Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 35 (2009) 69–75

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Effect of some nucleating agents on crystallizing phases and microstructure in Li_2O–BaO–Al_2O_3–SiO_2 system

G.A. Khater [1,*], M.H. Idris

Saudi Geological Survey, P.O. Box 54141, Jeddah 21514, Saudi Arabia

Received 1 June 2007; received in revised form 7 July 2007; accepted 20 September 2007
Available online 29 January 2008

Abstract

Different concentrations of LiF and Cr_2O_3 were incorporated in Li, Ba aluminosilicate glass to establish their effects on the crystallization process. The kinetics of phase transformations, the final crystalline phase assemblages and the microstructures formed were found to be dependent on the types and concentration of the nucleant involved. Cr_2O_3 was found to increase the melting temperature and favor crystallization of β-spodumene ss hexacelsian and traces of monoclinic celsian. It also favors volume crystallization of finer grained microstructure. LiF was found to decrease the melting temperature and favor crystallization of β-spodumene ss and monoclinic celsian. LiF in low concentrations greatly facilitates the crystallization process, the β-eucryptite ss/β-spodumene ss transformation and hexacelsian/monoclinic celsian transformation. It also stimulates surface crystallization with holocrystalline coarse non-uniform textures. The effects of various Cr_2O_3 concentrations were discussed on the basis of the increased viscosity and separation of Cr_2O_3 and/or chromium spinel phases. The role of LiF was 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.

Keywords: Crystallization; β-Eucryptite ss; β-Spodumene ss; Hexacelsian; Monoclinic celsian

1. Introduction

Glass-ceramics are crystalline materials formed through the controlled crystallization of glass during specific heat treatments. The bulk chemical composition, nucleant added, final phase assemblage and microstructure are the most important factors affecting their technical properties. Crystallization of glass from the surface or from a small number of sites in the interior usually results in low strength materials with coarse-grained microstructures; in contrast, efficient nucleation of crystals from numerous centers results in fine-grained microstructures and consequently high-strength materials. 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 [1–6].

The crystallization of some glasses, based on the spodumene with successive additions of celsian [7–10] showed that, although the tendency towards bulk crystallization increased with increase in celsian content, relatively non-uniform coarse-grained textures were produced. The resulting crystalline phase assemblages depend largely upon bulk chemical composition, crystallization parameters and the extent of isomorphous substitution as well as rate of cooling. Hexacelsian was the only $BaAl_2Si_2O_8$ phase that directly crystallized out from the glass. It may invert reversibly and rapidly into its orthorhombic modification with a detectable volume change around 225 °C or may be partly converted irreversibly and sluggishly to its stable low-expansion monoclinic modification through prolonged high temperature treatments [7,11].

Crystal nucleation is a fundamental process of phase transition in glass melts based on molecular level fluctuations under a regime of supersaturation. The time and temperature dependent kinetics of crystal nucleation are of crucial importance in determining the glass forming abilities of melts and play an important role in their wide ranging technological applications as glass ceramic materials.

---

* Corresponding author.
E-mail address: kater.ja@sgs.org.sa (G.A. Khater).

[1] Permanent address: National Research Centre, Glass Research Department, Dokki, Cairo, Egypt.

doi:10.1016/j.ceramint.2007.09.118

Table 1
Base glass composition

Nominal phase composition (wt%)	
Celsian	30
Spodumene	70
Calculated oxides constituents (wt%)	
BaO	12.25
Li_2O	5.62
Al_2O_3	27.33
SiO_2	54.81

Whereas for most devitrifications the composition of glass and crystal differ, a limited number of glass compositions crystallize isochemically, i.e. without changes in composition [7]. Nucleation can occur in such glasses on pre-existing surfaces and in the absence of any initial surface [12]. The nucleation kinetics of the latter process (homogeneous volume nucleation) has been described using the results of the classical nucleation theory [13–16].

The main objective of the present study was to investigate the various effects of different additions of the nucleating agents Cr_2O_3 and LiF, on the crystallizability, phase assemblages, isomorphism and polymorphism of the crystallizing spodumene or celsian, respectively, and on the resultant microstructures.

2. Experimental procedure

2.1. Glass composition and preparation

A base glass was prepared for the experimental work with the composition shown in Table 1.

Local Saudi silica sand and kaolin (Table 2) and chemically pure $BaCO_3$, Li_2CO_3, Cr_2O_3 and LiF were used as starting materials for batch preparation. The weighed batch materials, after thorough mixing were melted in Pt crucibles in an electrically heated globar furnace at temperatures ranging from 1300 to 1500 °C for 3.5–5 h depending upon the nucleant involved. The melts containing Cr_2O_3 were rather more viscous than those containing fluorides and therefore required (especially those containing the higher percentages of Cr_2O_3) higher temperatures and longer periods of melting. The homogeneity of the melt was achieved by swirling of the melt-containing crucible several times at about 20 min. intervals. After melting and refining, the bubble-free melt was cast onto a hot steel marver into buttons and rods. The hot glass samples were then transferred to a preheated electric muffle furnace for annealing.

