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Journal of the European Ceramic Society 27 (2007) 1829–1835

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Effect of fluoride nucleating catalysts on crystallization of cordierite from modified basalt-based glasses

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Abstract

Cordierite-anorthite phases were crystallized from modified basalt-based glasses by adding calculated amounts of reducing agent, TiO_2, kaolin and F^- ions in the form of Li, Mg and Al fluorides as nucleated agents. DTA, XRD and SEM were performed to study the crystallization of these glasses. It was noticed that, AlF_3 greatly encourage the formation of anorthite and has an opposite effect on spinel crystallization. The presence of MgF_2 decreases the onset of crystallization and enhance cordierite polymorphs and anorthite while LiF stimulates the crystallization of anorthite, β-quartz solid solutions (ss) and minor spinel. Sequence of crystallization is dependent on heat treatment parameters and type of fluorides added.

Keywords: Glass-Ceramics; Basalt; Cordierite; Fluoride

1. Introduction

The relatively high refractoriness and thermal stability, low coefficient of thermal expansion and excellent resistance to thermal chock as well as the high volume receptivity and low dielectric constants are some of the outstanding properties which have made cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) an industrial material. Several investigations have already been made to produce it via a glass-ceramic process.[1–5] Almost all these investigations used high purity chemical reagents or at least pure processed raw materials such as kaolin, magnesite and quartz sand as the starting batch materials.

From the commercial exploitation point of view of cordierite glass-ceramic, the main difficulty lies in the high viscosity and high melting temperatures of its ternary stoichiometric glass composition. Even in the presence of TiO_2 which acts as a nucleating agent and also facilitates melting, volume crystallization is not easily achieved.

However, it has been reported[6–8] that: (a) the melting temperature and crystallization temperature can be substantially reduced in presence of CaO; (b) iron cordierite $Fe_2Al_4Si_5O_{18}$ is well-known as a natural mineral occurring in different metamorphic rocks, and so Fe^{2+} can isomorphously substitute Mg^{2+} ions in pure cordierite $Mg_2Al_4Si_5O_{18}$ giving rise to cordierite ss; (c) anorthite, $CaAl_2Si_2O_8$, is the only lime-bearing phase compatible with cordierite; and (d) TiO_2 is the most effective nucleation catalyst for cordierite crystallization.

The present work aims at crystallizing cordierite from impure multi-component raw materials as basalt. It was decided to modify the basalt composition by adding a deliberately calculated amounts of: (i) a reducing organic agent (e.g., sucrose) to convert the Fe^{3+} ions present in basalt to the Fe^{2+} ions; since the capability of the latter to be isomorphously captured or shared in the cordierite structure is much more than the former (Fe^{3+}); (ii) adding TiO_2, because it has a significant reducing effect on the melting and viscosity of cordieritic glass compositions, in addition to its catalytic effect on formation of the cordierite crystals. The total percentage of TiO_2 approached the optimum values required for promoting nucleation process; (iii) alumina and/or alumina plus silica, in the form of alumina and kaolin, to compensate the deficiency of Al_2O_3 in basalt composition and consequently satisfying the requirements of cordierite solid solution formations. (iv) Making use of CaO, present in the basalt composition, in lowering the melting temperature and viscosity of molten glasses, and allotting most of it as anorthite ($CaAl_2Si_2O_8$) due to its compatibility with cordierite as well as its good thermal properties. (v) F^- ions, in the form of Li, Mg and Al fluorides, with the view to capture the remaining Ca^{2+}, after anorthite, to form a secondary nucleant phase of fluorite. The selected said cations of the added fluorides were used with the view that they could be easily accommodated or found place in the structure of the crystallizing cordierite polymorphs.

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0955-2219/$ – see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.jeurceramsoc.2006.05.062

2. Experimental

Cordierite ss molecules $(Mg,Fe)Al_4Si_5O_{18}$ and plagioclase molecules $CaAl_2Si_2O_8$ and $(Na,K)AlSi_3O_8$ as major phases according to CIPW norm were calculated.[7] The molecular norm calculations revealed that the crystalline phase assemblages are ~51% cordierite ss, 39% anorthitic plagioclase and the rest being TiO_2-bearing phases which may be crystallized out from this glass under conditions approaching the equilibrium.

