Effect of the nucleating agents Cr_2O_3 and LiF on crystallizing phases and microstructures of glass-ceramics prepared by using some industrial wastes

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Glass-ceramics in the system diopside–anorthite–orthoclase were prepared using the waste known as the by-pass cement dust in the amount of 36 % of the batch constituents. The effects of addition of the nucleating agents Cr_2O_3, LiF, and mixtures of them on the crystallizability, phase assemblages, and the resultant microstructures were investigated. Low concentration of Cr_2O_3 (0.5 wt%) causes volume crystallization and formation of fine-grained microstructures of microcline, anorthite and aluminous pyroxene. Higher concentrations of Cr_2O_3 favor formation of leucite and aluminous pyroxene and inhibit crystallization of anorthite. LiF causes the formation of microcline and its transformation into orthoclase. It also increases the crystallizability with the formation of nonuniform coarse-grained texture. A mixture of 0.5 % Cr_2O_3 and 1.5 % LiF causes a synergistic effect, where fine-grained microstructure is formed (due to Cr_2O_3) with orthoclase formation (due to LiF) in addition to aluminous pyroxene and anorthite. The effects of various Cr_2O_3 concentrations were discussed on the bases of the increased viscosity and separation of Cr_2O_3 and/or chromium-spinel phases. The effects of LiF were attributed to the role of fluorine ions in reducing the viscosity of the glasses, consequently facilitating crystallization of the structurally more complex silicate in addition to favoring reaching thermodynamic equilibrium.

Einfluß der Keimbildner Cr_2O_3 und LiF auf die Kristallisation und die Mikrostruktur bei der Herstellung von Glaskeramiken unter Zugabe von Industrieabfällen

Für die Herstellung von Glaskeramiken des Systems Diopsid–Anorthit–Orthoklas wurde ein Gemengeanteil von 36% durch Zementstaub, ein Abfallprodukt der Zementindustrie, ersetzt. Der Einfluß der zugegebenen Keimbildner Cr_2O_3, LiF und deren Mischungen auf die Kristallisation, Phasenzusammensetzung und die resultierenden Mikrostrukturen wird untersucht. Eine niedrige Konzentration von Cr_2O_3 (0,5 Gew.%) verursacht eine Volumenkristallisation und die Bildung von feinkörnigen Mikrostrukturen von Mikroklin, Anorthit und aluminiumhaltigem Pyroxen. Höhere Konzentrationen von Cr_2O_3 begünstigen die Bildung von Leucit und aluminiumhaltigem Pyroxen und verhindern die Kristallisation von Anorthit. LiF verursacht die Bildung von Mikroklin und seine Umwandlung in Orthoklas. Außerdem erhöht es die Neigung zur Kristallisation durch die Bildung einer ungleichförmigen, grobkörnigen Textur. Eine Mischung von 0,5% Cr_2O_3 und 1,5% LiF bewirkt einen synergistischen Effekt, wodurch eine feinkörnige Mikrostruktur (aufgrund von Cr_2O_3) mit Orthoklasbildung (aufgrund von LiF) zusätzlich zu aluminiumhaltigem Pyroxen und Anorthit gebildet wird. Der Einfluß der unterschiedlichen Cr_2O_3-Konzentrationen wird auf der Grundlage erhöhter Viskosität und der Abscheidung von Cr_2O_3- und/oder Chromspinellphasen diskutiert. Der Einfluß von LiF wird Fluorionen zugeschrieben, die die Viskosität der Gläser herabsetzen und dementsprechend die Kristallisation des strukturell komplexeren Silicats erleichtern und zusätzlich die Einstellung des thermodynamischen Gleichgewichts begünstigen.

