Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 37 (2011) 2193–2199

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Influence of Cr_2O_3, LiF, CaF_2 and TiO_2 nucleants on the crystallization behavior and microstructure of glass-ceramics based on blast-furnace slag

G.A. Khater [*]

National Research Center, Glass Research Department, Dokki, Cairo 12622, Egypt

Received 5 January 2011; received in revised form 2 March 2011; accepted 3 March 2011
Available online 9 March 2011

Abstract

Glass-ceramics based on blast-furnace slag (56.78 wt%) were prepared by mixing quartz sand, dolomite, limestone, clay as other batch constituents.

The nucleating agents Cr_2O_3, LiF, CaF_2 and TiO_2 were added to the batches to study their effects on the crystallization, phase assemblages, and microstructure. Glass-ceramics were obtained by single and double heat-treatment schedules and examined by DTA, XRD and polarizing microscope. The presence of Cr_2O_3, TiO_2, CaF_2 and LiF was found to enhance the crystallizability of the glass. Cr_2O_3 and TiO_2 are much better than LiF and CaF_2 in promoting homogeneous nucleation and the formation of extremely fine-grained microstructure of aluminous pyroxene and magnetite.

Keywords: Crystallization; Diopside; Anorthite; Fayalite; Glass-ceramics; Slag

1. Introduction

Glass-ceramics has been developed since the early 1960s, in Russia using waste materials, by employing slag of ferrous and non-ferrous metallurgy, ashes and wastes from mining and chemical industries [1]. Lately, the waste of coal combustion ash, fly ash and filter dusts from waste incinerators, mud from metal hydrometallurgy, by-pass cement dust, different types of sludge and glass cullet or mixtures of them have been considered for the production of glass-ceramics [2–4]. Using waste to prepare glass-ceramics is significant for industrial applications as well as for environmental protection and scientific importance with proper correction of the chemical composition [5,6].

Blast-furnace slag is formed in the processes of pig iron manufactured from iron ore, coke, fluxes of limestone and other materials. If the molten slag was cooled quickly by high-pressure water, fine grains glass of vitreous Ca–Al–Mg silicate can be formed [7]. This suggests that, blast-furnace slag can be used as a source to make glass-ceramics. Because glass and glass ceramics are known to have many commercial applications, the transformation of waste into glass or glass-ceramics provides the opportunity for making useful marketable products. The use of waste materials such as silicon–manganese slag, steel slag, blast – furnace slag and by-pass cement dust for the production of glass-ceramic materials is of great economic, technological and scientific importance with proper correction of the chemical composition.

Research and development investigations pertaining to glass-ceramic materials have been underway for more than three decades [8]. The fabrication technology of glass-ceramics, the glass composition, the nature of the nucleating agent and the thermal history, all greatly affect the microstructure and properties of these materials [9]. The internal crystallization can usually be achieved with a simple two-step heat treatment. In the first step, namely the nucleation step, the mobility of atoms in the glass is sufficient for embryo formation and subsequent nuclei stabilization. In the second step, the nuclei grow to crystals of desired sizes homogenously dispersed in the glass volume [10]. It is obvious that internal crystallization will be greatly facilitated by using suitable nucleating agents. Some investigations carried out in the field of nucleation in the ternary SiO_2–MgO–CaO and related

---

[*] Corresponding author at: P.O.Box 3893, Riyadh 11481, Saudi Arabia. Tel.: +966 505486245; fax: +966 14627569.
E-mail address: gamal.kh@saudiceramics.com.

0272-8842/$36.00 © 2011 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2011.03.011

systems have shown the relative difficulty of initiating internal nucleation and bulk crystallization in some glass-ceramic compositions of this system [11].

The composition of such glass-ceramics can mainly be located in the SiO_2–Al_2O_3–CaO–MgO system. Many investigators have studied the nucleation process in the SiO_2–Al_2O_3–CaO–MgO and related glass systems. Cr_2O_3 is one of the most recommended oxides which is able to induce effective bulk nucleation in the glasses of SiO_2–Al_2O_3–CaO–MgO and related systems. Rezvani et al. [12] found that Cr_2O_3, Fe_2O_3 and TiO_2 were more effective in inducing bulk crystallization. Omar et al. [13] suggested that, Cr_2O_3 favors pyroxene crystallization in quartz sand-dolomite–magnesite mixtures. Khater and Hamzawy [14] found that Cr_2O_3, CaF_2 and TiO_2 were more effective in SiO_2–Al_2O_3–CaO–MgO system based on industrial waste.