Table 1 lists the chemical composition of the raw materials used (viz, basalt and kaolin). Three compositions with deliberate amount of different fluorides viz., LiF, MgF_2 and AlF_3 as nucleating agents were prepared. These compositions (Table 1) were designated as BCL, BCM and BCA; where BC indicates the modified basaltic cordierite-anorthite base composition and L, M and A indicate the nucleating agents added; LiF, MgF_2 and AlF_3, respectively.

The aforementioned three cordierite basalt-based batches, were generally melted well in the range 1400–1470 °C (depending upon the nucleant added) for 3 h. The melts were cast in the form of rectangular specimens and transferred into a muffle furnace at 550 °C which is then switched off to cool to room temperature. The obtained specimens appeared blackish in color and seed-free.

Glass nucleated by LiF (BCL) showed a lower melting temperature and a better viscosity and workability. Glass containing AlF_3, showed somewhat higher melting temperatures and viscosity than those nucleated only by LiF or MgF_2. The latter, however, showed an intermediate character. These experimental observations revealed the reducing effect of Li^+ ions on the melting temperatures and viscosity of the melts and the opposite increasing effect of Al^{3+} ions on the viscosity and melting temperatures.

Differential thermal analysis was carried out using the computerized Perkin-Elemer (U.S., Norwalk, CT) DTA-7 Unix System Series. The DTA measurements were performed using ~70 mg of powdered glass sample (of 90–260 μm grain size), in a Pt crucible in a flowing (~50 cm^3/min) atmosphere of dry N_2 gas. The DTA instrument was calibrated periodically with Al and Au standards using powdered alpha Al_2O_3 as a reference material.

Table 1
Calculated chemical composition (in wt.%) of the raw materials used and the modified basaltic cordierite-anorthite base glasses

Oxide/glasses	Basalt	Kaolin	BC	BCA	BCM	BCL
SiO_2	50.46	50.7	43.44	42.08	41.89	42.14
Al_2O_3	14.79	43.23	27.39	26.52	26.40	29.56
TiO_2	3.47	2.11	10.43	10.10	10.06	10.12
FeO	10.97	0.96	6.6	6.39	6.36	6.4
CaO	10.84	0.94	6.51	6.3	6.27	6.31
MgO	6.28	–	3.7	3.58	3.57	3.59
Na_2O	2.47	1.32	1.49	1.45	1.43	1.44
K_2O	0.72	0.83	.44	0.43	0.43	0.43
LiF	–	–	–	–	–	3.01
MgF_2	–	–	–	–	3.59	–
AlF_3	–	–	–	3.15	–	–

BC = rectified basalt – Cordierite base composition; L, M and A indicate the addition of the fluorides of Li, Mg and Al either separate or mixed.

Thermal heat treatment to convert glasses into glass-ceramics were carried out in a programmable muffle furnace (Nabertherm), starting from room temperature up to the required temperature at a heating rate of 10 °C/min. Then the samples were soaked at that temperature for an intended period of time after which the furnace was switched off to cool to room temperature.

The identification of the crystallizing fine-grained phases in this work resides essentially on the X-ray powder diffraction analysis. A Philips PW 1390 X-ray Diffractometer, adopting Ni-filtered Cu radiation with tube 40 kV and a current of 30 mA, was used in the present investigation.

The microstructure and the possible mineralogical constituents were examined optically in thin sections using a polarizing Carl-Zeiss research microscope.

3. Results

Fig. 1 shows the DTA traces of the investigated glasses, from which it can be noticed that all the three DTA curves have a close resemblance and character (one endotherm and at least four exothermic effects). The endothermic dips are due to the transition temperature of the glass (Tg). The Tg endothermic effects of BCL, BCA and BCM glasses are located at 606°, 624° and 641 °C, respectively. These effects are followed by four exothermic successive peaks correspond to release of thermal energy as a result of crystallization of spinel plus fluorite (CaF_2), β-quartz solid solutions plus pseudo-brookite, anorthite, and α-cordierite, respectively.

The first exothermic effect is broad with a peak at about 682 °C in glass BCL, and at about 725 °C in glasses BCA and BCM. This peak appears sharper in glass BCM nucleated by MgF_2, it was attributed to the formation of both spinel and CaF_2; as verified by XRD analysis.