1. Introduction

The first practical glass-ceramic materials prepared by controlled crystallization of special glasses were developed nearly forty years ago [1]. Since that time a wide variety of applications of these versatile materials have been developed as a result of their many outstanding properties. The distinct advantages of the glass-ceramic method, in certain circumstances, over conventional ceramic processing routes are of particular importance in many applications with respect to the high uniformity of the microstructures of glass-ceramics, the absence of porosity and the minor changes in volume during the conversion of glass into glass-ceramic. Because the glass-ceramic process begins with a glass, all the well established glass forming techniques can be employed to manufacture components with a variety of complex

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shapes including blowing, casting, pressing and rolling. Subsequently the glass is readily converted into a fine-grained polycrystalline ceramic by a controlled nucleation and crystal-growth heat treatment schedule.

Glass-ceramics could be produced by the addition of nucleating agents. The role of nucleating agents in initiating glass crystallization from a multitude of centers was the major factor allowing the introduction of glass-ceramics into industrial applications [1 to 3].

It has been found that Cr_2O_3 is slightly soluble in certain glasses of the $CaO-MgO-Al_2O_3$ system at 1500 °C; and decreases the rate of crystal growth [4]. More than 0.3 wt% of Cr_2O_3 in such a system was found to cause surface and internal (bulk) crystallization [5]. It has been reported [2] that chromium-rich phase could be separated out from the glass as a result of its presence as interstitial cation of high field strength. Chromium containing melts were also found to have great ability to crystallize out pyroxene phase due to the low activation energy needed – 8.8 kJ/mol – for such process [6], The role of Cr_2O_3, LiF and their mixtures on the crystallizing phases of glasses, based on the celsian–diopside–anorthite system, were studied [7].

Fluorides are known to weaken the glass network structure [2]. This weakening decreases the melting temperatures, the temperatures at which crystallization occurs and the viscosities of the glasses. As a result of the decrease in viscosity, the mobility and diffusion of the different ions will be markedly increased, leading to higher crystallizability. In silicate glasses containing fluorine, glass-in-glass phase separation occurs which decreases the energy barrier necessary for crystallization [8]. In many cases, phase separation alone is not, however, sufficient to induce bulk crystallization in the glass [9]. The mode of crystallization, whether it is surface or bulk, depends essentially on both the actual chemical composition of the glass and the concentration of the fluoride added [10].

The aim of the present work is to prepare glass-ceramic materials in the system diopside–anorthite–orthoclase, and to investigate the effects of addition of the nucleating agents Cr_2O_3 and LiF, as individuals and as mixtures of both, on the crystallizability, phase assemblages, and on the resultant microstructures of the glass-ceramics produced. These nucleating agent were chosen to obtain fine-grained microstructure and to facilitate crystallization as expected by Cr_2O_3 and LiF, respectively.

One of the raw materials which will be used in the batch constituents is the waste known as the by-pass cement dust. It is formed in large quantities by Portland cement factories that use the dry-technology for cement production in Egypt. This waste causes pollution to the environment and serious problems to human health. The use of such waste as nonconventional raw material for the preparation of glass-ceramic materials may pave the way for its application in manufacturing of tiles and cladding products [11].

Table 1. Nominal compositions of the base glass and glasses with nucleating agents

	K_2O	CaO	MgO	Al_2O_3	SiO_2
composition of base glass K30 in wt%	5.08	16.28	7.55	16.28	54.66

nos. of glasses with nucleating agents	nucleating agent	amount added in g/100 g base glass K30
KCr.5	Cr_2O_3	0.5
KCr1	Cr_2O_3	1.0
KL.5	LiF	0.5
KL1.5	LiF	1.5
KL3	LiF	3.0
KCrL	Cr_2O_3 + LiF	0.5 + 1.5

Table 2. Chemical composition (in wt%) of the raw materials used for batch preparation

constituent oxides	by-pass cement dust	kaolin	magnesite	quartz sand	potash feldspar
SiO_2	13.30	55.16	0.72	99.20	70.81
Al_2O_3	3.08	28.31	0.76	0.28	16.25
TiO_2	–	1.89	–	0.001	0.10
Fe_2O_3	1.35	3.16	0.19	0.03	0.35
CaO	44.03	0.34	10.20	0.10	0.29
MgO	2.56	0.18	38.70	0.02	0.16
Na_2O	1.10	0.80	0.30	0.02	2.24
K_2O	1.04	0.20	0.20	0.01	9.20
Cl^-	1.79	–	–	–	–
SO_3^{2-}	9.50	–	–	–	–
LOI¹⁾	22.25²⁾	10.82²⁾	48.92³⁾	0.40	–

¹⁾ LOI = Loss on ignition.
²⁾ Humidity and adsorbed water.
³⁾ Carbon dioxide and humidity.