2.2. Differential thermal analysis (DTA)

Scans were carried out using a PerkinElmer (7 series) micro-differential thermoanalyzer using 60 mg of powdered glass sample, of grain size less than 0.60 mm and greater than 0.2 mm, Al_2O_3 powder as a reference material. A heating rate of 20 °C/min and sensitivity setting of 8 μv/cm were maintained for all the DTA runs which were performed in an atmosphere of pure nitrogen, flowing at a rate of 30 ml/min.

2.3. Heat-treatment

The glass samples were heated in a muffle furnace from room temperature to the required temperature (which was from 800 to 1050 °C at 50 °C intervals) at the rate of heating 5 °C/min. and kept at the intended temperature for 1 h, after which the furnace was switched off and the samples were allowed to cool inside it to room temperature.

A double-stage heat-treatment schedule was used to study its effect on the microstructure. Glass samples were first soaked at 680 °C for 1 h and then at 950 °C for 1 h.

2.4. X-ray diffraction analysis

Identification of crystals precipitating in the course of crystallization was conducted by the X-ray diffraction analysis of the powdered samples. The X-ray diffraction patterns were obtained using a Philips type (BW 1710) adopting Ni-filtered Cu Kα radiation. All instrument settings were maintained for all the analyses using a Si disk as an external standard, this was necessary to make the measurements based on the peak height more accurate.

2.5. Microscopy

The mineralogical constitution and microstructure of almost all the heat treated specimens were examined optically in thin sections using a polarizing Carl Zeiss research microscope.

3. Results

3.1. Effect of lithium fluoride (LiF)

LiF was incorporated in the glass G3 in amounts of 0.5, 1.5 and 3 g per 100 g of glass oxide (Table 3). The addition of LiF to the glass batch reduced the melting temperature (by about 100–200 °C) and also the viscosity of the resultant melt, as compared with fluoride-free batches. The effect of

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

Raw material	Oxide (wt%)								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	CaO	Na_2O	K_2O	L.O.I.
Silica sand	99.50	0.52	0.04	–	<0.05	<0.05	<0.05	<0.05	–
Kaolinitic clay	42.90	36.00	1.10	2.80	0.20	0.63	0.99	0.09	15.10

Table 3
Nucleating agent additions per 100 g base glass

Nucleating agent	Additions (g)
LiF	0.5, 1.5, 3.0
Cr_2O_3	0.5, 1.0, 1.5

this LiF addition on the mineralogical constitution and microstructures of the resultant crystalline materials can be outlined as follows.

The presence of LiF was found to enhance the crystallizability of the glass. This is clear from the DTA curves (Fig. 1, curves b–d) where the exothermic crystallization peak was increased in intensity and shifted at the same time, towards lower temperature (Table 4, Fig. 1). It is noteworthy that this effect of LiF on the crystallizability is more pronounced in (G3 L) glass. The lowering of the main exothermic crystallization peak temperature was about 64 °C in sample G0.5 L, 145 °C in sample G1.5 L and 183 °C in sample G3 L

XRD patterns of (G0.5 L, G1.5 L and G3 L) glasses treated at 680 °C for 1 h then at 950 °C for 1 h are shown in Fig. 2.

The presence of LiF, even in small quantities, greatly affects both the crystalline phase composition and the microstructure of the formed ceramic materials.