The second exothermic peak is strong and sharp, which appeared at about 913–925 °C (Fig. 1) mainly ascribed to the formation of μ-cordierite (β-quartz ss) and pseudo-brookite. The XRD patterns of samples treated above 900 °C revealed additional crystallization of predominant amounts of μ-cordierite and small amounts of pseudo-brookite besides minor spinel and fluorite phase. The intensity of this peak, which reflects the strength of the crystallization is progressively increased in the order BCM, BCA and BCL. In other words, the effectiveness of these nucleants on the formation of μ-cordierite increases on going from MgF_2 to AlF_3 to LiF. The letter one shows the maximum effectiveness which may be; due to the additional formation of a Li-bearing stuffed β-quartz ss variety.

The third exothermic peak, is located at 967°, 974° and 1005 °C for glasses BCL, BCA and BCM, respectively (Fig. 1). This peak is related essentially to crystallization of anorthite in accordance to the XRD analysis. This peak is displaced to higher temperatures and became more intense in the direction of using LiF, AlF_3, and, then MgF_2. This increase in intensity may indicate the enhancement effect of these nucleators on the crystallization of anorthite, which being more efficient with the

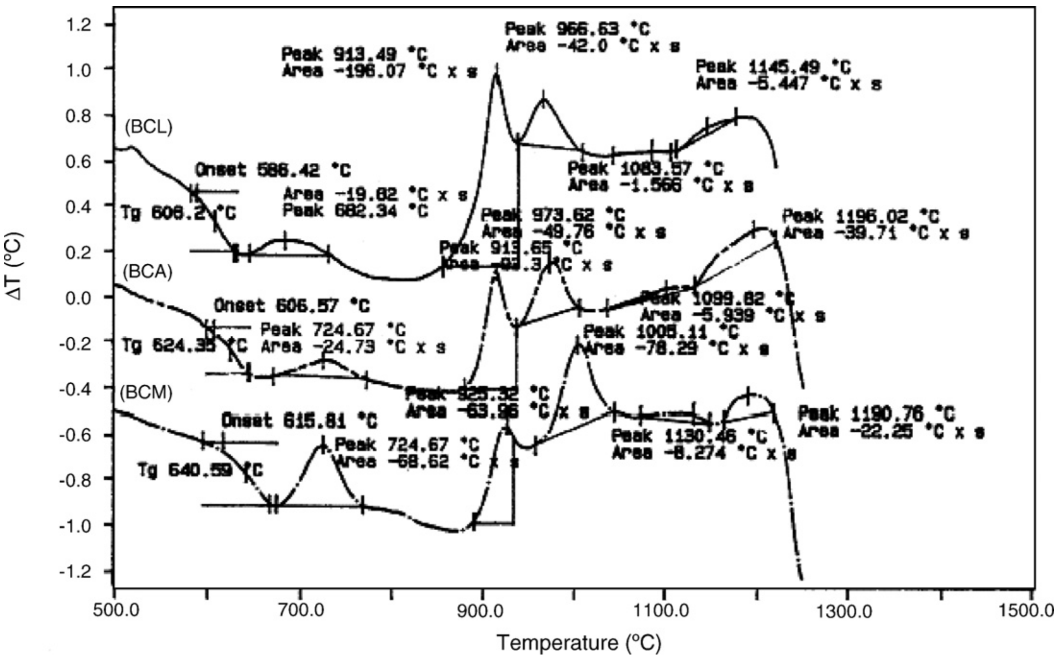

Fig. 1. DTA traces of cordiritic glasses nucleated by MgF_2 (BCM), AlF_3 (BCA), and LiF (BCL).

latter MgF_2; in spite of its cations not sharing in the anorthite formula ($CaAl_2Si_2O_8$).

The fourth exothermic peak is a broad ones, with diffused maximum located at 1084, 1100 and 1130 °C in glasses BCL, BCA and BCM, respectively. These peaks can be attributed to the formation of high-temperature α-cordierite phase, since the XRD analysis revealed its formation in samples isothermally treated at the same temperatures. This exotherm is followed by minor kink endothermic effects which may be related to the melting of a fluoride-bearing phase. This is immediately followed also by a very weak exothermic effect located at 1145, 1196 and 1191 °C in BCL, BCA and BCM, respectively. This very weak peak may be attributed to the separation of rutile, however, in amounts beyond the sensitivity of the XRD apparatus.

Table 2 lists a summary of the phases developed at different heat treatment conditions. Almost all XRD patterns of the studied samples are quite similar but with different intensity of the crystallized phases according to the nucleating agent added (Fig. 2 is responsible to it).

