Devitrification behavior and preferred crystallization mechanism of glasses based on fluorrichterite ($\text{Na}_2\text{CaMg}_5\text{Si}_8\text{O}_{22}\text{F}_2$) composition

R. Casasola, J.M. Pérez, M. Romero*

Group of Glass and Ceramic Materials, Instituto de Ciencias de la Construcción Eduardo Torroja, CSIC. C/ Serrano Galvache 4. 28033 Madrid. Spain.

* Corresponding author, Tel.: +34 91 302 04 40; Fax: + 34 91 302 07 00.

e-mail address: mromero@ietcc.csic.es

Abstract

This paper reports on the effect of different contents of fluorine on the thermal stability of glasses in the $\text{SiO}_2\text{-MgO-CaO-Na}_2\text{O-F}$ system. Four glass compositions, with experimental fluorine contents varying from 2.12 to 4.39 wt. %, were studied using differential scanning calorimetry (DSC). The devitrification behavior was assessed through the evaluation of both the glass stability (GS) and glass-forming ability (GFA) using different parameters calculated from the characteristic temperatures in non-isothermal DSC curves. The predominant crystallization mechanism was determined by the difference in the crystallization temperature (ΔT_p) between fine and coarse glass samples. The results indicate that the studied melts exhibit a low tendency to devitrify during cooling, although this trend is increased with the fluorine content. The glass thermal stability is affected by the particle size, with it being easier to crystallize a glass powder sample than a coarse glass sample. The surface crystallization mechanism is predominant at the beginning of the devitrification process; however, the volume crystallization acquires importance with an increase in the fluorine content.

Keywords: F-richterite; glass-forming ability; glass stability parameters; crystallization mechanism; DSC; oxyfluoride glasses.

1. Introduction

Generically, glasses can be defined as substances that have certain characteristics of solids, such as mechanical hardness and brittleness at room temperature, but that cannot be considered strictly as solids because they lack the characteristic crystalline structure of the solid state. [1].

Glass devitrification to develop a glass-ceramic material proceeds through a thermal process that usually occurs in two steps, nucleation (small seeds or nuclei emerge within the glass) and

crystal growth (the enlargement of crystals is facilitated). In turn, the nucleation of crystalline phases can occur through two different mechanisms, i.e., homogeneous nucleation, when the nuclei arise from their own melt composition in the absence of foreign boundaries, and heterogeneous nucleation, when crystalline phases develop from foreign boundaries, such as grain borders or interfaces [2].

Glass-ceramics have been shown to feature excellent thermal, chemical, biological and dielectric properties, which are due, in great extent, to the nature of the crystalline phases developed upon heating. Fluorrichterite (hereafter, F-richterite) is an amphibole with empirical formula $\text{Na}_2\text{CaMg}_5\text{Si}_8\text{O}_{22}\text{F}_2$. Glass-ceramics based on F-richterite are of great technological interest because of their excellent mechanical properties, chemical durability and crack propagation resistance. Hence, K-F-richterite glass-ceramics are used in the manufacture of hard drives [3] or high-quality tableware [4].

Another field in which F-richterite plays an important role is in dental restoration. F-richterite glass-ceramics are machinable and exhibit high strength and toughness, excellent acid and alkali chemical durability, and remarkable resistance to slow crack growth [4]. Denry and Holloway highlighted that these glass-ceramics were potential candidates as high-strength dental ceramics [5, 6, 7].

However, although F-richterite glass-ceramics have been demonstrated to exhibit promising properties, little is known regarding the ability of F-richterite-based melts to develop amorphous glasses and on the preferential crystallization mechanism that governs the devitrification of F-richterite glasses.

Differential scanning calorimetry (DSC) has proven to be a suitable technique to evaluate the main parameters required to understand both the glass stability and glass crystallization behavior [8-17]. The aim of the present paper was to study the effect of fluorine content on the glass-forming ability, glass stability and preferred crystallization mechanism of a series of glasses based on F-richterite composition ($\text{Na}_2\text{CaMg}_5\text{Si}_8\text{O}_{22}\text{F}_2$).

