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Crystallization of fluorcanasite–fluorrichterite glasses

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Abstract

The crystallization behavior of alkali-modified glasses in the fluorcanasite–fluorrichterite system was investigated using DTA, XRD, SEM, dilatometry and other techniques. The coefficient of thermal expansion, density, Vickers' microhardness and chemical durability of the obtained products were also evaluated. Limestone, magnesite, and quartz sand together with potassium and sodium carbonates, calcium and magnesium fluorides served as starting materials for glass preparation. The main crystalline phases formed after different heat-treatments were fluorcanasite, fluorrichterite, agrellite, fluorite and diopside ss. The microstructures of the crystalline products consisted of interlocking blade-like and acicular crystals with increasing degrees of fineness as the nominal fluorrichterite content was increased.

The coefficient of thermal expansion of the obtained glass-ceramic materials ranged between 79×10^{-7} and 109×10^{-7} °C^{-1}; and the density between 2.55 and 2.93 gm/cm^3. The crystalline products attained Vickers' hardness values of 508–743 kg/mm^2. The chemical durability of the materials was better in acidic than in alkaline solutions.

Keywords: D. Glass-ceramic; Fluorcanasite; Fluorrichterite; Agrellite

1. Introduction

Glass-ceramic materials, with double- and multi-chain silicate structures, were prepared and reported high values of flexural strength and fracture toughness. These glass-ceramics are composed of one or more of K-fluorrichterite (K Na Ca Mg_5 Si_8 O_{22} F_2), fluorcanasite (K_2 Na_4 Ca_5 Si_{12} O_{30} F_4) and agrellite (Na Ca_2 Si_4 O_{10} F_2) crystalline phases [1]. Glass-ceramics, based on either fluorcanasite or fluorrichterite, have great technological interest. Fluorcanasite was used in magnetic memory disk substrates [1]. These glass-ceramics exhibit highly crystalline microstructures of interpenetrating blades and possess a combination of high fracture strength and toughness [2,3]. The chemical durability of fluorcanasite glass-ceramics, however, is known to be low and is inferior, in acid resistance, to soda-lime-silica glass [1,4]. It was proposed that, the mechanism of fluorcanasite crystallization passes through two stages. At low temperatures, a devitrite-like phase and fluorite are developed and at high temperatures these two metastable phases react together and with the residual glass to form fluorcanasite [5].

On the other hand, potassium fluorrichterite ($KNaCaMg_5Si_8O_{22}F_2$) glass-ceramics have commercial applications in high performance dinnerware and as cups and mugs [1]. It was suggested that, the crystallization of glasses of stoichiometric K-fluorrichterite formula ($KNaCaMg_5Si_8O_{22}F_2$) starts by phase separation. Initially, at 550 °C, the glass separates into regions with composition close to that of mica. At higher temperatures (~700 °C), diopside is precipitated and these two metastable phases react together and with the residual glass to form K-fluorrichterite [1,6]. The increase of fluorine content, more than in the stoichiometric fluorrichterite composition, enhanced the early crystallization of this phase [7].

The present investigation deals with the crystallization behavior of glasses corresponding to different proportions of fluorrichterite and fluorcanasite (with different Na:K ratios). Crystalline phase formation and microstructures developed in these glasses and the properties of the resultant glass-ceramic materials were evaluated. Such properties include the coefficient of thermal expansion, density, Vickers' microhardness and chemical durability.

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2. Experimental technique

The batch compositions were based on stoichiometric fluorcanasite ($K_2Na_4Ca_5Si_{12}O_{30}F_4$) and fluorrichterite ($KNaCaMg_5Si_8O_{22}F_2$) in different weight ratios. Change of the alkali Na_2O:K_2O ratio, in the fluorcanasite formula, from 2:1 to 1:2, was also investigated. Limestone, magnesite, and quartz sand together with potassium and sodium carbonates, calcium and magnesium fluorides served as starting materials for glass preparation. To compensate for fluorine evaporation during the melting process, 10% excess of the amount of fluorine was added to the glass batch materials. Table 1 shows the chemical compositions of the used raw materials and Table 2 gives the compositions of two glass series. Well weighing and mixing of the batch materials were taken in consideration. The batches were melted in platinum (2% rhodium) crucibles in the 1250–1400 °C temperature range. The obtained glasses were annealed at 450–500 °C.