2. Experimental procedure

Table 1 lists the compositions of the base glass and glasses with nucleating agents. Magnesite, potash feldspar, quartz sand, kaolin and by-pass cement dust from Torah Cement Co., Helwan City (Egypt), were used as starting materials for the preparation of the glass-ceramics to be investigated. Table 2 shows the chemical composition of the materials used for batch preparation. The by-pass cement dust was used in the amount of 36 % of the batch constituents. The weighed batch materials after thorough mixing were melted in Pt crucibles in an electrically heated globar furnace at 1400 °C for 2 h, for batches containing fluorides, and at 1500 °C for 3 h, for batches containing chromium ions as nucleating

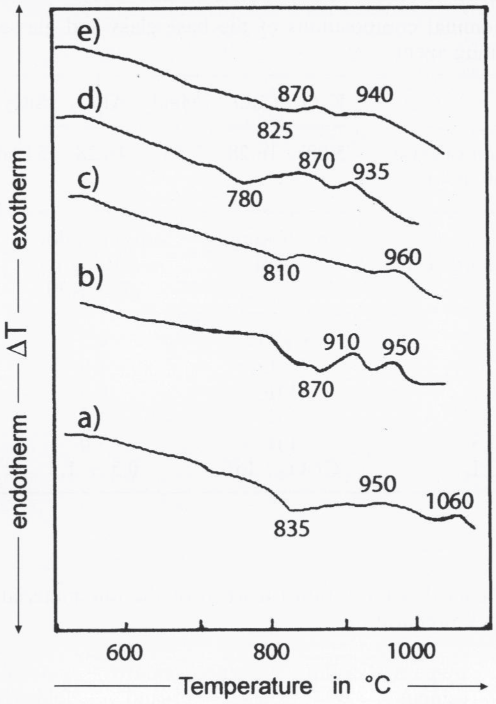

Figure 1. Differential thermal analysis curves of nucleant free specimen (curve a) and those with 0.5 % Cr_2O_3 (curve b), 1.5 % LiF (curve c), 3 % LiF (curve d), and 0.5 % Cr_2O_3 + 1.5 % LiF (curve e).

agents. The homogeneity of the melts was achieved by occasional swirling of their crucibles. After melting, bubble-free melts were cast into rectangular forms, then transferred into a muffle furnace at 550 °C, which was then switched off to cool to room temperature.

DTA scans were carried out with a Schimadzu DT-30 microdifferential thermal analyzer using 70 mg of the powdered glass of grain size of 0.6 to 0.18 mm against Al_2O_3 powder as the reference material. A heating rate of 20 K/min was maintained for all the DTA runs. Conversion of glass specimens into glass-ceramic was carried out by heat treating the specimens at 850 °C for 5 h followed by 3 h at 1100 °C in a muffle furnace.

X-ray diffraction patterns were obtained using a Philips type PW 1390 diffractometer with nickel-filtered CuK radiation. All the instrument settings were maintained for all the analysis using a silicon disc as an external standard.

A Zeiss Scanning Electron Microscope type DSM950 was used to examine selected specimens. The fractured surfaces of the samples were etched with 40 % HF for 10 s, then gold sputtering was performed on the surface, and finally the samples were examined.