2. Theory

In general, when a glass is subjected to a thermal treatment, devitrification takes place because of the energy decrease that occurs when the structurally amorphous glass crystallizes and results in a solid phase with a regular ordered geometry [18]. The glass stability (GS) indicates the strength of a glass against the nucleation and growth of crystalline phases during

thermal treatment. The GS of glasses can be easily evaluated from different parameters calculated from the characteristic temperatures in a DSC curve, including the glass transition temperature (T_g), onset crystallization temperature (T_x), peak crystallization temperature (T_p) and melting temperature (T_m) considered as the temperature at the minimum of the first endothermic peak.

Depending on the location where the first crystals form, the devitrification of a glass upon heating above T_g can evolve by two different mechanisms, volume and surface crystallization. In volume or bulk crystallization, crystals are regularly dispersed throughout the internal volume of the glass. However, in surface crystallization, crystals are first nucleated at the glass surface and subsequently extend inwards. In the early stages of devitrification, the positions in which the crystals are located can be evaluated by the difference between the crystallization temperatures of fine (powder) and coarse (bulk) glass samples, ΔT_p [18], as follows:

$$\Delta T_p = T_{p(\text{powder})} - T_{p(\text{coarse})}. \quad (1)$$

Thus, $\Delta T_p > 0$ indicates that the first crystals will develop at the surface of the glass particles, whereas if $\Delta T_p < 0$, the devitrification of the glass will begin with the development of nuclei in the internal volume of the glass. GS can also be evaluated based on other parameters, such as the following:

- Reduced glass transition temperature T_{gr} [19],

$$T_{gr} = \frac{T_g}{T_m} \quad (2)$$

- Working range ΔT_{TS} [20],

$$\Delta T_{TS} = T_x - T_g \quad (3)$$

- Weinberg (K_w) [21], Hruby (K_H) [22] and Lu-Liu [23, 24] parameters:

$$K_w = \frac{T_x - T_g}{T_m} \quad (4)$$

$$K_H = \frac{T_x - T_g}{T_m - T_x} \quad (5)$$

$$K_{LL} = \frac{T_x}{T_g + T_m}. \quad (6)$$

The capability of a melt to form a glass while quenched is designated its glass-forming ability (GFA). This ability can be assessed based on the critical cooling rate q_c , which is the minimum cooling rate from melting to T_g required to avoid crystal formation. This critical

cooling rate can be determined from the Weinberg, Hruby and Lu-Liu parameters using the following equations [25]:

$$\log_{10}q_W = 4.44 - 21.4 \cdot K_W \quad (7)$$

$$\log_{10}q_H = 3.17 - 2.26 \cdot K_H \quad (8)$$

$$\log_{10}q_{LL} = 17.7 - 34.6 \cdot K_{LL}. \quad (9)$$

The use of T_p instead of T_x to determine the K_W , K_H and K_{LL} parameters used in the q_c calculation should be noted, according to Nascimento et al. [25, 26].

3. Materials and methods

Four glasses in the SiO_2 - MgO - CaO - Na_2O - F system were formulated from high-quality reagents ($(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, CaCO_3 , Na_2CO_3 and MgF_2) and silica sand with low contents of iron oxide. The designated RE composition was prepared with the stoichiometric composition of F-richterite, $\text{Na}_2\text{CaMg}_5\text{Si}_8\text{O}_{22}\text{F}_2$. Moreover, three additional mixtures containing increased amounts of fluorine (6, 8 and 10 wt. %) were referred to as R6, R8 and R10, respectively.