In previous paper [2], the use of Saudi slag for the production of glass-ceramic materials was investigated. The aim of the present study is to prepare glass-ceramics based on waste material (blast–furnace slag) and to investigate the effects of different additions of the nucleating agents Cr_2O_3, LiF, CaF_2 and TiO_2 on the crystallizability, phase assemblages and microstructure.

2. Experimental procedure

2.1. Glass composition and batch preparation

The compositions of the base glass and the added nucleating agents are listed in Tables 1 and 2, respectively. Quartz sand, dolomite, limestone, clay and blast -furnace slag from Hadeed Company, Saudi Arabia, were used as starting materials for the preparation of the glass-ceramics to be investigated. 56.78 wt% of the blast-furnace slag was used in the batches of the glasses. The weighed batch materials were thorough mixed and melted in Pt crucibles in an electrically heated globar furnace at temperatures ranging from 1400 °C to 1500 °C for 2 to 2.5 h depending upon the nucleating agent added. It was noticed that, melts containing Cr_2O_3 were rather more viscous than those containing CaF_2 and LiF, therefore, higher temperatures and longer periods of melting was required. The homogeneity of the melts was achieved by swirling of the melt-containing crucible several times at about 20 min intervals. After melting and refining, the bubble-free melt were cast into a hot steel marver in the forms of buttons and rods, and then transferred to a preheated electric muffle furnace which is switched off to cool to room temperature.

2.2. Differential thermal analysis (DTA)

Scans were carried out using a Shimadzu DTG60 micro differential thermo analyzer 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 was used. A heating rate of 10 K/min was maintained for all the runs.

Table 2
Nucleating agent added/100 g glass.

Glass no.	Nucleating agent	Addition g/100 g glass
G30[a]	–	–
G30Cr	Cr_2O_3	0.5
G30T	TiO_2	2
G30Ca	CaF_2	2
G30L	LiF	2

[a] G30 = base glass.

2.3. Heat-treatment

In single-stage heat-treatment schedule glass samples were heated in a muffle furnace from room temperature to the required temperature and kept at the intended temperature for 2 h, after which the furnace was switched off and the samples were allowed to cool inside it to room temperature. In the double-stage heat-treatment schedule, glass samples were first soaked at 650 °C for 1 h and then at 850 °C and/or 1000 °C for 2 h.

2.4. X-ray diffraction analysis

Crystalline phase identification for the powdered glass-ceramic samples was conducted by the X-ray diffraction analysis using a Bruker D8 Advance, Germany adopting Ni-filtered CuKα radiation.

2.5. Microscopic investigation

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

3. Result

Fig. 1 shows differential thermal analysis curves of various compositions. From this figure it can be noticed that, the nucleation temperature occurs in the range 628–663 °C, while crystallization occurs in temperatures range between 742 and 882 °C. Table 3 lists the phases formed as identified by X-ray diffraction.

3.1. Effect of Cr_2O_3

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

Table 1
Composition of base glass G30.

Calculated oxides constituents (wt%)					Raw materials (wt%)				
FeO	CaO	MgO	Al_2O_3	SiO_2	Slag	Quartz sand	Clay	Dolomite	Limestone
21.17	16.45	7.52	10.79	44.07	56.78	24.92	14.66	1.20	2.43

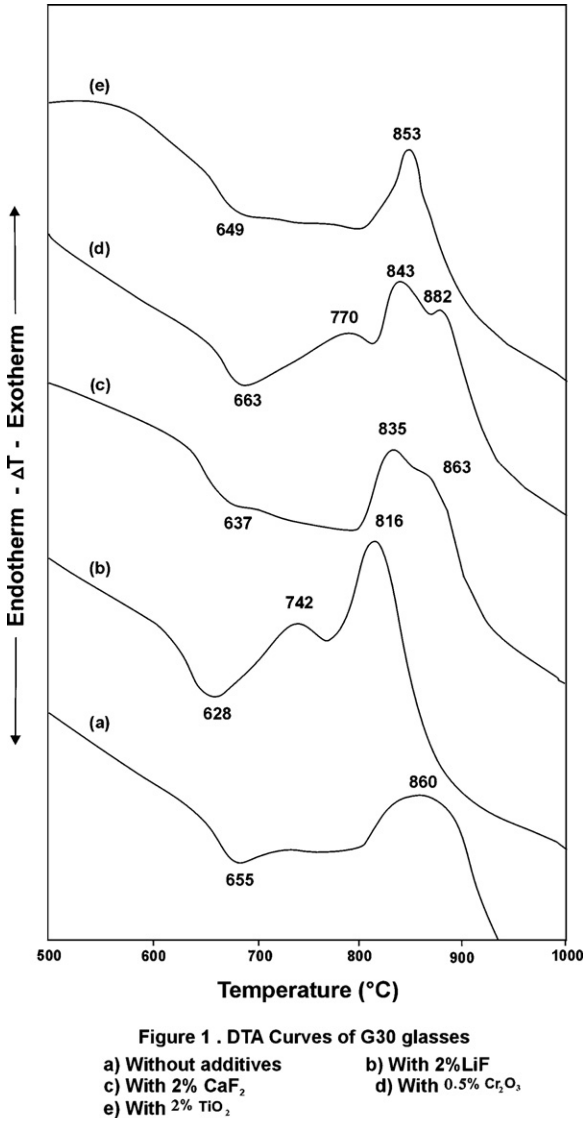

Fig. 1. DTA Curves of G30 glass.

