat-treatment for 5 min in the 1000–1100°C temperature interval.

Favors the development of germs, which grow and reach the average size of 500 nm. The X-ray pattern corresponding to this thermal treatment (Figure 4) allows recognizing these crystals as clinoenstatite (MgSiO$_3$, JPCDS file No. 35–0610). Thermal treatment of RE glass at 1100°C (Figure 5(e)) promotes the growth of the F-richterite crystallization shell to a greater extent but it suppresses the development of spherulites. The crystalline shell has been developed perpendicularly to the RE glass surface and it takes up the main part of the particle internal volume. Observation of RE glass thermal treated at 1100°C for 5 min at higher magnification (Figure 5(f)) shows that crystallization shell is comprised of F-richterite crystals but also including clinoenstatite crystals (Table 4), which reach an average size of 1.5 µm. EDS analyses collected from clinoenstatite crystals reveal lower MgO content together with enrichment in Al$_2$O$_3$, CaO and Na$_2$O compared to clinoenstatite stoichiometric composition. Clinoenstatite is a mineral belonging to pyroxene group and as amphiboles, isomorphic substitutions are recurring. Consequently, the results point out that devitrification in RE glass begins with the development of F-richterite crystals at the glass surface. As F-richterite growth is linked to magnesium consumption, the lack of Mg$^{2+}$ cations for the subsequent clinoenstatite crystallization is balanced out by means of their substitution by Ca$^{2+}$ cations and by the (Al$^{3+}$ + Na$^{+}$) pair [26]. Similar results are found in the devitrification study of R6 and R8 glasses.

As previously mentioned, the crystallization process of R10 glass shows some dissimilarities in the development of both crystallization shell and internal spherulitic crystals when compared with RE, R6 and R8 glasses. Figure 6 shows the microstructure of the fracture surface of the R10 glass heat-treated at 850°C for 5 min. It brings to light that the energy required for the development of crystals in the soft surface of glass should be high and thus, superficial crystallization mainly occurs through the nucleation of crystals along cracks previously existing in the parent glass (Figure 6(a,b)), where the energy requirement is lower [22,27,28]. Developed crystals, with sheet or scale shape, are arranged perpendicularly to the fracture surface of cracks, giving rise to crystalline assemblages that, both because of the shape of the crystals and of their spatial arrangement, resemble micas clusters. On the other hand, devitrification in the internal volume of R10 glass develops through the precipitation of small scales or sheets, ~ 1.5 µm thick, which merge giving rise to crystalline formations with spherulite appearance (Figure 6(c)). Unlike R6 and R8 glasses, crystals developed in the inner volume of R10 glass are not properly spherulites, as needle-shaped crystals growing subparallel from a central point. In this case, it seems rather that they are straight crystals that bend in their growth and give rise to spherical or sheaf-like crystalline clusters. This type of growth has been previously reported in the study of phlogopite type mica glass-ceramics [29], in which the development of curved crystals is a consequence of the substitution of aluminum by magnesium in octahedral positions. Figure 7 shows the X-ray pattern from R10 glass after heat treatment at 850°C for 5 min. The profile of the diffractogram indicates that after this treatment, the glass is in an initial state of its devitrification process, as is deduced by the presence of a high amorphous background on which wide peaks of crystallization overhang. X-ray pattern can be associated with the occurrence of preiswerkite (NaMg$_2$Al$_6$Si$_2$O$_{10}$F$_2$) and paragonite (NaAl$_2$Si$_2$AlO$_{10}$F$_2$) crystalline phases, both belonging to the mica group. However, semi-quantitative EDS analyses performed on the crystals of Figure 6 does not completely match the identified micas. The chemical composition of the micas is extremely variable and numerous
homo- and heterovalent isomorphic mixtures are recorded. In the case of R10 glass, these substitutions are also favored by the glass composition itself, which is scarce in alumina and it is no able to deal with the requirement of $\text{Al}^{3+}$ cations necessary for the development of mica crystals. In this sense, Veblen \cite{30} reported new ordered structures, called biopyriboles, which are intimately related to amphiboles. This term, derived from biotite, pyroxene, and amphibole, reflects the connection between these mineralogical phases.

The spatial layout of small crystals in the whole glass-ceramic matrix suggests that bulk crystallization in fluorrichterite glasses could progress through a phase separation process in the parent glass. For this possibility, the existence of liquid-liquid immiscibility in original glasses was observed by FESEM from original glasses (quenched) prepared in bulk form. FESEM observation were carried out on fresh fracture surfaces subjected to chemical etching (Figures 8–11). All glasses show the occurrence of phase separation and the degree of immiscibility increases with the fluorine content in glasses composition. Thus, RE

Table 4. EDS analyses (wt.%) collected from crystals developed after thermal treatment of RE glass. The error is ± 0.2 wt%.