The raw material mixtures were homogenized in a planetary ball mill (TURBULA) for 15 min. The batches were melted in alumina-silica crucibles in an electric furnace at a heating rate of $10^\circ\text{C}/\text{min}$ up to 1450°C and held at that temperature for 120 min for homogenization. Subsequently, the melts were cooled down to room temperature following two different cooling steps. Thus, frit glasses were achieved through a fast-cooling stage by pouring the melts into cool water. Meanwhile, the bulk glass samples were obtained by casting the melt onto brass molds followed by subsequent annealing for 2 h at 100°C below their respective glass transition temperatures (T_g). After annealing, the glasses were cooled to room temperature inside the furnace. Differential scanning calorimetry (DSC) analyses were conducted previously on the glass samples with the same composition to determine the T_g value for each glass.

The chemical composition of the glasses was determined by X-ray fluorescence (XRF) from pressed pellets of powder glass samples ($<63 \mu\text{m}$) using a BRUCKER S8 Tiger spectrometer. The glass transition temperature (T_g), onset crystallization temperature (T_x), maximum crystallization peak temperature (T_p) and melting temperature (T_m) were evaluated by DSC on both fine ($< 63 \mu\text{m}$ powder) and coarse ($\sim 3 \times 3 \times 4 \text{ mm}$ coarse) samples. The DSC runs were performed in a SETARAM Labsys Thermal Analyzer. The samples were heated from room temperature to 1400°C at a heating rate of $50^\circ\text{C} \cdot \text{min}^{-1}$ under flowing air. Samples of $\sim 40 \text{ mg}$

were placed in platinum crucibles, and calcined Al_2O_3 was used as the reference material. All the DSC curves were normalized with respect to the sample weight. The temperature precision of the equipment is ± 0.1 °C. Each measurement was reproduced three times to estimate the experimental errors.

The effect of the fluorine content on the GFA of the glasses studied in the present work was corroborated by *in situ* DSC examinations that replicated the melting program applied in the preparation of these glasses. For this purpose, a mix of raw materials of each glass composition was heated in the DSC equipment from ambient to 1450°C, applying a heating rate of 50 °C/min. The melt was held at the melting temperature for 30 min, and afterwards, the samples were cooled to room temperature at a rate of 50°C/min. Right away, the samples were subjected to a new heating process at 50°C/min up to 1450°C. Hence, the GFA of the melts can be evaluated from DSC curves recorded during the first cooling step, and the GS of the glasses can be determined from the DSC curves recorded during the second heating ramp.

To ascertain the crystalline phases developed upon cooling, a batch of each glass composition was melted in an electric furnace under the same schedule followed for the *in situ* DSC runs. To facilitate the development of crystalline phases, the melts were cooled at 50°C/min from 1450°C to the temperature of their maximum exothermic effect of the *in situ* DSC curves recorded during the first cooling step and then held for 30 min. Afterwards, the samples were extracted from the kiln and cooled in air.

The evaluation of the amorphous nature of the as-melted glasses and the mineralogical study of the crystalline phases devitrified after thermal treatment was achieved using X-ray diffraction (XRD) using BRUKER D8 Advance equipment with Ni-filtered Cu K α radiation operating at 30 mA and 40 kV. Data were recorded in the 5–60° 2 θ range (step size 0.019732° and 0.5 s counting time for each step).

To confirm the effect of fluorine on the preferential crystallization mechanism, samples of glass frit of the different compositions were subjected to a heat treatment at 850°C for 10 minutes to support the formation of crystals within the glass. The microstructure of the resulting glass-ceramic materials was studied by field-emission scanning electron microscopy (FESEM) with a HITACHI S-4800P microscope using an acceleration voltage of 20 kV. Glass-ceramic 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 ethylic alcohol, dried and coated with Au-Pd in a Balzers SCD 050 sputter.

4. Results and Discussion

After the cooling of the melts, the glasses obtained by both frit and bulk form appeared homogeneous to the naked eye; XRD analysis confirmed their glassy nature.