Differential thermal analysis (DTA) was conducted for glass powders (0.25–0.6 mm) using PerkinElmer thermoanalyzer (DTA-7 Series) under dynamic nitrogen gas atmosphere and at a heating rate of 10 °C/min. Crystallization of the glasses was accomplished by heat-treatment through double-stage schedules (at 600 °C/1–2 h then at 700–900 °C/2–6 h). X-ray powder diffraction spectra (XRD) of the obtained crystalline products were recorded using X-ray diffractometer (Brukur D8 Advanced, Germany) employing Ni-filtered Cu Kα radiation.

Polarizing microscopy (PM, CarlZeiss) of thin sections and scanning electron microscopy (SEM, Philips, model XL30) were used for microstructural characterization of the obtained glass-ceramic products. For SEM examinations, fresh fractured samples were etched by 1% HNO_3–HF solution.

The coefficients of thermal expansion (CTE) of the obtained glass-ceramic samples (0.3 cm × 0.3 cm × 2 cm) were determined using dilatometer (Linseis, model L76/1250, Germany) at 5 °C/min heating rate. The densities of the glass-ceramic samples were determined at room temperature by the Archimedes method using distilled water.

3. Results and discussion

Batch melting was accomplished in the 1250–1400 °C temperature range. In both glass series, CN-R and CK-R, as the nominal amount of richterite was increased, the melting temperature shifted to higher values within the above-mentioned range.

3.1. Thermal analysis (DTA) of the glasses

The DTA traces of the 1st glass series (CN-R) show endothermic and exothermic peaks in the 541–622 °C and 730–813 °C temperature ranges, respectively (Fig. 1). The DTA traces of the 2nd glass series (CK-R) show endothermic and exothermic peaks in the 580–650 °C and 721–870 °C temperature ranges, respectively (Fig. 2).

Table 1
Chemical composition of the raw materials (wt.%)

Raw material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	LOI
Limestone	0.15	0.22	–	55.7	0.10	–	–	44.02
Magnesite	0.72	0.76	0.19	10.20	38.70	Trace	Trace	48.92
Quatrz sand	99.20	0.28	0.03	0.10	–	–	–	0.4

Table 2
Compositions of the investigated glasses

Sample code	Nominal phase ratio in wt.% canasite:richterite	Constituent oxides wt.%						
		SiO_2	CaO	MgO	K_2O	Na_2O	MgF_2	CaF_2
1st series (CN-R)								
CN($K_2Na_4Ca_5Si_{12}O_{30}F_4$)-R	100:00	57.0	13.30	–	7.50	9.80	–	12.40
CN8R2	80:20	57.08	11.94	3.84	7.12	8.64	1.48	9.90
CN7R3	70:30	57.12	11.32	5.76	6.93	7.97	2.22	8.68
CN6R4	60:40	57.16	10.68	7.68	6.64	7.38	2.96	7.40
CN5R5	50:50	57.20	10.00	9.60	6.55	6.75	3.70	6.20
CN3R7	30:70	57.28	8.68	13.44	6.17	5.53	5.18	3.72
R	00:100	57.40	6.70	19.20	5.60	3.70	7.40	–
2nd Series (CK-R)								
CK($K_4Na_2Ca_5Si_{12}O_{30}F_4$)-R	100:00	55.60	13.00	–	14.50	4.80	–	12.10
CK8R2	80:20	56.00	11.74	3.84	12.72	4.54	1.48	9.70
CK7R3	70:30	56.14	11.11	5.76	11.83	4.47	2.22	8.47
CK6R4	60:40	56.36	10.48	7.68	10.94	4.38	2.96	7.30
CK5R5	50:50	56.50	9.85	9.60	10.05	4.25	3.70	6.05
CK3R7	30:70	56.86	8.59	13.44	8.27	4.03	5.18	3.63
R	00:100	57.40	6.70	19.20	5.60	3.70	7.40	–