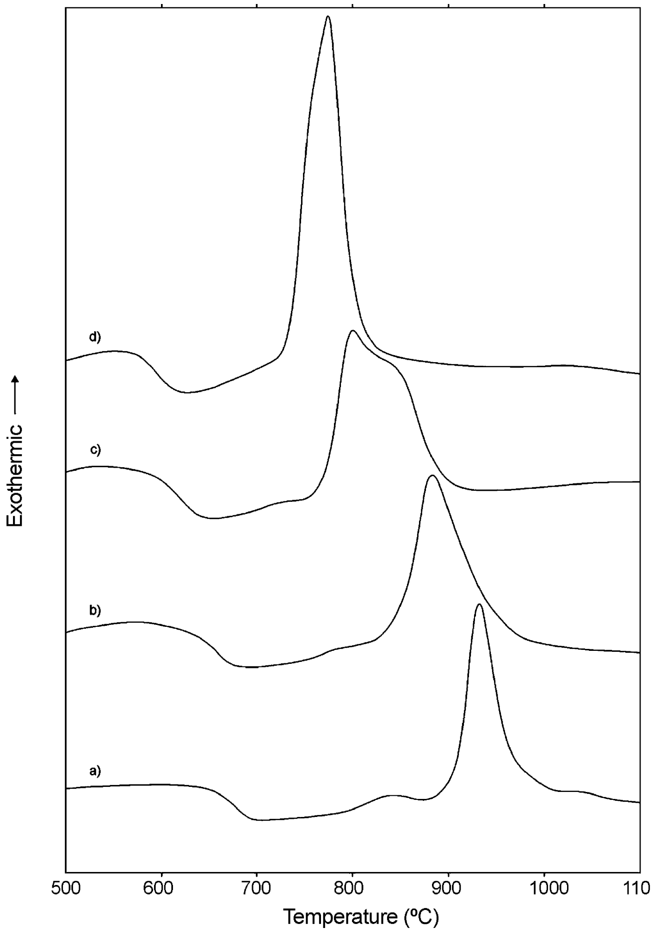

Fig. 1. DTA curves of G3 glasses: (a) without additives, (b) with 0.5% LiF, (c) with 1.5% LiF and (d) with 3.0% LiF.

Table 4
Summary of DTA results of glasses with and without additions of the nucleation catalysts LiF and Cr_2O_3

Glass no.*	Nucleator used (g/100 g glass)	Endothermic peak temperature (°C)	Exothermic peak temperature (°C)
G3	–	702	860,945
G0.5 L	0.5 LiF	683	881,897
G1.5 L	1.5 LiF	646	800,845
G3 L	3.0 LiF	624	762,775
G0.5 Cr	0.5 Cr_2O_3	705	866,913
G1.5 Cr	1.0 Cr_2O_3	712	925,935
G1.5 Cr	1.5 Cr_2O_3	718	974

*L = LiF and Cr = Cr_2O_3.

From the mineralogical point of view, the presence of LiF in G3 glass favored monoclinic celsian and β-spodumene ss formation and inhibited β-eucryptite ss and hexacelsian crystallization. The X-ray diffraction analysis (Fig. 2, pattern a, Table 5) indicated that the G3 glass (free of catalyst) yielded β-eucryptite ss and hexacelsian (at 680 °C for 1 h and then at 950 °C for 1 h). Meanwhile, for the LiF containing samples (0.5 L, 1.5 L and 3 L), yielded β-spodumene ss and monoclinic celsian when it was treated at the same conditions (Table 5, Fig. 2, patterns b–d). The formation of monoclinic celsian together with β-spodumene ss was only achieved after treatment at 1050 °C for 40 h in base glass (free of catalyst) [8]. Therefore, this small percentage (0.5 g) of LiF incorporated

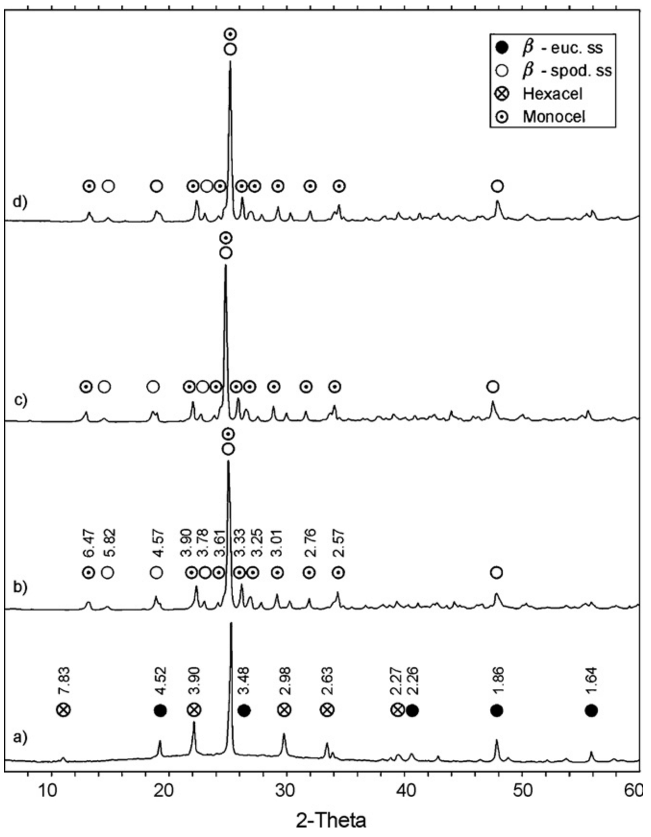

Fig. 2. X-ray diffraction patterns of G3 glasses heat-treated at 680 °C for 1 h and then at 950 °C for 1 h: (a) without additives, and (b) with 0.5% LiF, (c) with 1.5% LiF and (d) with 3.0% LiF.