3. Results

Table 3. Summary of DTA results for glasses with and without nucleating agents

glass no.	endothermic peaks, temperature in °C	exothermic peaks, temperature in °C	crystalline phases
K30	835	950, 1060	Di (ss), An + Mic
KCr.5	870	910, 950	Di (ss), An (m) + Leuc
KL1.5	810	960	Di (ss), An, Mic + Orth (m)
KL3	780	870, 935	Di (ss), An, Mic + Orth (m)
KCrL	825	870, 940	Di (ss), An + Orth

Note: Di = diopside, An = anorthite, Mic = microcline, Leuc = leucite, Orth = orthoclase, ss = solid solution, m = minor.

Table 4. Crystalline phases identified by X-ray in specimens heat-treated for 5 h at 850 °C followed by 3 h at 1100 °C

glass no.	phases identified by X-ray
K30	diopside (ss) + anorthite + microcline
KCr.5	diopside (ss) + leucite + anorthite (m)
KCr1	diopside (ss) + leucite
KL.5	diopside (ss) + anorthite (m) + microcline + orthoclase (m)
KL1.5	diopside (ss) + anorthite + microcline + orthoclase (m)
KL3	diopside (ss) + anorthite + microcline + orthoclase (m)
KCrL	diopside (ss) + anorthite + orthoclase

Note: ss = solid solution, m = minor.

Figure 1 shows DTA curves of various specimens studied. Table 3 lists a summary of the DTA results with the corresponding crystalline phases identified. From this table it can be noticed that the nucleation occurs in the range 780 to 870 °C, while crystallization occurs in temperatures ranging between 935 to 1060 °C. Bulk specimens ((1 x 2 x 1) cm^3) were tested for nucleation at 750 and 850 °C for 5 h. The latter condition (850 °C for 5 h) showed high nucleation density. Due to the large thickness of the bulk specimens a higher temperature (1100 °C) than that recorded by DTA was used as the crystallization temperature. All glasses were treated for 5 h at 850 °C followed by 3 h at 1100 °C, and table 4 depicts the phases formed as identified by X-ray diffraction.

The effect of Cr_2O_3 addition on the crystallization behavior and the textures of the investigated glasses can be outlined as follows:

a) As revealed from DTA studies (figure 1 and table 3) the addition of 0.5 % Cr_2O_3 to the base glass K30 tends to shift the temperatures of endothermic DTA dips to higher temperatures. The DTA curves of the base glass K30 (figure 1, curve a) show that the endothermic dip occurs at 835 °C, whereas in the glass with 0.05 % Cr_2O_3 this dip occurs at 870 °C (figure 1, curve b).

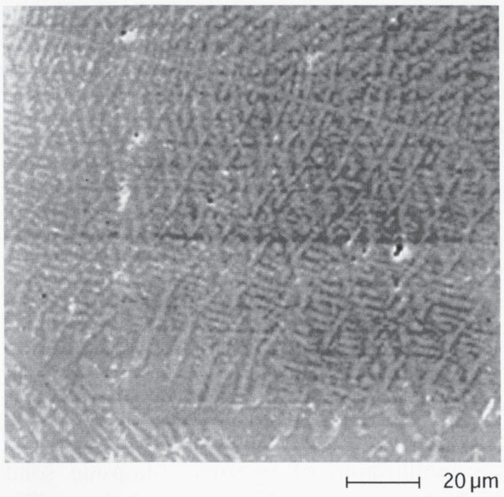

Figure 2. SEM micrograph of nucleant free glass K30 after heat treatment for 5 h at 850 °C followed by 3 h at 1100 °C.

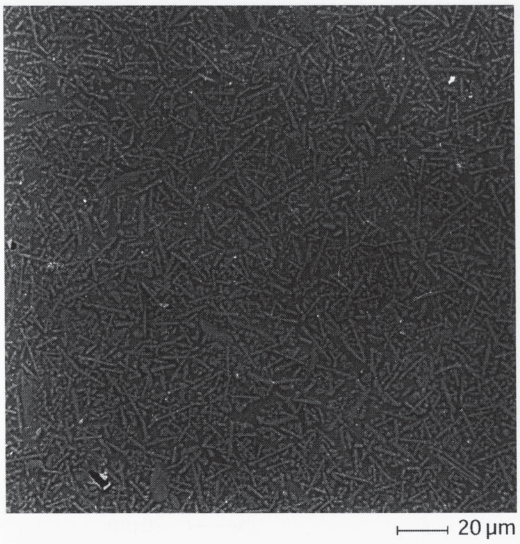

Figure 3. SEM micrograph of glass KCr1 after heat treatment for 5 h at 850 °C followed by 3 h at 1100 °C.