Table 3
X-ray identification of the crystalline phases developed in the glasses containing different nucleating agents at selected heat-treatment temperatures.

Glass no.	Heat-treatment parameters (°C, h)	[a]Phases identified by X-ray
G30	850°C, 2 h	Diop.ss. + Mag.
	1000°C, 2 h	Diop. + Anor. + Fay.
G30Cr	850°C, 2 h	Diop.ss. + Mag.
	1000°C, 2 h	Diop. + Anor. + Fay.
G30T	850°C, 2 h	Diop.ss. + Mag.
	1000°C, 2 h	Diop. + Anor. + Fay.
G30Ca	850°C, 2 h	Diop.ss. + Mag.
	G30Cr	Diop. + Anor. + Fay.
G30L	850°C, 2 h	Diop.ss. + Mag.
	G30Cr	Diop. + Anor. + Fay.

[a] Diop.ss. = diopside solid solution, Mag = magnetite, Anor = anorthite, Fay = faylite, Diop = diopside.

(a) The addition of 0.5% Cr_2O_3 to the base glass G30 tends to shift Tg, glass transition temperature, towards higher values (Fig. 1). Comparing the base glass G30 (Fig. 1, curve a) with glass containing 0.5% Cr_2O_3 (Fig. 1, curve d) it can be noticed that, the Tg value shifts from 655 °C to 663 °C, respectively.

(b) The presence of Cr_2O_3 helps to generate three exothermic crystallization peaks, as revealed from the DTA curves of the base glass G30 and glass G30Cr are compared. Fig. 1 shows that the exothermic peak occurs at 860 °C for the base glass G30 (Fig. 1, curve a), whereas in the corresponding chromium–oxide nucleated glass G30Cr (Fig. 1, curve d) exothermic peaks occur at 770, 843 and 882 °C.

(c) Mineralogically, the presence of Cr_2O_3 in glass G30 generally increases the formation of diopside solid solution and magnetite (Table 3). X-ray diffraction analysis of the crystallized glasses (Fig. 2, curve a) indicates that glass G30 (free of catalyst) developed diopside solid solution and magnetite after heat-treatment at 850 °C for 2 h. Meanwhile, for Cr_2O_3 – containing glass G30Cr (Fig. 2, curve b) heat-treatment under the same conditions, caused the intensities and explicitly of both diopside solid solution lines (e.g. lines 3, 23, 3.01, 2.57 and 2.54 nm) and magnetite lines (e.g. 2.95, 2.54 and 1.48 nm) to increase. After treatment at a higher temperature at 1000 °C for 2 h (Fig. 3, curves a and b) the picture of the X-ray patterns became more explicit and nearly approaching the nominal phase condition. It can be said that heat heat-treatment at 1000 °C for 2 h leads to crystallization of diopside, anorthite and fayalite. Table 3 gives a summary of the crystalline phases developed after the various heat treatment conditions as identified by XRD.

(d) From the microstructures point of view, the results (Figs. 4 and 5) show that $Cr_2O_{3,}$ effectively stimulated the formation of a very large uniform bulk crystallization of extremely fine-grained microstructures. For the same crystallization conditions glasses G30 (free of catalyst) showed a non-uniform coarse grained texture (Fig. 4) while the glass containing Cr_2O_3 glass G30Cr, exhibit uniform fine-grained microstructures (Fig. 5) is formed.

3.2. *Effect of lithium fluoride (LiF)*

Lithium fluoride was used in amount of 2 g per 100 g glass. It facilitates the melting process by decreasing viscosity as revealed by the shift of Tg from 655 °C (G30, Fig. 1, curve a) to 628 °C (Fig. 1, curve b) and the decrease of the temperature of beginning of crystallization of the glasses. The effect of LiF on the crystallization behavior and microstructure of the investigated glasses can be summarized as follows: °C

(a) The presence of LiF in the glass greatly facilitates diopside solid solution phase and magnetite when heat-treated at 850 °C/2 h (Fig. 2 curve d). After heat-treatment at higher temperature 1000 °C/2 h, diopside solid solution transforms into diopside, magnetite transforms into fayalite in addition to formation of anorthite (Fig. 3 curve d).