Table 5
X-ray identification of the crystalline phases developed in the glasses containing Cr_2O_3 and LiF at selected heat-treatment temperatures

Glass no.	Heat-treatment parameters (°C, h)	Phases identified by X-ray
G3*	680 °C 1 h, 800 °C 1 h	β-Euc. ss + hexacel
	680 °C 1 h, 900 °C 1 h	β-Euc. ss + hexacel
G0.5 L	680 °C 1 h, 800 °C 1 h	β-Spod. ss + monocel.
	680 °C 1 h, 900 °C 1 h	β-Spod. ss + monocel
G1.5 L	680 °C 1 h, 800 °C 1 h	β-Spod. ss + monocel
	680 °C 1 h, 900 °C 1 h	β-Spod. ss + monocel
G3.0 L	680 °C 1 h, 800 °C 1 h	β-Spod. ss + monocel
	680 °C 1 h, 900 °C 1 h	β-Spod. ss + monocel
G0.5 Cr	680 °C 1 h, 950 °C 1 h	β-Spod. ss + hexacel + traces of monocel
G1.0 Cr	680 °C 1 h, 950 °C 1 h	β-Spod. ss + hexacel + monocel
G1.5 Cr	680 °C 1 h, 950 °C 1 h	β-Spod. ss + monocel + traces of hexacel

* G, base glass; L, LiF; Cr, Cr_2O_3; β-euc., β-eucryptite; β-spod., β-spodumene; ss, solid solution; hexacel., hexacelsian; monocel., monoclinic celsian.

in the glass proved to be greatly effective in catalyzing monoclinic celsian and β-spodumene ss even at the earliest stages of crystallization, and in lowering their crystallization temperature. Its addition affects the transformations of the metastable hexacelsian → stable monoclinic celsian and metastable β-eucryptite ss → stable β-spodumene ss. It could be seen from (Fig. 2), that the lowest amount of LiF used (0.5 g) showed a great enhancement effect on this process, also the higher amounts (1.5 and 3 g) showed the same effect. Therefore, the main exothermic peaks given by the DTA curves at 881, 800 and 775 °C for the glasses G0.5 L, G1.5 L and G3 L, respectively (Fig. 1) can be attributed to the co-crystallization of β-spodumene ss and monoclinic celsian

Microscopic examination of the double-stage heat-treatment glasses showed that the LiF additions are mostly effective on the nucleation process. These are translated by the high crystallizability of the glasses and the relatively coarser textures (Figs. 3 and 4).

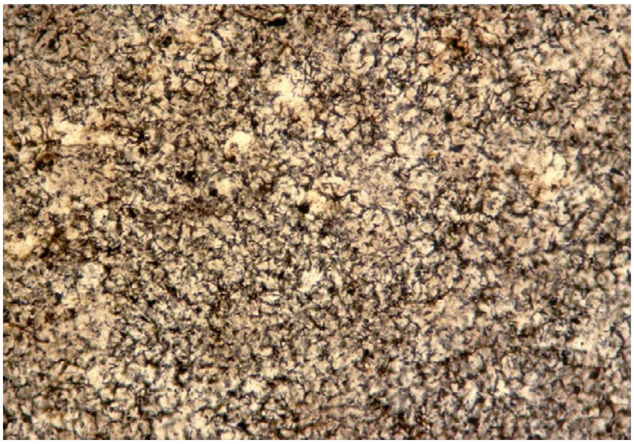

Fig. 3. G3 (680 °C, 1 h + 9500 °C, 1 h) Fine crystallization of β-eucryptite ss with hexacelsian, P.N. 400×.

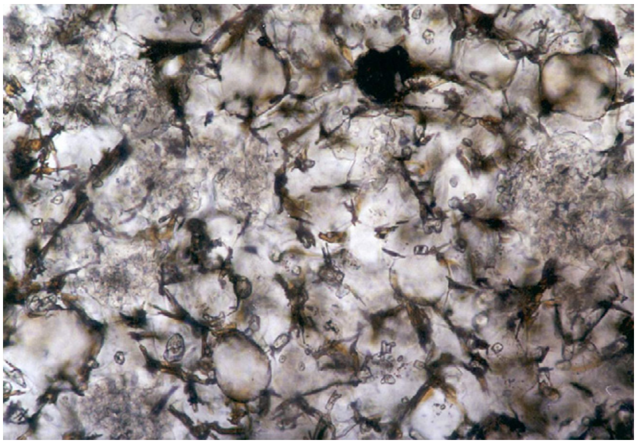

Fig. 4. Glass G0.5 L heat-treated at 680 °C, 1 h + 950 °C, 1 h Holocrystalline coarse-grained texture of rounded aggregates of β-spodumene ss with micro-litres of monoclinic celsian, P.N. 400×.