Table 1 presents the theoretical and experimental chemical analysis results determined by XRF of the parent glasses. In all the analyzed compositions, the following effects were observed: the silica content is slightly increased; alumina is observed in the experimental compositions although it had not been considered in the glass formulations as richterite lacks Al_2O_3 in its composition; and a considerable decrease in the percentage of fluorine and sodium oxide is also observed. These results are attributed to the joint effect of the corrosion of the inner surface of the Si-Al crucibles by the melted glass [27] and the fluorine volatilization in the form of SiF_4 and NaF [28]. It is observed that the higher the initial fluorine content in the mixture, the greater the proportion in which the fluorine evaporates from the melt. Similar results have been reported in the literature in fluoride glasses belonging to the $\text{SiO}_2\text{-CaO-K}_2\text{O-F}$ [13] and $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-K}_2\text{O-F}$ [14] systems.

Table 1. Theoretical composition and experimental chemical analysis as determined by FRX method (wt.%) of the studied glasses.

		Si₂O	Al₂O₃	MgO	CaO	Na₂O	F₂
RE	Theoretical	57.35	0.00	24.03	6.69	7.40	4.53
	Experimental	57.68	5.33	20.89	7.84	6.15	2.12
R6	Theoretical	56.46	0.00	23.66	6.59	7.28	6.00
	Experimental	57.50	6.78	20.31	7.06	5.60	2.76
R8	Theoretical	55.26	0.00	23.16	6.45	7.13	8.00
	Experimental	55.86	7.88	19.95	6.83	5.44	4.04
R10	Theoretical	54.06	0.00	22.66	6.31	6.97	10.00
	Experimental	55.74	8.65	19.23	6.69	5.30	4.39

Figure 1 depicts the DSC curves of F-richterite glasses recorded from samples with different particle sizes, i.e., fine (<63 μm powder) and coarse (~3 x 3 x 4 mm fragment) extracted from glasses obtained in both bulk and frit form. Regardless of the cooling step followed in the

preparation of the glass and the particle size of the sample, all the DSC curves present an exothermic peak after T_g , which indicates that the investigated glasses are susceptible to crystallization in subsequent heating stages.

Figure 1. DSC curves from fine ($< 63 \mu\text{m}$) and coarse ($\sim 3 \times 3 \times 4 \text{ mm}$ fragment) glass samples recorded at a heating rate of $50^\circ\text{C}\cdot\text{min}^{-1}$.

By evaluating both the height and shape of the crystallization peaks, it is observed that the exothermic effects associated with the devitrification of RE glass (Fig. 1a) are relatively wider and less intense than those corresponding to the other glasses. This finding indicates that among the glasses studied, the devitrification of RE glass will result in glass-ceramic materials with a lower crystallinity degree. Regarding the granulometry of the sample, maximum crystallization peaks in RE glass are highly affected by the particle size corresponds to surface crystallization. The more noticeable effect that the fluorine content exerts on the devitrification of F-richterite-based glasses is the enhancement of the volume crystallization with respect to the surface mechanism as the percentage of fluoride in the glass composition increases. Thus, in RE glass, the exothermic peaks corresponding to coarse samples are located at higher temperatures than those in powder samples; however, the difference between the crystallization temperatures

of fine and coarse glass samples decreases with the increasing content of fluorine, such that in R10 glass, all the crystallization exotherms overlap (Fig. 1d). At the same time, the intensities of the exothermic effects in coarse samples are higher than their equivalent of powder samples ($h_{\text{bulk fragment}} > h_{\text{bulk powder}}$ and $h_{\text{frit fragment}} > h_{\text{frit powder}}$).