Table 3 lists a summary of the crystalline phases developed after the various heat-treatment conditions as identified by XRD.

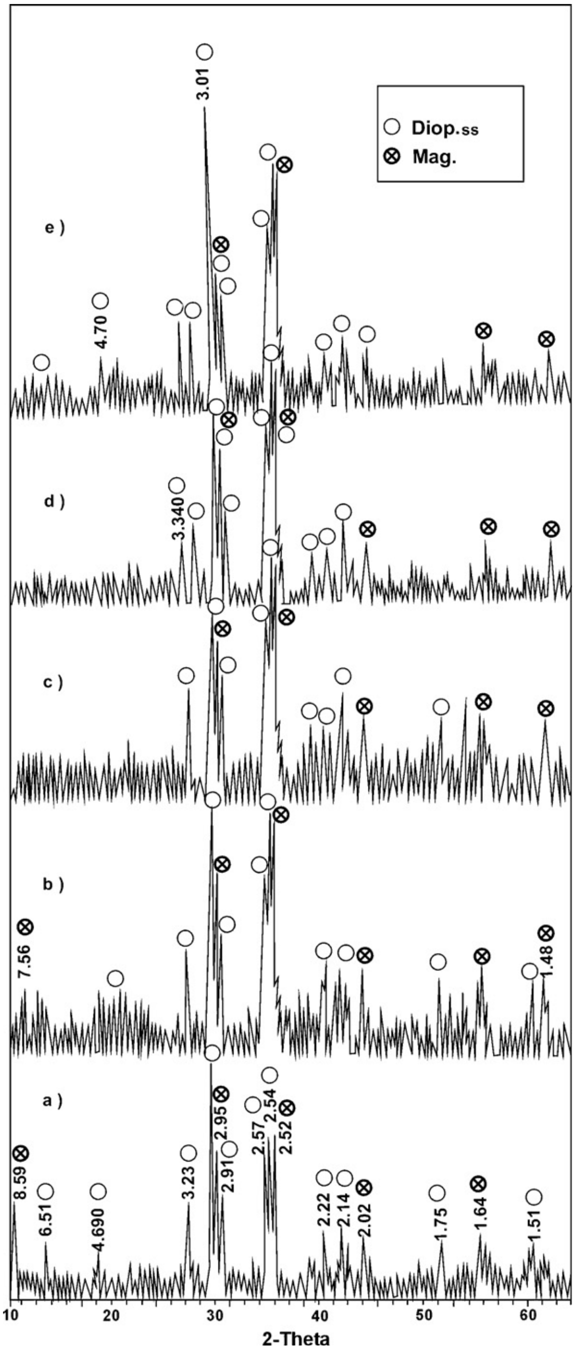

Fig. 2. X-ray diffraction patterns of G30 glass heat-treated at 850°C for 2 h.

(b) Microscopic examination of the double-stage heat–treatment showed that glass with LiF addition is mostly effective on the nucleation process. As indicated by the high crystallizability of the glass and the relatively coarser texture (Fig. 6).

3.3. *Effect of calcium fluoride (CaF_2)*

Calcium fluoride was used in amount of 2 g per 100 g glass. It facilitates the melting process by decreasing viscosity as revealed from the shift of Tg from 655 °C (G30, Fig. 1, curve a) to 637 °C (Fig. 1, curve c) and the decrease of the temperature of beginning of crystallization of the glasses.