3.2. Effect of the chromium oxide (Cr_2O_3)

Chromium oxide was incorporated in the glass G3 in amounts of 0.5, 1.0 and 1.5 g per 100 g glass (Table 3). The incorporation of Cr_2O_3 in the base glass composition practically increased the viscosity of the resultant melts, as compared with that free of this oxide. The effect of these Cr_2O_3 additions on the crystallization behavior of the investigated glasses and on microstructure formed can be outlined in the following.

The presence of Cr_2O_3 slightly increases the temperature at which the glass transition occurs and also the endothermic peak temperature. This is clear from the DTA curves of the Cr_2O_3-nucleated glass compared with Cr_2O_3-free glass (Fig. 5 and Table 4).

The addition of Cr_2O_3 was found to decrease the crystallizability of the glass. This is clear on the DTA curves (Fig. 5) where the exothermic crystallization peak was decreased in intensity and slightly shifted at the same time, towards higher temperature (Table 4). It is noteworthy that this effect of Cr_2O_3 on the crystallizability is more pronounced in glass (G1.5 Cr). XRD patterns of glasses (G0.5 Cr, G1 Cr and G1.5 Cr) treated at 680 °C for 1 h then at 950 °C for 1 h, are shown in Fig. 6.

From the mineralogical point of view the presence of Cr_2O_3 in glass G3 favors the β-spodumene ss and monoclinic celsian formation and inhibits β-eucryptite ss and hexacelsian crystallization. The X-ray diffraction analysis (Fig. 6, pattern a and Table 5) indicated that the glass G3 (free of catalyst) yielded β-eucryptite ss and hexacelsian after treated at 680 °C for 1 h and then at 950 °C for 1 h. Meanwhile, for the Cr_2O_3-containing glasses G0.5 Cr and G1 Cr (Fig. 6, patterns b and c, Table 5) β-spodumene ss was formed and monoclinic celsian appeared after treatment at the same conditions. For glass with high concentration of Cr_2O_3 (G1.5 Cr), monoclinic celsian and β-spodumene ss were developed after treatment at 680 °C for 1 h and then at 950 °C for 1 h (Fig. 6, pattern d and Table 5). Glass G3 (free of catalyst), yielded hexacelsian and β-eucryptite ss plus a small amount of residual glass

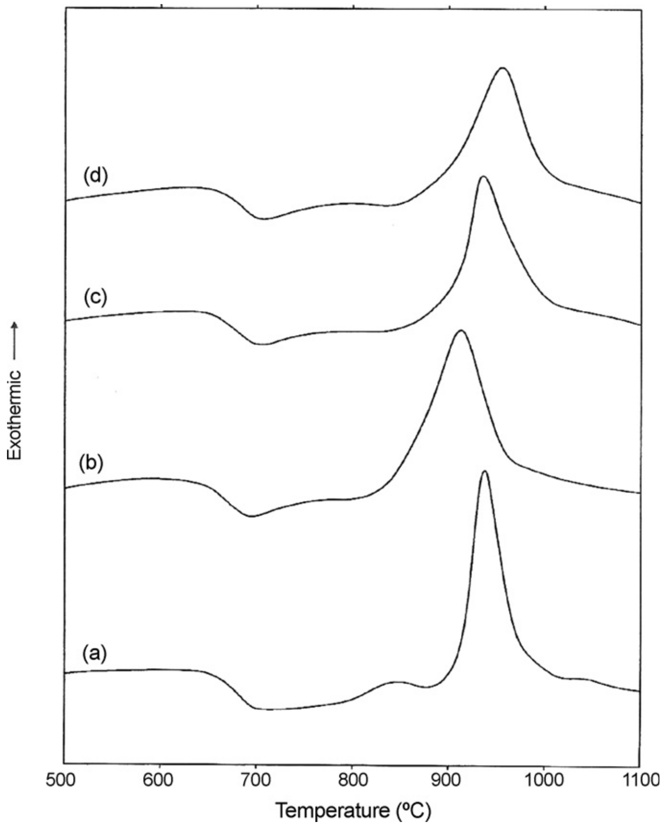

Fig. 5. DTA curves of G3 glasses: (a) without additives, (b) with 0.5% Cr_2O_3, (c) with 1.0% Cr_2O_3 and (d) with 1.5% Cr_2O_3.