CN = stoichiometric fluorcanasite ($K_2Na_4Ca_5Si_{12}O_{30}F_4$), CK = alkali-modified fluorcanasite ($K_4Na_2Ca_5Si_{12}O_{30}F_4$), R = fluorrichterite ($KNaCaMg_5Si_8O_{22}F_2$).

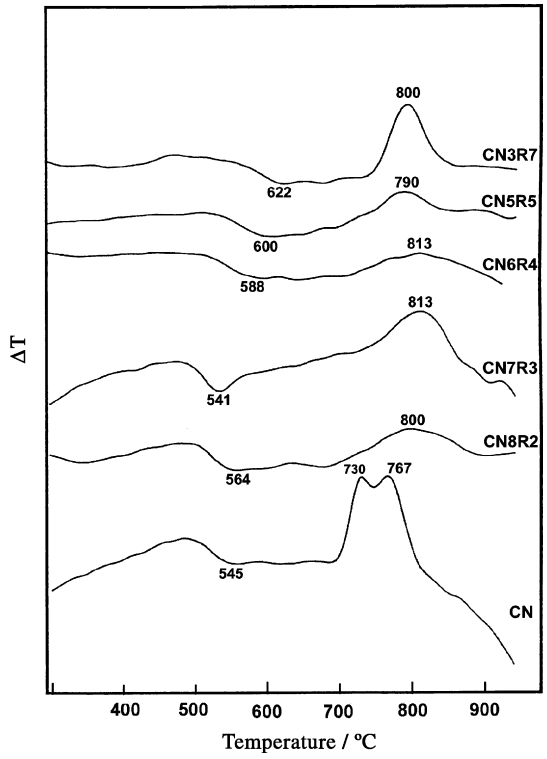


Fig. 1. DTA of the investigated CN-R glasses.

In the DTA of the first series (CN-R), as the nominal richterite content in the investigated glasses was increased, the endothermic dip, generally, shifted to lower temperatures till composition CN7R3 and then increased up to 622 °C in CN3R7 composition. The exothermic peaks, which refer to the process of crystallization, occurred in the 730–813 °C temperature range and varied in intensity and temperature span. Both intensity and span have significant crystallization meanings. Peak splitting in the CN sample reflects the crystallization of two fluorcanasite forms [8]. The exothermic peak temperatures shifted to higher values as the nominal fluorrichterite content in the glass was increased up to CN6R4 and then slightly decreased in glasses containing higher nominal fluorrichterite contents (Fig. 1).

The DTA traces of the second series (CK-R) showed the same general trend, as that of the first series, for the endothermic and exothermic peak temperatures. The temperature of the endothermic effect first decreased from 650 °C in CK to 580 °C in CK7R3 sample and then increased again up to 610 °C in sample CK3R7 (Fig. 2). The exothermic peak temperatures first shifted to higher temperatures and then back to lower temperatures as the nominal fluorrichterite percentage was increased. Diffused exothermic peak splitting took place at 721 and 748 °C in CK5R5 sample, and at 732 and 753 °C in CK3R7 sample. The other glasses, CK6R4 and CK7R3, showed broad exothermic peaks at 790 and 870 °C, respectively. This splitting reflects the crystallization of more than one phase and the peak broadening reflects crystallization over a wide temperature range. Generally, the exothermic peaks of glasses of both series are broad in the middle compositional range and are relatively sharp in either high nominal fluorcanasite or fluorrichterite compositions (Figs. 1 and 2).