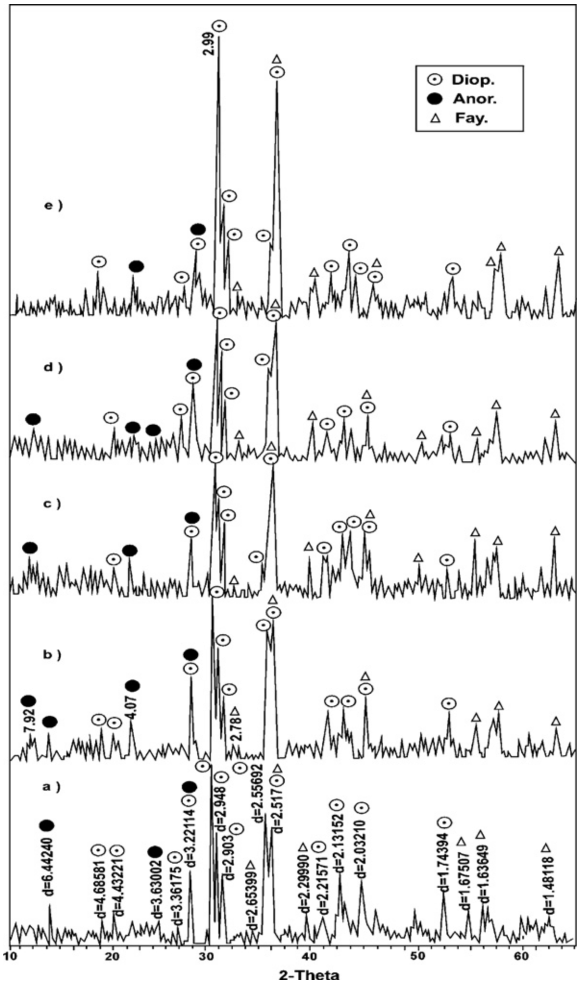

Fig. 3. X-ray diffraction patterns of G30 glass heat-treated at 1000°C for 2 h.

The effect of CaF_2 additions on the crystallization behavior and the textures formed can be outlined as follows:

(a) The presence of CaF_2 in the glass greatly facilitated diopside solid solution as the major crystalline phase and magnetite at lower temperature 850 °C/2 h (Fig. 2 curve e).

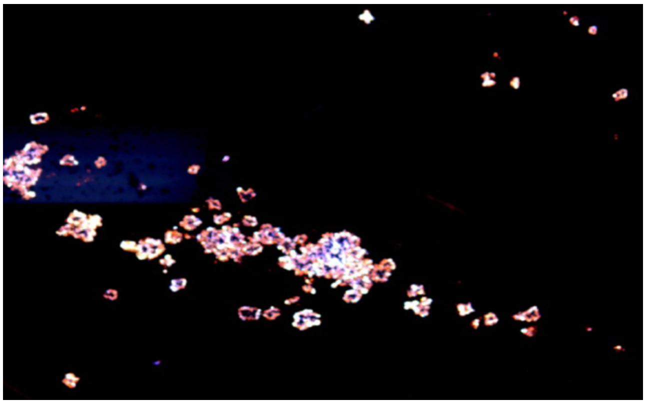

Fig. 4. Photomicrograph of glass G30 at 650 °C, 1 h +850 °C, 2 h.

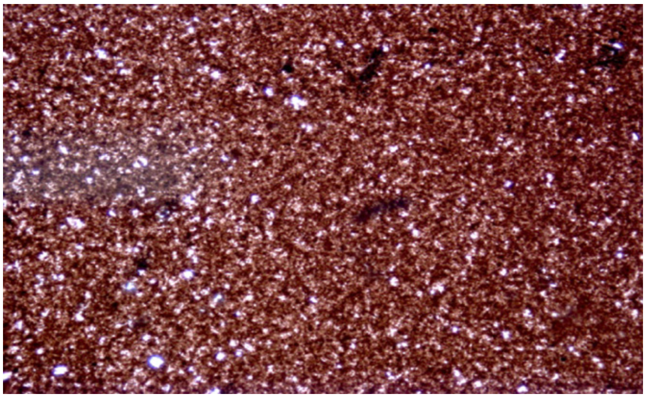

Fig. 5. Photomicrograph of glass G30Cr at 650 °C, 1 h +850 °C, 2 h.

After heat-treatment at higher temperature 1000 °C/2 h, diopside solid solution transformed into diopside, magnetite transformed into fayalite in addition to anorthite formation (Fig. 3 curve e).

Table 3 gives a summary of the crystalline phases developed after the various heat-treatment conditions as identified by XRD.

(b) Microscopic examination of the double-stage heat–treatment glass showed that the CaF_2 addition has a little effect on the texture and led to relatively coarser texture.

3.4. Effect of titanium dioxide (TiO_2)

From DTA studies (Fig. 1) the addition of titanium dioxide to the base glass G30 tends to shift Tg towards lower values. Comparing base glass G30 (Fig. 1, curve a) with glass containing TiO_2 (Fig. 1, curve e) shows that, the Tg of these glasses are recorded at 655 °C and 649 °C, respectively.

The effect of titanium dioxide additions may be summarized as follows:

(a) The addition of 2% TiO_2 to the glass batch G30 improves the melting of the batch and crystallizability of the glass.

(b) The presence of TiO_2 in the glass stabilizes both the aluminous pyroxene and magnetite when heat – treated at 850 °C for 2 h. (Fig. 2, curve c). While heat – treatment at higher temperature 1000 °C for 2 h (Fig. 3, curve c) aluminous pyroxene transforms into diopside, also magnetite transforms into fayalite in addition to anorthite formation.

The presence of TiO_2 in the glass greatly enhances volume crystallization with the formation of uniform fine-grained microstructure.