3.1. Effect of AlF_3

XRD analysis and thin section examination of BCA samples heat treated for 3 h at 900 °C indicated the existence of μ-cordierite, pseudo-brookite ss, spinel, minor fluorite and Mg petalite-like phase. Thin section examination (Fig. 3) shows the identified phases with lesser amount of spinel. Increasing the temperature from 900 to 1050 °C, fine anorthitic plagioclase microlites together with intergrowths of the already mentioned phases (except Mg petalite-like phase) was developed (Fig. 3). On increasing soaking time to 30 h, at 1050 °C, the

Table 2
Phases developed from some cordierite – basalt glasses

Glass	Heat treatment °C, hour	Phases developed
BCA	900 °C/3 h	β − qz ss + Sp + Fl + Mg − p?
	1050 °C/3 h	An + β − qz ss + Sp + Fl
	1050 °C/30 h	An + β − qz ss + Fl + Sp + α − cord
	1050 °C50 h + 1100 °C/14 h	An + β − qz ss + α − cord + Fl + Sp
	1100 °C/24 h powdered	An + β − qz ss + α − cord + Fl + Sp
	1200 °C/24 h	An + β − qz ss + Sp + Fl
	1200 °C/24 h powdered	An + β − qz ss + α − cord + Fl + Sp
	850 °C/14 h + 1200 °C/8 h	An + β − qz ss + Sp + Fl
	850 °C/14 h + 1200 °C/8 h powdered	An + β − qz ss + α − cord + Fl + Sp
BCM	950 °C/3 h	β − qz ss + Sp + Fl
	1000 °C/3 h	β − qz ss + An + Sp + Fl
	1050 °C/3 h	An + β − qz ss + Sp + Fl
	1050 °C/30 h	An + β − qz ss + α − cord + Fl + Sp
	1050 °C/50 h + 1100 °C/14 h	An + β − qz ss + α − cord + Fl + Sp
	1200 °C/24 h	An + β − qz ss + α − cord + Fl + Sp
	1200 °C/24 h powdered	An + β − qz ss + Fl + α − cord. + Sp
	850 °C/14 h + 1200 °C/8 h	β − qz ss + An + α − cord. + Fl + Sp
	850 °C/14 h + 1200 °C/8 h powdered	An + β − qz ss + α − cord. + Fl + Sp
BCL	850 °C/3 h	Mg-P? + β − qz ss + Sp + Fl
	900 °C/3 h	β − qz ss + An+Sp + Fl + Mg − p?
	1050 °C/3 h	An + β − qz ss + Sp + Fl
	1050 °C/30 h	An + β − qz ss + Fl + α − cord + Sp
	1050 °C/50 h + 1100 °C/14 h	An + β − qz ss + Fl + α − cord
	1200 °C/24 h	An + β − qz ss + Fl +Sp
	1200 °C/24 h powdered	An + β − qz ss + Fl + α − cord + Sp
	850 °C/14 h + 1200 °C/8 h	An + β − qz ss + Fl + α − cord + Sp
	850 °C/14 h + 1200 °C/8 h powdered	An + β − qz ss + Fl + α − cord + Sp

An = Anorthite; Sp = Spinel; Fl = fluorite. β − qz ss = + β − quartz ss; α − cord = α − cordierite; Mg − P = Mg − petalite and ? uncertainly.