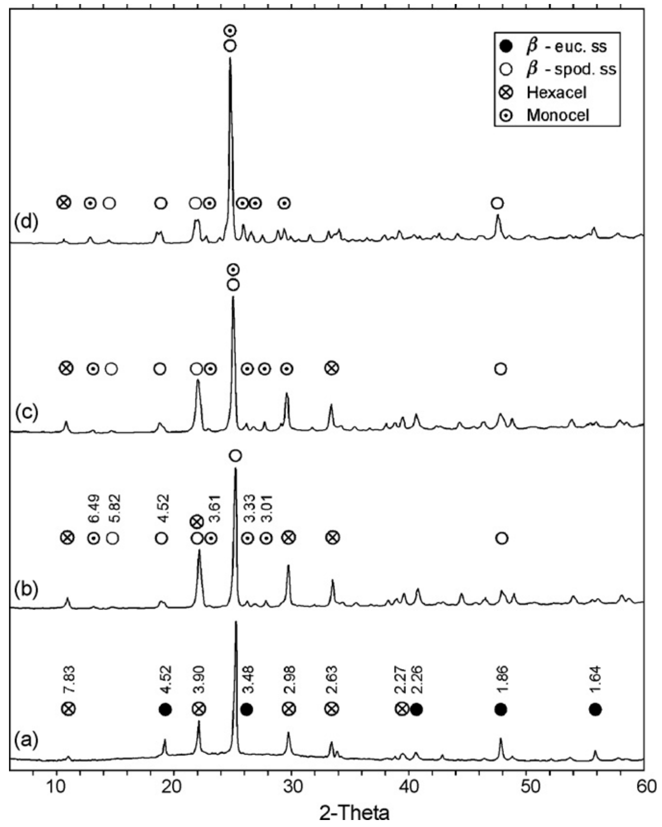

Fig. 6. X-ray diffraction patterns of G3 glasses heat-treated at 680 °C, 1 h and then 950 °C, 1 h: (a) without additives, (b) with 0.5% Cr_2O_3, (c) with 1.0% Cr_2O_3 and (d) with 1.5% Cr_2O_3.

when it was treated at 680 °C for 1 h and then at 950 °C for 1 h (Fig. 6, pattern a). The formation of β-spodumene ss and monoclinic celsian was only achieved after treatment at 1050 °C for 40 h (free of catalyst) [8]. Therefore, this percent 1.5% of Cr_2O_3 incorporated in glass proved to be greatly effective in catalyzing β-spodumene ss and monoclinic celsian.

The presence of (1.5 g) Cr_2O_3 reduced the time of formation of β-spodumene ss and monoclinic celsian from 40 h at 1050 °C to 1 h at 680 °C followed by 1 h at 950 °C. The addition of Cr_2O_3 affects the transformations of metastable β-eucryptite ss → stable β-spodumene ss. It can be seen from (Fig. 6) that the highest amount (1.5 g) Cr_2O_3 enhances on this process, but not the lower amounts, i.e. 1.0 or 0.5 g.

From the micro-structural point of view, microscopic examination revealed that Cr_2O_3 induces a great number of crystallization centers which lead to fine-grained microstructures (Figs. 7 and 8). Therefore, glass G3 (free of catalyst) develops relatively non-uniform coarse grained texture when it was treated at same conditions (Fig. 3). Meanwhile, glass with 0.5 Cr_2O_3 yielded uniform volume crystallization of tiny aggregates of β-eucryptite ss and hexacelsian ss. Glass with 1.5 Cr_2O_3 shows uniform volume crystallization of tiny aggregates of β-spodumene ss and monoclinic celsian when it was treated under the same conditions (Fig. 8).

4. Discussion

4.1. Role of lithium fluoride (LiF)

The effect of fluoride additions on the crystallization behavior and the textures formed can be outlined as follows.

Fluoride may act as network breaker in the glassy anionic structure. The bridging oxygen can be replaced by fluoride ions due to their radius similarity without causing too great

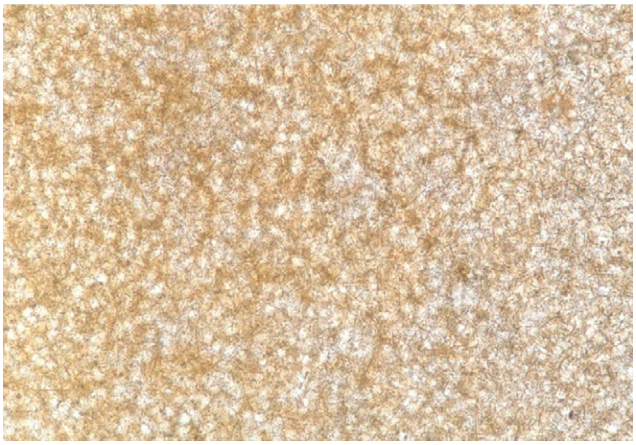

Fig. 7. Glass G0.5 Cr heat-treated at 680 °C, 1 h and then 950 °C, 1 h. Very fine crystallization of β-spodumene ss with hexacelsian and monoclinic celsian, P.N. 400×.