b) The presence of Cr_2O_3 lowers the temperatures of the exothermic crystallization peaks. This may be clearly seen when the DTA curves of the base glass K30 and glass KCr.5 are compared. Figure 1 shows that the exothermic peaks occur at 950 and 1060 °C for the base glass K30 (curve a), whereas in the corresponding chromium-oxide nucleated glass KCr.5 (curve b) these peaks occur at 910 and 950 °C.

c) The presence of Cr_2O_3 in the glass generally facilitates and favors the formation of diopside solid solution ($CaMgSi_2O_6 \cdot CaAl_2SiO_6$) and leucite and inhibits anorthite formation (especially with 1 % Cr_2O_3, table 4). X-ray examination of the base glass K30 indicated the development of microcline, diopsidic pyroxene and anorthite [12], whereas for the glass with 0.5 % Cr_2O_3 leucite and diopside with minor amounts of anorthite are formed. For the glass of higher concentration of Cr_2O_3, (KCr1) the formation of anorthite is inhibited (table 4).

d) The presence of Cr_2O_3 in the glass greatly enhanced volume crystallization with the formation of uniform fine-grained microstructure. This can be noticed when the SEM micrograph of glass-ceramic specimen of the base glass K30 (figure 2) is compared with that of glass KCr1 (figure 3).

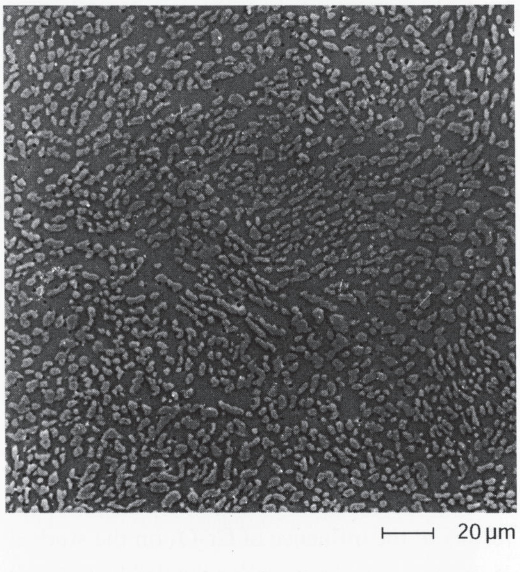

Figure 4. SEM micrograph of glass KL3 after heat treatment for 5 h at 850 °C followed by 3 h at 1100 °C.

Lithium fluoride was used in amounts of 0.5, 1.5 and 3 g per 100 g glass. Generally, it facilitates the melting process and decreases the temperature of beginning of crystallization of the glasses. The effect of LiF on the crystallization behavior of the investigated glasses can be summarized as follows:

- It reduces the melting temperature and also the viscosity of the resultant melt in comparison with LiF-free glass.
- It greatly enhances the crystallizability of the glass. The DTA curves (figure 1, curves a, c and d) show that the exothermic crystallization peaks (table 3) shift from 835 to 810 to 780 °C, i.e. to lower temperatures when LiF was increased from 0.0 to 1.5 to 3.0 wt%, respectively. Figure 4 illustrates the enhancement in the crystallizability noticed in specimen KL3, where a relatively nonuniform coarse-grained texture is obtained (compare with that of LiF-free specimen figure 2).
- It favors the formation of microcline and orthoclase in addition to diopside and anorthite (table 4).