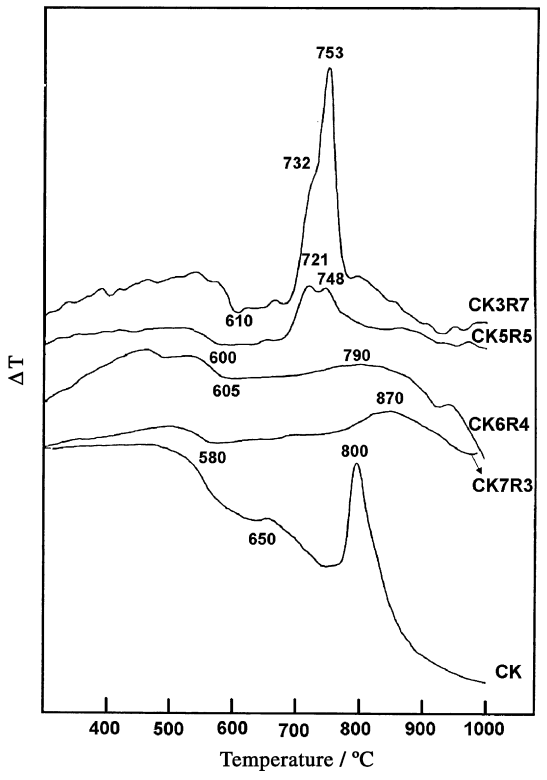


Fig. 2. DTA of the investigated CK-R glasses.

3.2. X-ray diffraction analysis of the crystallized glasses

The heat-treatment parameters applied were suitable to give sufficient dense crystallization in the investigated glasses. Generally, the phases developed in the crystallized glasses were fluorcanasite, fluorrichterite, agrellite, diopside ss and fluorite. Crystallization of the stoichiometric fluorcanasite glass (sample CN) at 600 °C/2 h + 900 °C/2 h yielded both fluorcanasite and agrellite, whereas, high K-fluorcanasite glass (sample CK) developed only fluorcanasite. Fluorrichterite and some diopside ss were developed in the stoichiometric fluorrichterite glass (sample R) after the same heat-treatment.

The crystalline phases developed in the CN-R glasses after different heat-treatments are outlined, as deduced from the corresponding X-ray diffraction patterns in Table 3. Diopside ss and/or fluorrichterite were the main crystalline phases in CN6R4, CN5R5 and CN3R7 samples heat-treated at lower temperatures (at 600 °C/1 h + 700 °C/6 h or 600 °C/1 h + 750 °C/6 h). CN-R glasses, heat-treated at 600 °C/2 h + 900 °C/2 h, developed fluorcanasite as a major phase up to 40% nominal fluorrichterite. No fluorcanasite was developed in samples containing nominal fluorrichterite greater than 50% after any of the heat-treatments applied. Fluorrichterite started to appear in the heat-treated glasses containing 30% of its nominal composition and became a major phase, together with diopside ss, in glasses containing 50% or more of its nominal amount. Agrellite developed in samples containing more than 50% nominal fluorcanasite.

Table 3
Crystalline phases developed in the investigated glasses after different heat-treatments

Sample no.	Heat-treatment (°C/h)	Crystalline phases*
CN	600/2 + 900/2	Cn + Ag
CN8R2	600/2 + 900/2	Cn + Ag
CN7R3	600/2 + 900/2	Cn + R + Ag
CN6R4	600/1 + 700/6	Di ss + Cn + R
	600/1 + 750/6	R + Cn + Di ss
	600/2 + 900/2	Cn + R + Ag
CN5R5	600/1 + 700/6	Di ss + R + Cn + F
	600/1 + 750/6	Di ss + Cn + R
	600/2 + 900/2	Di ss + R + Cn
CN3R7	600/1 + 700/6	Di ss + R (m)
	600/1 + 750/6	Di ss + R
	600/2 + 900/2	Di ss + R
R	600/2 + 900/2	R + Di ss
CK	600/1 + 700/6	Cn
	600/2 + 900/2	Cn
CK8R2	600/1 + 700/6	Cn + F
	600/2 + 900/2	Cn + R
CK7R3	600/1 + 700/6	Cn
	600/2 + 900/2	Cn + R + Di ss
CK6R4	600/1 + 700/6	Cn + R
	600/2 + 900/2	R + Di ss + Cn
CK5R5	600/1 + 700/6	Di ss + R
	600/2 + 900/2	R + Di ss + Cn
CK3R7	600/1 + 700/6	Di ss + R
	600/2 + 900/2	R + Di ss
R	600/2 + 900/2	R + Di ss