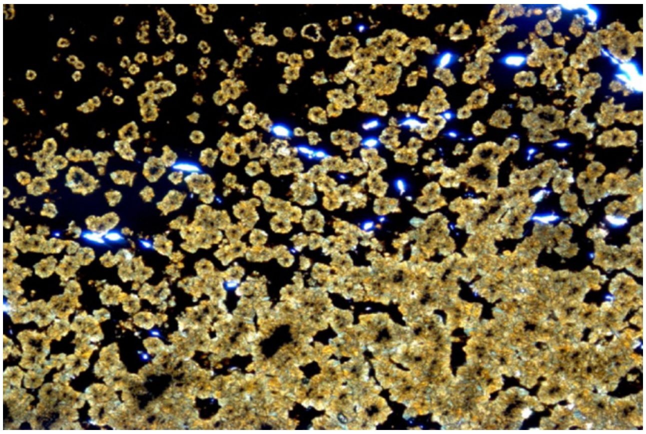

Fig. 6. Photomicrograph of glass G30L at 650 °C, 1 h +850 °C, 2 h.

4. Discussion

4.1. Role of chromium oxide (Cr_2O_3)

The beneficial effect of Cr_2O_3 additions is the formation of fine-grained bulk crystallization as well as the preferential formation of diopside solid solution and magnetite. This may be due to one or more of the following reasons. It is well known that in some super cooled silicate melts and glasses, Cr_2O_3 may be completely miscible at high temperatures but rapidly separates out at lower temperatures, either in the form of Cr-containing minute crystalline phases [15] or as Cr-rich amorphous colloidal droplets [16,17] which act as sites for the subsequent crystallization of the major phases. According to McMillan [16], chromium can exist in the glass as an interstitial cation of high field strength having trivalent and hexavalent states. The Cr^{3+}/Cr^{6+} ratio depends upon the melting conditions and the glass composition and may increase by increasing the melting temperatures and soaking times. Chromium in the hexavalent state (Cr^{6+}) has higher field strength and hence it would occupy an interstitial position, exerting a marked ordering effect upon the oxygen ions surrounding it. Under these circumstances an amorphous chromium-rich phase separates out from the glass.

Sawai [17] reported that 1–3% of chromic oxide was successfully used to catalyze the crystallization glass containing Lithia, potash and calcium oxide by inducing two-phase separation in the glasses followed by crystallization of other phases. Keyworth [18] has studied the effect of addition of Cr_2O_3 on both nucleation and crystal growth rates. He found that Cr_2O_3 is only slightly soluble in certain glasses in the SiO_2–Al_2O_3–CaO–MgO system. At 1500 °C approximately 0.6 wt% of Cr_2O_3 dissolved in the melt.

The preferential formation of aluminous pyroxene over plagioclase in the Cr_2O_3- containing glass studied is in accordance with Omar' s results [19], which was attributed to the very low activation energies for pyroxene crystallization, (2–6 kcal/mol) when compared with those for plagioclase (8–13 kcal/mol). Thus, Cr_2O_3 may increase the extent of isomorphous substitution of the Ca-containing Tschermak's molecule, $CaAl_2SiO_6$, into the pyroxene structure, leading to enhancement of aluminous-pyroxene formation, at the expense of the basic ingredients of the plagioclase. Moreover, the viscosity of the crystallizing glass may be increased in the presence of chromium to the extent that the formation of more complex structures, like those of the plagioclases, becomes difficult relative to the simpler pyroxene crystal structures. The great tendency for pyroxene (diopside solid solution) formation in Cr_2O_3 – containing glasses may also be favored by the high degree of registry between the lattice parameters of the pyroxene and those of the catalyst phase.

4.2. Role of fluorides (LiF and CaF_2)

The results have shown that the introduction of fluoride produced a marked lowering of the temperature at which crystallization begins 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 [16]. 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 fluoride used is less than 5% [20], which account for the non-uniform coarse-grained character of the fluorine-containing glass G30L (Fig. 6). The addition of fluorides (LiF or CaF_2) led to the formation of non-uniform coarse grained microstructures. These effects may be explained by some or all, of the following:

Fluorides may act as network breakers in the glassy anionic structure [16]. The bridging oxygen can be replaced by fluoride ions due to their similarity in radius without causing too great a 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 may explain the decrease in the melting temperatures and the temperatures at which crystallization occurred as well as the viscosities of the glasses (indicated by the DTA endothermic peak temperature corresponding to M_g °C) with successive increases in fluoride addition. As a result of the decrease of the viscosity, the mobility and diffusion of the different ions and ionic complexes of the glasses during the crystallization process will be markedly increased, leading to the higher crystallizabilities.