Figure 2 plots the characteristic temperatures determined by DSC analyses from fine and coarse samples extracted from glasses prepared in frit and bulk form as a function of the fluorine content in the glass composition. Overall, T_g and T_m are characteristic temperatures that exhibit similar values; meanwhile, the variations in T_x and T_p are more pronounced. As is usual in fluoride glasses, a higher fluorine content results in decreased T_g values (Fig. 2a) due to the fluidizing effect of F^- anions [1, 13]. However, T_g varies for a given composition depending on the cooling process. Hence, the fast cooling of the melt on water (frit) leads to glasses with higher T_g values than bulk form glasses, which are subsequently annealed. This result occurs because T_g is greatly affected by the thermal story of the glass. In quenched glasses, the mobility of the melt constituents is limited by the abrupt increase in viscosity, such that the glass reaches the supercooled liquid state with a more open structure than the glass obtained by casting (slower cooling process), where the increase of viscosity is gradual, and the lattice units take longer to be grouped in a more compact manner [1].

Figure 2. Evolution of the glass transition temperature (T_g), onset crystallization temperature (T_x), peak crystallization temperature (T_p) and melting temperature (T_m) with fluorine content.

The fluorine content plays a greater effect on T_x (Fig. 2b) than on T_g . Thus, while T_g varies within a interval of $\sim 40^\circ\text{C}$, this gap in T_x is greater with a difference of $\sim 230^\circ\text{C}$ between the minimum and maximum values. The increase in the fluorine content exerts a similar effect on T_x as that for T_g . Therefore, although a slight increase in the values of T_x is observed in R6 glass, the general trend for T_x is to decrease with increasing fluorine concentration in the glass composition. This result indicates that, in general, the increased presence of fluorine in the vitreous network favors the glass devitrification, which begins at lower temperature. Concerning the effect of the thermal history of glass on T_x , Fig. 2b shows that crystallization in annealed glasses begins at temperatures significantly lower than in fast-cooled glasses, which is more noticeable in coarse samples, although the trend is to converge as the fluorine content increases. Annealed glasses exhibit a more compact and ordered lattice network than frits, and therefore, it is easier to begin the crystallization process. Nevertheless, it appears that the crystallization onset in R10 glass is independent of its thermal history as T_x bulk glass $\sim T_x$ frit glass. This behavior could be associated with the higher fluorine content in its composition. It is known that an elevated fluorine percentage increases the tendency of a melt to crystallize during cooling [13]. The fast quenching of the R10 melt leads to a non-crystalline material, as denoted by its X-ray diffraction pattern, typical of amorphous solids. However, molecular aggregates may be formed during fast cooling, which would be in a pre-crystalline state with higher internal order than the glass matrix [1]. This fact would justify the decrease of T_x in quenched R10 glass to a value similar to that shown by the annealed glass. Fig. 2b also shows the pronounced effect of the glass particle size on the onset crystallization temperature, as T_x values are always lower in powder samples. However, T_x of the bulk glasses considerably decreases upon increasing the fluorine percentage in the glass compositions, such that $\Delta T_x \sim 120^\circ\text{C}$ for RE glass, whereas $\Delta T_x \sim 40^\circ\text{C}$ for R10 glass. This behavior indicates that crystallization in these glasses preferentially begins at the particles' surface; however, as the fluorine content increases, the formation of crystals in the internal volume of the particles will spread.

Among the different characteristic temperatures, T_p is the most affected by the fluorine content in the base glass (Fig. 2c). T_p in both fine and coarse samples tends to decrease with increasing fluorine in the composition. However, similar to T_x , the largest differentiation in T_p is observed in coarse samples, with a variation interval of $\sim 280^\circ\text{C}$. Figure 2d presents the variation of T_m in the studied glasses. It can be seen that the values of T_m are very similar (except for R10, which differs from the rest of the samples) which means that both the crystalline and glassy matrix developed are the same for all samples. Thus, even if the crystalline phases would develop in different amounts depending on the fluorine content, the melting would vary a few