Cn = fluorcanasite, Ag = agrellite, R = fluorrichterite, Di ss = diopside solid solution, F = fluorite, m = minor.
* Arranged according to their relative abundance.

The crystalline phases developed in the CK-R glasses after different heat-treatments are also outlined in Table 3. Crystallization of the CK sample yielded only fluorcanasite after any of the heat-treatments applied. Samples with more nominal richterite (CK8R2, CK7R3, CK5R5 and CK3R7) showed a gradual increase and dominance of fluorrichterite and diopside ss as major phases. It should also be noted that, similar to compositions of the first series, no fluorcanasite phase was developed in the second series samples containing more than 50% nominal fluorrichterite after any of the heat-treatments applied.

These results indicate that during the crystallization of glasses containing more than 50% nominal fluorrichterite, in the investigated system, elemental redistribution takes place whereby single-chain silicates (Ca-Mg metasilicates possibly with alkali metasilicates in solid solution) preferentially form together with fluorrichterite to such an extent that fluorcanasite does not crystallize even in the more fully crystallized samples. Moreover, as the nominal richterite increases, above the before mentioned limit (50%), the enstatite component ($MgSiO_3$) increases in the crystallizing pyroxene solid solution.

3.3. Microstructure of the obtained glass-ceramics

The microstructures, of the obtained glass-ceramic samples, vary with composition of the original glass and heat-treatment parameters. PM and SEM micrographs of the investigated glasses after heat-treatment at 600 °C/2 h + 900 °C/2 h are shown in Figs. 3 and 4.

Almost volume crystallization with rather fine-grained microstructures was observed in compositions with more than 20 wt.% nominal fluorrichterite. The CN sample showed evenly distributed spherulitic growths of fluorcanasite, however, 30–40% residual glass was still present (Fig. 3a). In the CNR82 sample, coarse anhedral and prismatic crystals developed in glassy groundmass (about 30–40%, Fig. 3b). The microstructure of sample CN7R3 exhibits interlocked lath-like and fibrous crystals of about 50–100 μm in size (Fig. 3c). Sample CN5R5 developed a microstructure composed of interlocked randomly oriented rod-like crystals (about 1–2 μm in size) in a dense crystalline groundmass (Fig. 3d). Glass-ceramic sample CN3R7 exhibited a more uniform dense microstructure with crystals size less than 1 μm (Fig. 3e).

As can be seen from the micrographs, a relatively coarse-grained microstructure was developed in the glass-ceramic of stoichiometric fluorcanasite composition. On the other hand, the increase of fluorrichterite resulted in the formation of fine- and ultra fine-grained microstructures.

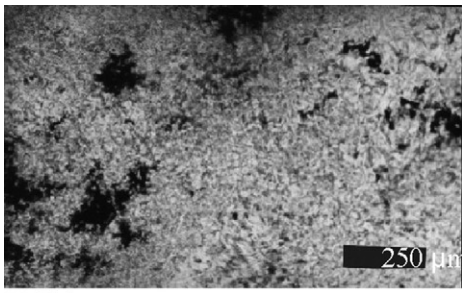
PM and SEM micrographs of CK-R samples are depicted in Fig. 4. Polarizing microscopic examination showed fine randomly oriented prismatic and acicular crystals in CK8R2 sample (Fig. 4b). Other samples, examined by the scanning electron microscope, showed fine-grained and ultrafine-grained microstructures of interlocked prismatic crystals of fluorcanasite alone (sample CK, Fig. 4a) or with fluorrichterite and diopside ss (samples CK5R5 and CK3R7, Fig. 4c and d).