Fluorides are also known to be immiscible in silicate melts, especially at lower temperatures, leading to two-phase 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, it has been found by Nikandrov [21] that phase separation alone is not sufficient to induce volume crystallization in the glass. The mode of crystallization whether it is surface or volume depends mainly both on the actual chemical composition of the glass and concentration of the fluoride additions. Danilova [20] recommended this concentration to be 5 wt% in the case of glass with 57% SiO_2 and 15–16% Al_2O_3. Deviation from such compositional optimum percentages, i.e., at lower or higher Al_2O_3%, leads to surface and non-uniform crystallization giving rise to coarse heterogeneous microstructures and not mentioned making problems during melting the batch formulation.

The presence of fluorides helps in the formation of diopside solid solution and magnetite at low temperature and transformation of diopside solid solution into diopside and favored formation of anorthite and fayalite at high temperature. 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 which can take place, e.g. the anorthite and fayalite formation.

4.3. Role of titanium dioxide (TiO_2)

According to the results obtained from TiO_2-containing glasses, it is quite evident that TiO_2 is greatly effective in the nucleation and crystallization processes.

In glasses containing TiO_2 as nucleation catalysts, it is generally agreed that TiO_2 leads to liquid un-mixing, which may be referred to as phase separation [22]. On the other hand, several investigators [23,24] showed that in glasses containing appreciable amounts of TiO_2 the effective nuclei and small crystallites of titanium are compound such as titanates.

For glass in which the ratio of oxygen ions/network forming cations is greater than 2, there must be non-bridging oxygen ions, a lowering of the free energy will follow, if chemical differentiation occurs to give domains in which the silica network is continuous and which are separated from each other by the non-bridging oxygen [25]· Such a microstructure will provide a larger number of potential nuclei for phases whose structural elements are related to the short-range order within the domains. It is postulated here that Ti^{4+} ions can create such domains by their tendency to occupy the non-bridging surface sites associated with non-bridging oxygen ions. This tendency is consistent with the limited ability of Ti^{4+} ions to form stable tetrahedral network. Moreover, the rejection of the Ti^{4+} ions to the periphery is expected since the solubility of Ti^{4+} in the network silicate structure is very low. These criteria of considerations may be reflected on facilitating the melting process, decreasing the viscosity of the resultant melts and increasing the crystallizability of the corresponding glasses investigated. Hillig [26] pointed out that, the mechanism of the action TiO_2 does not lie in the TiO_2 crystals acting as nuclei, but rather in the fact that TiO_2 speeds up the liquid–liquid phase separation in the glass and its subsequent crystallization. From the mineralogical point of view, the TiO_2 effect can be summarized in the followings:

The presence of TiO_2 in the glass leads to catalyzation of diopside ss (diopside + Ca-Tschermak's) → diopside transformation and also magnetite → fayalite transformation. Its presence also enhances the formation of anorthite and fayalite at high temperatures.

These results are in good agreement with the literature concerning the nature of crystallization of calcium magnesium aluminosilicates [14,27].

5. Conclusions

Diopside ss (aluminum pyroxene) ($CaAl_2SiO_6$) and magnetite (Fe_2O_3) are crystallized at low temperature, in glasses based on blast furnace slag and natural raw materials, while diopside, anorthite and fayalite are the main phases developed at high temperature. The presence of Cr_2O_3 and TiO_2 are highly effective as catalyst for initiating crystallization centers that induce volume crystallization and formation of fine-grained glass-ceramics. Whereas the presence of LiF or CaF_2 helps in the formation of diopsidic solid solution and magnetite at lower temperatures and leads to the formation of coarse-grained microstructures. Glass G30Cr heat-treated at 650 °C, 1 h + 850 °C, 2 h shows the best microstructure and phases developed among the glasses studied.

References

[1] E. Bernardo, R. Castellan, S. Herglich, Sintered glass-ceramics from mixtures of waste, Ceram. Int. 33 (2007) 27.

[2] G.A. Khater, The use of Saudi slag for the production of glass-ceramic materials, Ceram. Int. 28 (2002) 59.

[3] JiaKuan Yang, DuDu Zhang, Jian Hou, BaoPing He, Bo Xiao, Preparation of glass-ceramics from red mud in the aluminum industries, Ceram Int. 34 (2008) 125.

[4] G.A. Khater, Glass-ceramics in the $CaO–MgO–Al_2O_3–SiO_2$ system based on industrial waste materials, J. Non-Cryst. Solids 356 (2010) 3066.

[5] Hongyu Liu, Hongxia Lu, Deliang Chen, Hailong Wang, Hongliang Xu, Rui Zhang, Preparation and properties of glass-ceramics derived from blast furnace slag by a ceramic-sintering process, Ceram. Int. 35 (2009) 3181.