degrees. This difference is hardly detected taking the peak temperature. In this way, a variation in this peak temperature would yield differences more noticeable, as it has been mentioned in R10 sample. In powder samples, crystallization occurs at lower temperatures and values of T_p seem to be almost independent on the fluorine content of the base glass. This result is likely due to the fact that surface crystallization is initiated at lower energy surface sites. Thus, nuclei formation is almost independent of light fluctuations in the glass composition. T_p indicates the temperature at which the crystallization rate is the highest. As the fluorine content in the glass composition increases, the T_p values for the powder and coarse samples converge. In RE glass with lower fluorine content, the gap in T_p of samples with different particle sizes implies that for short-time thermal treatment, the crystal growth at the surface of glass particles will be favored over the development of nuclei within the internal volume ($T_{p \text{ coarse}} \gg T_{p \text{ fine}}$). In contrast, in glasses with higher fluorine content (R8, R10), both crystallization mechanisms will occur simultaneously ($T_{p \text{ coarse}} \sim T_{p \text{ fine}}$). This behavior is also supported by ΔT_p ; regardless of the cooling rate used in the preparation of the glass, it varies from $\Delta T_p \sim -200$ in RE glass to $\Delta T_p \sim 0$ in R10 glass.

Figure 3 depicts the values of T_{gr} for different glass compositions in coarse and fine ($<63 \mu\text{m}$) samples separated from both monolithic and frit glasses. The highlighted region in the diagram distinguishes the prevalence regions of surface and volume crystallization [29, 30, 31]. Fig. 3 shows again a slight predominance of the surface crystallization mechanism because in all cases, T_{gr} is greater than 0.60.

Figure 3. Progress of T_{gr} for the different glass compositions in both coarse and fine ($<63 \mu\text{m}$) samples separated from both annealed monolithic and frit glasses. The highlighted region establishes the gap between the surface ($T_{gr} > 0.58\text{--}0.60$) and bulk ($T_{gr} < 0.58\text{--}0.60$) crystallization. The errors in T_{gr} are approx. $\pm 2\text{--}3^\circ\text{C}$.

To corroborate the preferred crystallization mechanism, coarse samples of annealed glasses were heated for 5 minutes in the range of temperature 850–1000°C to induce the development of crystals.

Figure 4 shows the microstructure observed by FESEM in the heat-treated samples. It is apparent that RE glass begins to devitrify through a surface crystallization mechanism, resulting in the development of a crystallization shell in the glass surface. Crystallization in R6 glass is also initiated at the surface of glass particles; however, simultaneously, small spherulitic crystals are developed in the internal body of glass fragments. The crystalline density of spherulitic crystals increases upon increasing the fluorine content in the glass composition (R8 and R10 glasses), which confirms that in the early stages of devitrification of F-richterite-based glasses, crystal growth begins with the development of crystals through a surface crystallization process, and the volume mechanism becomes more important upon increasing the fluorine content in the glass composition.

Figure 4. FESEM images of polished and etched surfaces showing the microstructure in the early stages of crystallization of F-richterite-based glasses: a) RE treated at 1000°C for 5 min; b) R6 treated at 950°C for 5 min; c) R8 treated at 950°C for 5 min; and d) R10 treated at 850°C for 5 min.

The thermal stability of the glasses was estimated by calculating both the working range (ΔT_{TS}) using Eq. (3) and the Hrubý (K_{H}), Weinberg (K_{W}) and Lu-Liu parameters (K_{LL}) (Eqs. (4), (5) and (6), respectively).

Figure 5 shows the values of ΔT_{TS} as a function of the fluorine content for different particle size samples of glasses obtained in both annealed and frit form. Smaller values of this temperature interval indicate a lower thermal stability of the glass, and the development of crystalline phases on heating is favored [32]. The ΔT_{TS} values determined from fine samples are, in all cases, inferior to those corresponding to coarse samples. This result indicates that the thermal stability of these glasses is highly affected by the particle size and that fine samples exhibit a greater capability for glass devitrification in subsequent thermal treatments [20]. However, the ΔT_{TS} of fine and coarse samples tend to be equal as the percentage of fluorine in the glass composition increases. This fact indicates that increased fluorine content may involve a variation in the thermal stability of samples with different particle sizes, such that coarse samples become more unstable. Likely, it is due to the ability of fluorine ions to promote bulk nucleation by phase separation, which favors the development of crystalline phases. Indeed, the initiation of phase separation represents the beginning of mica glass-ceramic development in base glasses of the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-Na}_2\text{O-K}_2\text{O}$ system [3].