It is obvious that, glass-ceramics derived from CK-R series compositions exhibit bulk crystallization. The increase of the nominal percentages of fluorrichterite gives crack-free highly crystalline glass-ceramic samples with finer microstructures.

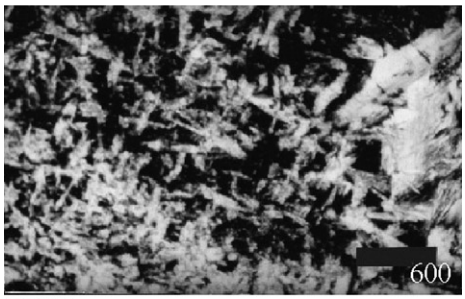
3.4. Physical and mechanical properties the glass-ceramics

The density values of the obtained glass-ceramic samples resulting after heat-treatment of the corresponding glasses at 600 °C/2 h + 900 °C/2 h are listed in Table 4. It can be easily noticed that the density increases with increasing the nominal fluorrichterite in the glass-ceramic composition.

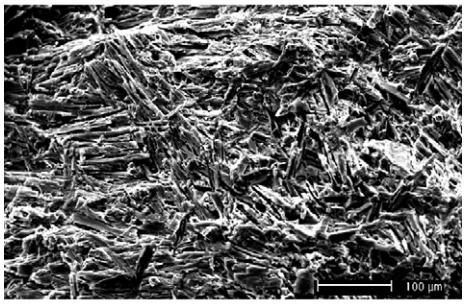
The coefficients of thermal expansion (CTE) of the investigated glass-ceramics obtained after heat-treatment at 600 °C/2 h + 900 °C/2 h are given in Table 4. The CTE values range from 79 to 109 $\times 10^{-7}$ °C^{-1}. Samples with nominal K-rich fluorcanasite (2nd series) showed slightly higher CTE values than those containing Na-rich fluorcanasite (1st series). The change of CTE values of the investigated glass-ceramic samples is governed by the type and quantity of the developed crystalline phases, as well as, by the amount and composition of the residual glass.