[6] G.A. Khater, Diopside–Anorthite–Wollastonite glass-ceramics based on waste from granite quarries, Glass Tech.-Europe. J. Glass Sci. Tech. part A. V.51, No.1 (2010)6.

[7] T.W. Cheng, J.P. Chiu, Fire-resistant geopolymer produced by granulated blast furnace slag, Miner. Eng. 16 (2003) 205.

[8] M.L. Ovecoglu, B. Kuban, H. Ozer, Characterization and crystallization kinetics of a diopside-based glass-ceramic developed from glass industry raw materials, J. Eur. Ceram. Soc. 17 (1997) 957.

[9] J.I. Chu, H.C. Park, C.C. Sorrell, DTA study of nucleation and crystallization of $MgO–CaO–SiO_2–P_2O_5$ glass-ceramics containing ZrO_2, $BaCO_3$ and Li_2CO_3, Int. Ceram. Monogr. 1 (1994) 585.

[10] C. Leonelli, T. Manfredini, M. Paganelli, Crystallization of some anorthite–diopside glass precursors, J. Mat. Sci. 26 (1991) 5041.

[11] G. Baldia, E. Generali, Effects of nucleating agents on diopside crystallization in new glass-ceramics for tile-glaze application, J. Mat. Sci. 30 (1995) 3251.

[12] M. Rezvani, B. Eftekhari-Yekta, M. Solati-Hashjin, V.K. Marghussian, Effect of Cr_2O_3,Fe_2O and TiO_2 nucleants on the crystallization behavior of $SiO_2–Al_2O_3–CaO–MgO(R_2O)$ glass-ceramics, Ceram. Int. 31 (2005) 75.

[13] A. Omar, A.W. Elshennawi, G.A. Khater, The role of Cr_2O_3,LiF and their mixtures on crystalline phase formation and microstructure in Ba, Ca, Mg aluminosilicate glass, Br. Ceram. Trans. J. 90 (1991) 179.

[14] G.A. Khater, E.M.A. Hamzawy, Effect of different nucleation catalysts on the crystallization behavior within the $CaO–MgO–Al_2O_3–SiO_2$ system, Silic. Indus. 73 (2008) 103, Nr-7-8.

[15] L.A. Zhunina, V.N. Shara, V.F. Tsikov, N.N. Khripkova, Crystallization of glasses of composition $CaO-MgO-Al_2O_3-SiO_2$ in the presence of Cr_2O_3 with formation of a stable pyroxene phase, The Structure of Glass, 3, Consultant Bureau, New York, 1964, p. 192.

[16] P.W. McMillan, Glass-Ceramics, 2nd ed., Academic Press, London, England, 1979.

[17] I. Sawai, Glass technology in Japan, Glass Tech. 2 (1961) 243.

[18] B. Keyworth, P.S. Rogers, Crystallization phenomena in glasses containing chromium oxide, in: Proc.10th Conf. on Silicate industry, Budapest, 1962, p. 260.

[19] A.A. Omar, Influence of isomorphous substitutions in pyroxene on the crystallization of synthetic basaltic melts, Ph.D. Thesis, Moscow State University (1965).

[20] N.P. Danilova, Dependence of the temperature range of crystallization in the $Na_2O–CaO–MgO–Al_2O_3–SiO_2$ system on the composition, The Structure of Glass, 3, Consultant Bureau, New York, 1964 , p. 195.

[21] V.S. Nikandrov, The Structure of Glass "Catalyzed Crystallization of Glass", 3, Consultant Bureau, New York, 1964, p. 188.

[22] S.D. Stookey, Catalyzed crystallization of glass in theory and practice, Ind. Eng. Chem. 51 (1959) 805.

[23] R.D. Maurer, Crystal nucleation in glass containing titania, J. Appl. Phys. 33 (1962) 2132.

[24] P.E. Doherty, D.W. Lee, R.S. Davis, Direct observation of the crystallization of $Li_2O–Al_2O_3–SiO_2$ glasses containing TiO_2, J. Am. Ceram. Soc. 50 (2) (1967) 77.

[25] T.I. Barry, D. Clinton, L.A. Lay, R.A. Morrell, R.P. Miller, Crystallization of glasses based on eutectic compositions in the system $Li_2O–Al_2O_3–SiO_2$, J. Mat. Sci. 5 (2) (1970) 117.

[26] W.B. Hillig, Engineering Progress at the University of Florida 21 (1962) 2–26.

[27] D.R. Stewart, TiO_2 and ZrO_2 as nucleation in a lithium alumino silicate glass-ceramic. Advances in nucleation and crystallization in glasses, Ed. Hench and Freiman, J. Am.Ceram.Soc. (1972) 83.