The greater ability of fine glass samples to crystallize is also deduced from Figure 6, in which the Weinberg, Hrubý and Lu-Liu parameters are displayed. Lower values of these parameters indicate further ease in obtaining a crystallized material from the parent glass. Regardless of the cooling rate used in the preparation of the glasses, fine samples always exhibit the lowest K_{H} , K_{W} and K_{LL} values, which explain their greater capability to develop crystalline phases upon heating. Figure 6 agrees with Kozmidis –Petrovic [33] showing that $\Delta K_{\text{H}} > \Delta K_{\text{W}} > \Delta K_{\text{LL}}$ ($\Delta K = K_{\text{coarse}} - K_{\text{fine}}$), so K_{LL} can be used as a reference.

Figure 5. Evolution of ΔT_{TS} with fluorine content for different particle size samples of glasses obtained in both annealed and frit form. The errors in ΔT_{TS} are approximately $\pm 2\text{--}3^\circ\text{C}$

Figure 6. Evolution of Hrůby, Weinberg and Lu-Liu parameters with fluorine content.

Table 2 lists the critical cooling rates of the melts determined from Eq. (7), (8) and (9). These values reveal the GFA of the molten glasses. The studied compositions result in melts with low capacity to crystallize during cooling, except for the R10 melt, which presents critical cooling rates above 65°C/min. Therefore, a high fluorine percentage in the raw materials mixture decreases the GFA of the melts.

Table 2. Critical cooling rates for F-richterite based glasses determined from Weinberg, Hrubý and Lu-Liu parameters.

	q_W (°C/min)	q_H (°C/min)	q_{LL} (°C/min)
RE	15	29	8
R6	15	29	8
R8	15	32	9
R10	70	125	68

Figure 7 presents the in situ DSC graphs recorded from raw material mixtures. The curves confirm the effect of the fluorine content on GFA of the melts (Fig. 7a) and the thermal stability of the resulting glasses in a subsequent heating process (Fig. 7b). Table 3 lists the values of the characteristic temperatures determined from the curves in Fig. 7. It is evident that the molten composition resulting from R10 is the only one resulting in the formation of crystalline phases upon cooling, as evidenced by the existence of two exothermic peaks in its corresponding curve (Fig. 7a). This result indicates that the cooling rate ($50^\circ\text{C}/\text{min}$) is not high enough to avoid crystallization. This behavior is consistent with the critical cooling rates determined for the different glasses (Table 2), where $q_c < 50^\circ\text{C}/\text{min}$ for the RE, R6 and R8 compositions, whereas $q_c > 50^\circ\text{C}/\text{min}$ for R10. The DSC curves recorded upon heating of RE, R6 and R8 glasses (Fig. 7b) present the typical profile of a glass with a high trend for devitrification. The endothermic jump in the $630\text{--}660^\circ\text{C}$ range represents the glass transition temperature (T_g), and the exothermic effect at higher temperatures is consistent with a devitrification process. Conversely, the DSC curve corresponding to R10 glass presents neither T_g nor crystallization exothermics, which indicates that the preceding cooling process resulted in a high devitrification degree.

Figure 7. In situ DSC curves recorded from a mixture of raw materials of each glass composition. The batches were up to 1450°C and held for 30 min. Subsequently, the melts were cooled to room temperature at $50^\circ\text{C}/\text{min}$ (Fig. 7a) and immediately exposed to a re-heating ramp at $50^\circ\text{C}/\text{min}$ up to 1450°C (Fig. 7b).

Table 3. Characteristics temperatures derived from DSC curves recorded during a) the cooling step after the melting of raw materials and b) subsequent heating of the resulting material. The errors in the characteristics temperatures are approximately $\pm 2\text{--}3^\circ\text{C}$.