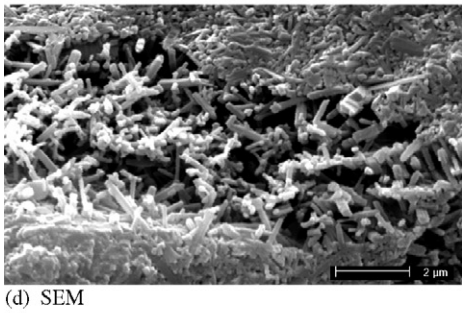
(a) PM



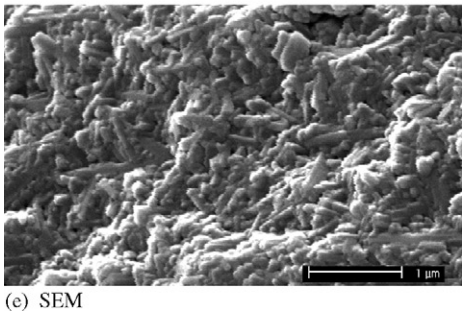
(b) PM



(c) SEM

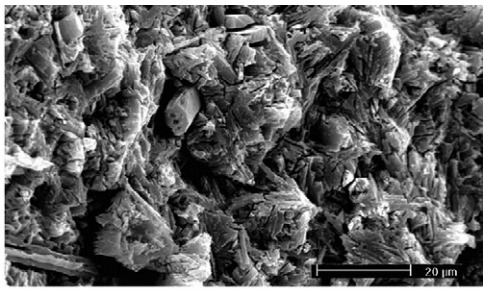


(d) SEM



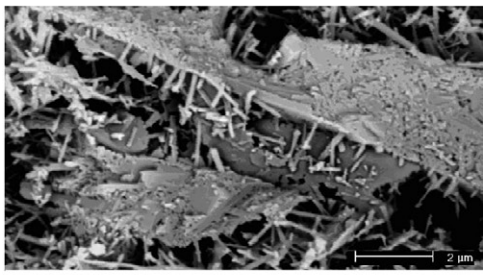
(e) SEM

Fig. 3. Photomicrographs of the investigated glasses (1st series): (a) CN, (b) CN8R2, (c) CN7R3, (d) CN5R5 and (e) CN3R7 heat-treated at 600 °C/2 h + 900 °C/2 h.

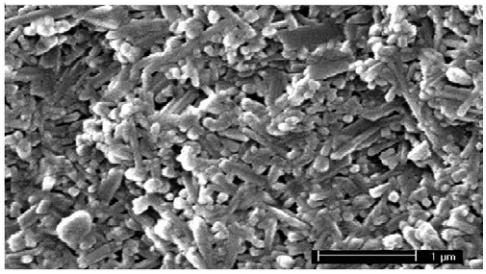


(a) SEM

(b) PM



(c) SEM



(d) SEM

Fig. 4. Photomicrographs of the investigated glasses (2nd series): (a) CK, (b) CK8R2, (c) CK5R5 and (d) CK3R7 heat-treated at 600 °C/2 h + 900 °C/2 h.

The reported CTE value of fluorcanasite glass-ceramic is about 125×10^{-7} °C^{-1} [3] and about 115×10^{-7} °C^{-1} for K-fluorrichterite containing cristobalite [9]. Enstatite has a relatively medium CTE ~75–100 $\times 10^{-7}$ °C^{-1} [10]. The same applies for diopside.

Table 5 gives the Vickers' microhardness values of the obtained glass-ceramic samples. Crack-free and homogeneous glass-ceramic samples were selected for measurements. For this reason, glass samples heat-treated at 600 °C/1 h + 700 °C/6 h and 600 °C/1 h + 750 °C/6 h were most adequate for this testing. The obtained values reflect the impact of the heat-treatment parameters and type of developing phases on the microhardness of the material. The Vickers' microhardness values, generally, increased, by increasing the heat-treatment

Table 4
Thermal expansion coefficients and densities of the investigated glasses heat-treated at 600 °C/2 h + 900 °C/2 h

Sample code	Developed phases	Expansion coefficient $\alpha \times 10^{-7}$ °C^{-1} (20–500 °C)	Density (g/cm^3)
CN	Cn + Ag	79	2.59
CN8R2	Cn + Ag		2.60
CN7R3	Cn + R + Ag	94	2.64
CN6R4	Cn + R + Ag		2.71
CN5R5	Di ss + R + Cn	103	2.80
CN3R7	Di ss + R	100	2.83
R	R + Di ss		2.93
CK	Cn	94	2.55
CK8R2	Cn + R		2.58
CK7R3	Cn + R + Di ss	108	2.61
CK6R4	R + Di ss + Cn	109	2.69
CK5R5	R + Di ss + Cn	107	2.80
CK3R7	R + Di ss	109	2.90

Cn = fluorcanasite, Ag = agrellite, R = fluorrichterite, Di ss = diopside solid solution.

Table 5
Vickers hardness values of some glasses heat-treated at 600 °C/1 h + 700 °C/6 h and 600 °C/1 h + 750 °C/6 h

Heat-treatment	Sample code	Developed phases	Hv (kg/mm^2)
600 °C/1 h + 700 °C/6 h	CN6R4	Di ss + Cn + R	519
	CN5R5	Di ss + R + Cn + F	606
600 °C/1 h + 750 °C/6 h	CN6R4	R + Cn + Di ss	525
	CN5R5	Di ss + Cn + R	579
	CN3R7	Di ss + R	743
600 °C/1 h + 700 °C/6 h	CK8R2	Cn + F	508
	CK5R5	Di ss + R	642
	CK3R7	Di ss + R	613
600 °C/1 h + 750 °C/6 h	CK6R4		514
	CK5R5		560
	CK3R7		743