Fig. 8. Glass G1.5 Cr heat-treated at 680 °C, 1 h and then 950 °C, 1 h. Uniform very fine-grained texture, P.N. 400×.

disturbance in the arrangement of the other ions. Consequently, the replacement of the strong ≡Si–O–Si≡ linkage by a pair of the weak ≡Si–F can result in the weakening of the glass network structure. This can be reflected in facilitating the melting process of the fluoride-containing charges as well as in decreasing the viscosity of the resultant melts and glasses. As a result of the decrease of viscosity the diffusion of the different ions and ionic complexes of the glasses during the crystallization process will be markedly increased.

Fluoride are also known to be immiscible in silicate melts, specially at lower temperatures, leading to two phase glass-in-glass separation; comprising numerous droplets of one glass dispersed in another. The formation of such phase separation decreases the energy barriers necessary for crystallization. In this respect, the phase separation alone is not sufficient to induce volume (internal) crystallization in the glass and cases are known where glasses having a tendency for phase separation, exhibit opalescence during the heat-treatment, and do not show volume crystallization [17].

The above mentioned positive effect of LiF on the mineral constitution of the crystallizing glasses can be attributed to their great influence in lowering the viscosity of the melts and glasses as discussed before. This may result in subsequent ease of migration and diffusion of ions and ionic complexes present to such an extent that the crystallization of the structurally more complex silicates and/or some structural transformations such as hexagonal → monoclinic celsian can take place. The presence of a relatively small amount of lithium fluoride has been shown to markedly induce the transformation of the hexagonal phase or to enhance largely crystallization of the barium feldspars (celsian). The structure of the hexagonal phase requires the presence of a divalent ion, although has nearly the same size as the barium ion, would have a tendency to weaken the structure when present between the Si and Al sheets of the barium hexagonal phase [18,19].

4.2. Role of chromium oxide (Cr_2O_3)

In some silicate melts, Cr_2O_3 may be completely miscible at high temperatures, whereas at lower temperatures, it rapidly separates out in the form of chromium-containing minute crystalline phases or as chromium-rich amorphous colloidal droplets (glass-in-glass phase separation) which act as sites for the subsequent crystallization of the major phases. The great affinity of Cr_2O_3 to combine with other cations such as Mg^{2+}, Fe^{2+}, Fe^{3+}, and Al^{3+} helps the formation of minute spinel-like phase, which can readily crystallize out, and act as crystallization centers or nuclei for the main crystallizing phases.

Cr_2O_3 is only slightly soluble in certain glasses in the CaO–MgO–Al_2O_3–SiO_2 system. At 1500 °C approximately 0.6 wt% of Cr_2O_3 dissolved in the melt. Cr_2O_3 has been found to decrease the crystal growth rates [20]. When Cr_2O_3 is greater than 0.3 wt% in such a system with MgO content greater than 6 wt% yields bulk crystallization.

The presence of 1–3% of chromic oxide was successfully used to catalyze the crystallization of an aluminosilicate glass containing lithia, potash and calcium oxide by inducing two-phase separation in the glasses followed by crystallization of other phases [21].

Glass ceramic from a glass made by melting oil shale found that the parent glass exhibited only surface crystallization. By the addition of about 1% chromic oxide, however they were able to produce a material that was approximately 90% crystalline with an average grain size less than 10 μm. In this case the nuclei formed were found to be a mixed spinel type of crystals of the general formula (Mg, Fe)(Al, Fe, $Cr)_2O_4$ [22].

The great tendency for pyroxene formation over the other crystallizing phases in Cr_2O_3-containing glasses is most probably due, on one hand, to the great decrease of the activation energy of pyroxene crystallization. The activation energy of synthetic chromaugites, containing small amounts of Cr_2O_3, was decreased to the order of 2.1 kcal/mole which is greatly lowers than the mean value of the ordinary augites in general (6 kcal/mole). On the other hand, the pyroxene formation may be favored by the high degree of registry between their lattice parameters with those of Cr_2O_3 and/or chromo-spinels [23]. Spinellides (Mg, Fe)(Al, Fe, $Cr)O_4$ were the early-formed catalyst phase, which acted as crystallization nuclei mainly for the pyroxene phase during the crystallization of glasses based on calcareous clay [24].

The addition of 0.5–1.5 wt% of Cr_2O_3 in the BaO–CaO–MgO–Al_2O_3–SiO_2 system yielded volume crystallization of hexacelsian and diopside ss resulting in a uniform ultra fine-grained textures [11]. The low concentration (0.5 wt% Cr_2O_3) caused the formation of great number of crystallization centers that induce volume crystallization and formation of fine-grained microstructures [18]. The role of Cr_2O_3, LiF and their mixtures on crystalline phase formation and microstructure in Ba, Ca and Mg aluminosilicate glass found Cr_2O_3 alone is much better than LiF in promoting homogenous nucleation and growth of extremely fine-grained microstructures [11] Consequently, in the presence of Cr_2O_3, even in such small amounts used in the glass, pyroxenes (lithium aluminium silicate) having much lower values of activation energies can be greatly stimulated and in the same time are preferentially formed than plagioclases (barium aluminium silicate) which posses much higher values of activation energy (8–13 kcal/mole).