The effects produced by a mixture of 0.5 % Cr_2O_3 and 1.5 % LiF added per 100 g glass can be summarized as follows:

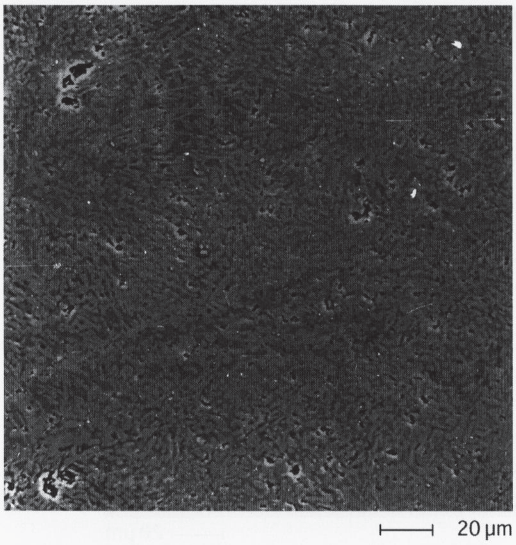

Figure 5. SEM micrograph of glass KCrL after heat treatment for 5 h at 850 °C followed by 3 h at 1100 °C.

- The melting temperature and viscosity of the resultant melt were decreased when compared with those of the base glass or Cr_2O_3-containing glasses.
- The mixture enhances the crystallizability of the glass. From figure 1 it can be noticed that for the DTA curve of the glass containing 0.5 % Cr_2O_3 and 1.5 % LiF (curve e) the exothermic crystallization peaks are displaced to lower temperatures when compared with those containing 0.5 % Cr_2O_3 alone (curve b).
- The mixture causes the development of uniform fine-grained microstructures (figure 5) of orthoclase with anorthite and diopside phases (table 4).

4. Discussion

From the results of the influence of Cr_2O_3 on the studied glasses, it is evident that it is greatly effective as a nucleating agent and favors fine-grained bulk crystallization. This effect may be due to one or both of the following reasons:

a) the rapid separation of Cr_2O_3 in the form of minute chromium-containing crystalline phase (spinel) or as chromium-rich amorphous droplets during heat-treatment which act as sites for the subsequent crystallization of the major phases;

b) the great affinity of Cr_2O_3 to combine with other cations such as Mg^{2+}, Fe^{2+}, Fe^{3+} and Al^{3+} and formation of minute spinel-like phases which can readily crystallize out and act as crystallization centers or nuclei for the major crystallizing phases.

The formation of the great number of crystallization centers by the above mentioned reasons, especially by the latter one, may account for the volume crystallization and fine-grained textures, observed during the heat-treatment of the investigated Cr_2O_3-containing glasses (figures 3 and 5).

Chromium-spinel crystallites, most probably of $Mg(Al,Cr)_2O_4$ composition may be created and separated out in very great numbers. Moreover, the small amounts of iron oxides brought into the glass by the raw material used may also form additional spinellide centers or nuclei. The present assignment is in agreement with the assumption that spinellides of the composition $(Mg, Fe) (Al, Fe, Cr)_2O_4$ are formed during the first stages of heat-treatment in Cr_2O_3-containing glasses based on the $CaO-MgO-Al_2O_3-SiO_3$ system [13]. The formation of these spinellide centers is followed by crystallization of pyroxene (diopside solid solution $CaMgSi_2O_6 \cdot CaAl_2SiO_6$) around them. The presence of Cr_2O_3 in the glasses studied favors pyroxene (diopside solid solution) formation and inhibits anorthite crystallization (table 4). This may be due to one or more of the following reasons:

a) The low value of the activation energy for crystallization of pyroxene (8.8 kJ/mol) from chromium-containing melts may cause its preferential formation compared to the plagioclases which possess much higher values of activation energy (33.5 to 54.4 kJ/mol) [6].

b) Pyroxene formation may be favored by the high degree of match in its unit cell parameters with those of Cr_2O_3 and/or chromospinel phases.

The mechanism of formation of pyroxenes in the studied specimens is in agreement with the findings that the early formed spinellides act mainly as crystallization nuclei for the pyroxene phases during the crystallization of glasses based on calcareous clays [13], and that Cr_2O_3 stimulates the formation of the pyroxenes and retards plagioclase crystallization [14].