Cn = fluorcanasite, Ag = agrellite, R = fluorrichterite, Di ss = diopside solid solution, F: fluorite.

parameters due to the development of more crystalline phases. The microhardness also increased by increasing the nominal percentage of fluorrichterite. Generally, Samples based on Na-rich fluorcanasite showed better microhardness than those with nominal K-rich fluorcanasite. The development of pyroxene phases in compositions with high nominal fluorrichterite percentages contributes to the hardness of the obtained glass-ceramics. This is clearly exemplified by samples CN3R7 and CK3R7 heat-treated at 600 °C/1 h + 750 °C/6 h.

3.5. Chemical resistively of the glass-ceramics

The results of the chemical durability of the investigated glass-ceramics resulting after heat-treatment at 600 °C/2 h + 900 °C/2 h are given in Table 6.

The glass-ceramics showed an obvious general trend of decreasing the weight loss % in HCl solution (increase in chemical durability) with increasing the nominal percentage of fluorrichterite.

Table 6
The chemical durability of both glass-ceramic series

Sample code	Developed phases after treatment at 600 °C/2 h + 900 °C/2 h	wt. loss % of glass-ceramic (after 1 h at 95 °C)	
		Leaching by 0.1 N HCl	Leaching by 0.1 N NaOH
CN	Cn + Ag	6.32	7.48
CN8R2	Cn + Ag	3.44	10.82
CN7R3	Cn + R + Ag	4.28	8.28
CN6R4	Cn + R + Ag	3.12	7.17
CN5R5	Di ss + R + Cn	0.96	6.60
CN3R7	Di ss + R	0.42	12.70
CK	Cn	5.54	9.62
CK8R2	Cn + R	2.58	6.80
CK7R3	R + Cn + Di ss	1.94	6.76
CK6R4	R + Di ss + Cn	2.18	7.66
CK5R5	R + Di ss + Cn	–	9.52
CK3R7	R + Di ss	0.16	8.56

Cn = fluorcanasite, Ag = agrellite, R = fluorrichterite, Di ss = diopside solid solution.

Generally, these glass-ceramic samples showed better chemical durability in the acidic medium than in the alkaline one. K-rich samples showed better chemical durability in HCl solution than Na-rich compositions.

4. Conclusion

Glasses based on fluorcanasite, with different Na_2O:K_2O ratios, and fluorrichterite were prepared using low cost abundant natural raw materials to produce cheap glass-ceramics with the inherent properties of both fluorcanasite and fluorrichterite phases. The developed crystalline phases after different heat-treatments were fluorcanasite, fluorrichterite, agrellite, fluorite and diopside ss. The crystalline phases developed in the fluorcanasite–fluorrichterite glasses depend on CaO/MgO ratio. Elemental redistribution takes place during the crystallization of glasses containing more than 50% nominal fluorrichterite whereby single-chain silicates (Ca–Mg metasilicates possibly with alkali metasilicates in solid solution) preferentially form together with fluorrichterite to such an extent that fluorcanasite does not crystallize even in the more fully crystallized samples.

The microstructures of the crystalline products consisted of interlocking blade-like and acicular crystals with increasing degrees of fineness as the nominal fluorrichterite content was increased.

The coefficients of thermal expansion of the obtained glass-ceramic materials range between 79×10^{-7} and 109×10^{-7} °C^{-1}; and the density between 2.55 and 2.93 gm/cm^3. The crystalline products attained Vickers' hardness values of 508–743 kg/mm^2. The chemical durability of the materials was better in acidic than in alkaline solutions.

The increase of potassium relative to sodium in the nominal composition of fluorcanasite, generally, enhances many properties of the resulting glass-ceramics.

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