Also Cr_2O_3 may increase the extent of the isomorphous substitution of the silica molecules, SiO_2, into the structure leading to an enhancement effect of β-eucryptite ss and/or β-spodumene ss formation on the expense of basic components of the celsian.

Some of the silica left from β-spodumene ss formation may probably enter in solid solution with hexacelsian. This incorporated silica may be responsible for the sluggishness of the transformation of hexacelsian into monoclinic celsian.

The present results agree with those in the literature concerning the nature of crystallization and the type of barium aluminosilicate phases. The solubility of silica in the hexagonal form of celsian (hexacelsian) amounts to about 4%, whereas, in the monoclinic form (celsian) it does not exceed 2%. They also confirm that, when hexacelsian contains silica in solid solution its transformation into monoclinic celsian becomes more sluggish [25].

5. Conclusions

It is concluded that the characteristics of glass ceramics depend, to a great extent, on the type and amount of the nucleant used.

The presence of LiF favors the monoclinic celsian and β-spodumene ss and hexacelsian crystallization and leads to the formation of non-uniform coarse grained microstructures. While Cr_2O_3, even in small concentrations induces the formation of very fine-grained microstructures and favors the formation of β-spodumene ss and monoclinic celsian.

Acknowledgement

The authors are greatly indebted to H.E. Dr. Zohair A.Nawab, President of Saudi Geological Survey, for his valuable support, encouragement and the facilities provided.

References

[1] S.D. Stookey, Ind. Eng. Chem. 51 (1959) 805.
[2] P.W. McMillan, Glass-Ceramics, second ed., Academic Press, London, England, 1979.
[3] G.H. Beall, L.L. Freiman, Am. Ceram. Soc., Special pub. 5 (1971) 251 (Special pub.).
[4] G.A. Khater, M.H. Idris, Ceram. Int. 33 (2007) 233.
[5] M.M. Morsi, G.A. Khater, K.J. Range, Glass Technol. 42 (2001) 160.
[6] G.A. Khater, M.H. Idriss, Glass Sci. Technol. 78 (2005) 189.
[7] G.A. Khater, Preparation and study of glass-ceramics containing celsian, Ph.D. Thesis, Ain Shams University, Cairo, Egypt, 1990.
[8] M.H. Idris, The use of some Saudi sands for the production of glass-ceramic materials, Ph.D. Thesis, Cairo University, Cairo, Egypt 2002.
[9] G.A. Khater, M.H. Idris, Ind. Ceram. 24 (2004) 43.
[10] M.H. Idris, G.A. Khater, Phys. Chem. Glasses 45 (2004) 141.
[11] A.W.A. El-Shennawi, A.A. Omar, G.A. Khater, Glass Technol. 32 (1991) 131.
[12] R. Müller, E.D. Zanotto, V.M. Fokin, J. Non-Cryst. Solids 274 (2000) 208.
[13] E.G. Rawlands, P.F. James, Phys. Chem. Glasses 20 (1) (1979) 1.
[14] P.F. James, J. Non-Cryst. Solids 73 (1985) 517.
[15] E.D. Zanotto, P.F. James, J. Non-Cryst. Solids 74 (1985) 373.
[16] M.C. Weinberg, E.D. Zanotto, J. Non-Cryst. Solids 108 (1989) 99.
[17] V.S. Nikandrov, The structure of glass, 3, Consultant Bureau, New York, 1964, pp. 188.
[18] G.A. Khater, M.M. Morsi, K.J. Range, Glastech. Ber. Glass Sci. Technol. 74 (7) (2001) 192.
[19] C.A. Sorrell, Am. Mineral. 47 (1962) 291.
[20] B. Keyworth, P.S. Rogers, Proc. 10th Conf. On Silicate Industry, Budapest, (1962), p. 260.
[21] I. Sawai, Glass technology in Japan, Glass. Technol. 2 (1961) 243.
[22] L.J. Shelestak, R.A. Chavez, J.D. Mackenzie, B.S. Dunn, J. Non-Cryst. Solids V 27 (1) (1978) 83.
[23] A.A. Omar, Influence of isomorphous substitutions in pyroxene on the crystallization of synthetic basaltic melts. Ph.D. Thesis, Moscow State University, 1965.
[24] L.A. Zhunina, V.N. Sharai, V.F. Tsitko, N.N. Khripkova, The Structure of Glass, 3, Consultant Bureau, New York, 1964, pp. 192.
[25] J.S.M. Corral, Y.A.G. Verduch, Trans. J. Br. Ceram. Soc. 77 (1978) 40.