<table>
<thead>
<tr>
<th>Thermal treatment Zone</th>
<th>Crystalline phase</th>
<th>SiO$_2$</th>
<th>O$_2$</th>
<th>MgO</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>F$^-$_1</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000$^\circ$C for 5 min</td>
<td>F-richterite</td>
<td>57.3</td>
<td>10.4</td>
<td>20.5</td>
<td>5.5</td>
<td>4.4</td>
<td>2.0</td>
</tr>
<tr>
<td>1100$^\circ$C for 5 min</td>
<td>F-richterite</td>
<td>53.7</td>
<td>8.2</td>
<td>23.8</td>
<td>6.1</td>
<td>4.8</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>Clinoenstatite</td>
<td>59.1</td>
<td>9.0</td>
<td>22.6</td>
<td>5.7</td>
<td>3.5</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Figure 5. Secondary electron images on cross-sections of RE glass prepared in bulk form after heat treatment at a) and b) 1000$^\circ$C for 5 min; c) and d) 1050$^\circ$C for 5 min; e) and f) 1100$^\circ$C for 5 min.
Figure 6. Secondary electron images on cross-sections of R10 glass prepared in bulk form after heat treatment at 850°C for 5 min. a) and b) nucleation of crystals along cracks previously existing in the parent glass; c) scales with spherulite appearance developed in the internal volume of glass particle.

Figure 7. XRD pattern for R10 glass heat-treated at 850°C for 5 min.

Figure 8. Secondary electron images on an etched fresh fracture of parent RE glass prepared in bulk form. a) Overview at 50 k magnification; b) agglomerates of small droplets in isolated regions observed at 20 k magnification.
glass mostly exhibits a homogeneous fracture surface (Figure 8(a)), in which a texture indicative of liquid immiscibility is not observed. However, the presence in isolated regions of agglomerates of small droplets, with a diameter comprised in the range 300–350 nm (Figure 8(b)) indicates phase separation through a nucleation and growth mechanism.

Phase separation in R6 glass is more noticeable (Figure 9(a)) and regions with different microstructure are distinguished. The observation at higher magnification (Figure 9(b)) shows that liquid-liquid immiscibility conduct to the segregation of small droplets with size within the range 40–60 nm, which in certain regions agglutinate and lead to larger aggregates (200–400 nm). The degree of phase separation in R8 glass (Figure 10) is greater than in glasses with lower fluorine content. Separation of phases clearly occurs through a nucleation and growth mechanism resulting in the formation of isolated droplets, of homogeneous size and average diameter of 175 μm.

Figure 9. Secondary electron images on an etched fresh fracture of parent R6 glass prepared in bulk form. a) Overview at 50 k magnification; b) detailed observation at 90 k magnification.

Figure 10. Secondary electron images on an etched fresh fracture of parent R8 glass prepared in bulk form. a) Overview at 50 k magnification; b) detailed observation at 70 k magnification.

Figure 11. Secondary electron images on an etched fresh fracture of parent R10 glass prepared in bulk form. a) Overview at 35 k magnification; b) detailed observation at 70 k magnification.
Finally, a change in the development of phase separation is observed in R10 glass, which results in a spinodal decomposition mechanism (Figure 10) where phases separate as two continuous interpenetrated phases, with high connectivity and worm-like morphology. In this case, the separated phase has a maximum diameter of 125 nm in the widest part and 75 nm in the drop necks.

4. Conclusions
The crystallization of fluorrichterite-based glasses was studied by means of DSC, XRD, and FESEM. From the current results, the next conclusions can be pointed out:

- Fluorine content weakly affects the crystallization mechanism and surface crystallization mechanism is slightly prevalent.
- Fluorine exerts high influence in the spatial position at which crystals develop in the early stage of glass devitrification. In RE glass with lower fluorine content (2.12 wt.%) the first crystals grow on the surface of glass grains but in R10 glass (4.39 wt.% fluorine), crystals are developed in the glass internal volume.
- Both, the thickness and crystallization rate of the crystallization shell decreases as the fluorine content in glass composition increases.
- In RE, R6 and R8, crystallization shell is comprised of fluorrichterite (KNaCaMg₃Si₂O₇F₃)/crystals but also including clinoenstatite(MgSiO₃) crystals.
- In R10 glass, crystallization shell is comprised of preiswerkite (NaMg₂Al(Si₂Al₂)O₁₀F₂) and paragonite (NaAl₂(Si₂Al)O₁₀F₂) simultaneously to crystallization shell expansion, volume crystallization develops through the growth of spherulitic crystals in the bulk volume of glasses.
- Bulk crystallization in fluorrichterite glasses could progress through a phase separation process in the parent glass.

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Disclosure statement
No potential conflict of interest was reported by the authors.
based on fluorrichterite (Na₂CaMg₅Si₈O₂₂F₂) composition. Thermochim Acta. 2015;619:32–40.