	Cooling step (Graph a) in Fig. 7)	Heating (Graph b) in Fig. 7)			
		T_g ($^\circ\text{C}$)	T_x ($^\circ\text{C}$)	T_p ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)
RE	-	657	924	1036	1171
R6	-	652	889	970	1200
R8	-	630	896	1008	1190
R10	Exothermics at 1150°C ; 1013°C	-	-	-	1013; 1202

The overall analysis of Fig. 7 reveals the antagonist effect of fluorine in glasses. At low concentrations, fluoride ion exerts a fluidizing action and decreases the glass viscosity, as evidenced by the decrease in T_g with increasing fluorine content (Table 3). However, fluoride ions at higher concentrations increase the molecular mobility in the melt, which favors the reorganization of basic units, resulting in the formation of crystalline phases upon cooling [28].

To identify the crystalline phases devitrified upon cooling of the R10 melt, a mixture of raw materials was subjected to melting at 1450°C , and afterwards, the melts were cooled at $50^\circ\text{C}/\text{min}$ to the temperature corresponding to the two exothermic effects in Fig. 7b (1150°C and 1013°C). After holding for 30 minutes, to promote the growth of crystalline phases, the samples were removed from the furnace and cooled in air. Figure 8 presents the diffractograms of the resulting materials. As expected, melt crystallization occurred and resulted in glass-ceramic materials composed of F-richterite (PDF 25-0808) as the main crystalline phase and mica (PDF 25-0155) to a minor extent. The diffractogram corresponding to stopping the cooling at 1150°C consists of more intense and better defined peaks and a lower amorphous background. This effect is related to the difference in the intensity of the exothermic peaks in the DSC curves recorded upon melt cooling (Fig. 7a).

Figure 8. XRD patterns of the glass-ceramic materials resulted after discontinuing the R10 melt cooling for 30 min at the temperatures of its corresponding exothermic effects in Fig. 7a.

5. Conclusions

Four F-richterite-based glasses in the $\text{SiO}_2\text{-MgO-CaO-Na}_2\text{O-F}$ system were obtained in both frit and annealed form. The glasses were evaluated by DSC to determine the effect of the fluorine content on the glass-forming ability, glass stability and predominant devitrification mechanism of the base glasses. The main conclusions of the present work are as follows:

- The crystallization process of F-richterite glasses proceeds through both surface and volume mechanisms.
- The characteristic temperatures (T_g , T_x , and T_p) decrease upon increasing the fluorine content because of its fluidizing effect.
- The variation of the temperature of crystallization (ΔT_p) with the particle size increases with the fluorine content, varying from $\Delta T_p \ll 0$ ($\Delta T_p = T_{p \text{ fine}} - T_{p \text{ coarse}}$) in RE glass to $\Delta T_p \sim 0$ in R10 glass. This tendency indicates a variation in the crystallization mechanism, such that the devitrification process in glasses with low fluorine percentages will begin with the development

of crystals in the surface of the glass particles, whereas the volume crystallization achieves more importance upon increasing the fluorine content.

- The reduced glass transition temperature (T_{gr}) shows a slight predominance of the surface crystallization mechanism at the beginning of the devitrification process because all the glasses present a value of $T_{\text{gr}} > 0.60$.

- The glass thermal stability (ΔT_{TS}) is affected by the particle size, such that a glass powder sample ($< 63 \mu\text{m}$) exhibits a superior ability for glass crystallization.

- The critical cooling rates of the melts are always below $35 \text{ }^\circ\text{C}/\text{min}$ for RE, R6 and R8 glasses and above $65 \text{ }^\circ\text{C}/\text{min}$ for R10 glass. These values indicate that the raw material mixtures of these compositions yield melts with a low tendency to devitrify during cooling, although this trend is increased with increasing fluorine content in the melt composition.

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