The minor amounts of anorthite or its absence (table 4) in the crystalline products of the glasses KCr.5 and KCr1, respectively, and the presence of leucite in these specimens can be attributed to the observed increase in the viscosity of their melts. The increased viscosity is expected to make the formation of complex structures, like those of the plagioclases (anorthite), difficult whereas minerals of relatively simple crystal structure (pyroxenes) can be easily formed [15 and 16]. The structure of leucite ($KAlSi_2O_6$) is relatively simple when compared with that of orthoclase ($KAlSi_3O_8$), so it crystallizes out as a result of the prevailing conditions. Excess silica is expected to be formed as a result of the formation of leucite at the expense of orthoclase.

The introduction of LiF or mixture of Cr_2O_3 and LiF produces a marked lowering of the temperature at which crystallization begins (figure 1) and consequently a widening of the crystallization range. The observed decrease in the melting temperatures and the temperatures at which crystallization occurs indicate a decrease in the viscosities of the glasses. This decrease in viscosity can be attributed to the weakening of the glass network structure brought about by fluorides [2]. Consequently, the mobility and diffusion of the different ions will be markedly increased leading to higher crystallizability. It is reported that surface crystallization is expected to occur if the amount of LiF used is less than 5 % [10], which account for the nonuniform coarse-grained character of the fluorine-containing glass KL3 (figure 4). The presence of other anions introduced by the waste by-pass cement dust (table 2), such as Cl^- and SO_3^{2-}, seems to have no role in the nonuniformity of the observed texture.

The presence of LiF favored the formation of orthoclase and transformation of microcline to orthoclase. This variability of mineral formation can be ascribed to the strong effect of fluorine ions on reducing the viscosity of the crystallizing glass. As a result it facilitates migration and diffusion of the ions and ionic complexes present to such an extent that crystallization of the structurally more complex silicates and/or some structural transformation such as microcline-orthoclase transformation can take place [17].

It has been reported [18] that leucite is the first phase to crystallize from K-feldspar melt. With continuous falling of temperature the liquid reacts with the leucite transforming it into orthoclase, the reaction being approximately represented by:

$$\underset{\text{leucite}}{5\,KAlSi_2O_6} + 5\,SiO_2 \rightarrow \underset{\text{K-feldspar (orthoclase)}}{5\,KAlSi_3O_8}$$

Therefore, in presence of LiF excess silica, formed after the formation of aluminous pyroxenes and anorthite, may react with leucite transferring it into orthoclase.

The fine-grained texture and presence of orthoclase in addition to diopside and anorthite in the crystallized glass KCrL (figure 5) confirm the synergistic effect of the mixed nucleants Cr_2O_3 and LiF. The present findings indicate that Cr_2O_3 causes bulk nucleation and growth of extremely fine-grained microstructures even in presence of LiF. On the other hand, LiF affects the phases crystallized out in presence of Cr_2O_3, where it causes orthoclase formation. The development of anorthite in fluorine-containing glasses (table 4) can be attributed to the effect of fluorine ions on facilitating the crystallization process and favoring reaching thermodynamic equilibrium.

5. Conclusions

The presence of low concentration of Cr_2O_3 (0.5 wt%) is highly effective as catalyst for initiating crystallization centers that induce volume crystallization and formation of fine-grained microstructures in the system diopside–anorthite–orthoclase studied. When Cr_2O_3 is present in higher concentrations (1.0 wt%), it favors leucite and aluminous pyroxene formation and inhibits crystallization of anorthite.

The presence of LiF helps in the formation of microcline and its transformation into orthoclase, and leads to the formation of nonuniform coarse-grained microstructures. Mixture of the nucleant species 0.5 % Cr_2O_3 and 1.5 % LiF can lead to the formation of fine-grained microstructure due to Cr_2O_3, and the formation of orthoclase due to LiF, which also facilitates the crystallization process and favors reaching thermodynamic equilibrium.

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