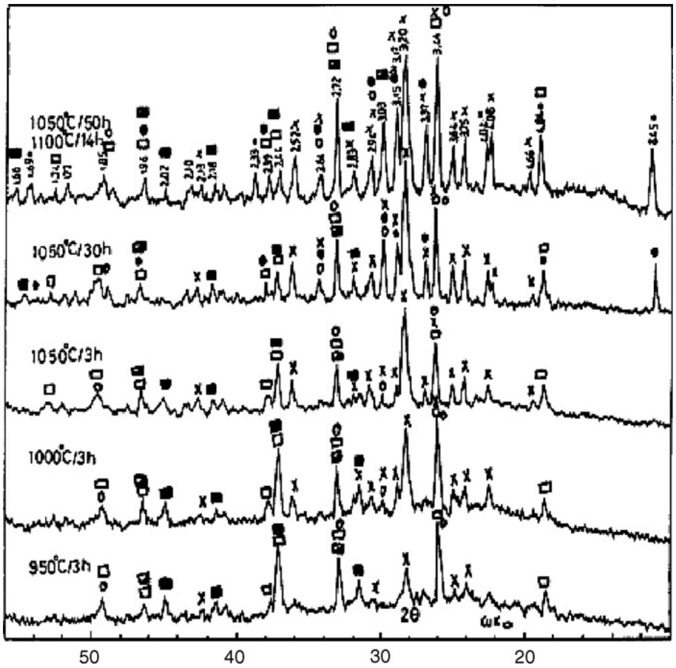

Fig. 2. XRD patterns of BCM glasses heat-treated at 950 °C/3 h, 1000 °C/3 h, 1050 °C/3h, 1050 °C/30h, and 1050 °C/50 h + 1100 °C/14 h. (●) α-Cordierite, (0) μ-cordierite, (×) anorthite, (□) pseudo-brookite, (■) spinel, (◪) fluorite.

intensities of the diffraction lines of the above phases (except spinel) were increased, indicating more advanced state of development and a higher degree of crystallinity, together with the appearance of the 8.45 diffraction line characteristic to the development of α-cordierite. By increasing the crystallization soaking time to 50 h at 1050 °C and then for 14 h at 1100 °C, the development of α-cordierite was considerably enhanced with a decrease in the crystallization of spinel, μ-cordierite, and less intergrowths of anorthite. It was noticed that, anorthite was developed in larger amounts during single stage rather than successive heat treatments and the reverse holds for the α- and μ-cordierite.

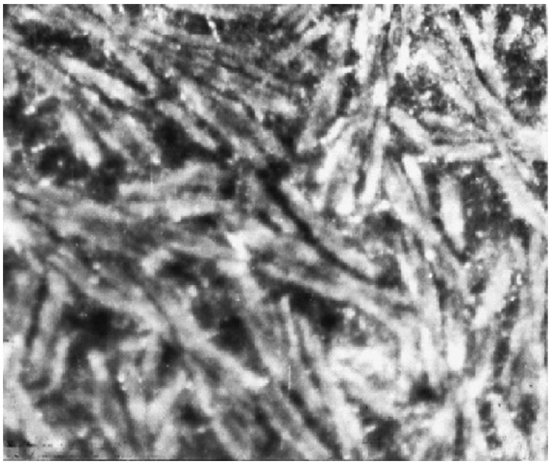

Fig. 3. Photomicroograph of BCA glass heat-treated at 1050 °C/3 h, showing fair-sized anorthitic polagioclase microlites enclosing in between μ-cordierirte, spinel, pseudo-brookite and fluorite intergrowths. (X = 350, polars+).

3.2. Effect of MgF_2

XRD patterns (Fig. 2) shows the isothermal single stage heat treatments for 3 h at 950 °C which leads to the crystallization of phases essentially of β-quartz ss, spinel, anorthite, pseudo-brookite and fluorite; arranged in decreasing order of abundance. Increasing the temperature from 950 to 1000 °C encourages the formation of anorthite which being the second major phase after β-quartz ss in the said phase assemblages. The thin section examination of this sample exhibited a uniform fine-grained texture of anorthite, β-quartz ss, pseudo-brookite and spinel crystallites as well as some interstitial glass. On further heating to 1050 °C, for the same soaking time, a more increase of anorthite content could be observed (note diffraction lines 3.20 and 3.18; Fig. 2). On prolonged heating for 30 h, at 1050 °C α-cordierite crystallized out in large amounts, whereas spinel is greatly decreased. It is worth mentioning that the appearance of α-cordierite is concomitantly accompanied with the disappearance of spinel. This may indicate that the formation of α-cordierite is a result of the interaction between the spinel components and residual non-crystallized siliceous glassy phase, and not via transformation of the initially formed μ-cordierite. A more development and/or maturity of anorthite crystals takes place on prolonged heating for 30 h. This was evidenced by the clearer and more resolutions of their XRD peaks characterizing it (3.20 and 3.18).

Increasing the heat treatment for longer periods as 50 h, at 1050 °C followed by another 14 h at a higher temperature as 1100 °C resulted into a higher quantity of cordierite polymorphs, as α-cordierite phase (diffraction lines note 8.45 and 3.03 in Fig. 2) and μ-cordierite. The amount of the latter reaches its maximum crystallization density and hence becoming in comparable to that of the major anorthite phase. Consequently, the sample is composed essentially of α-cordierite, μ-cordierite and anorthite as major phases.

The two stage heat treatment process enhances the formation of the very fine randomly oriented, interlocking crystals of approximately uniform sizes bonded by residual glassy matrix (Fig. 4).

3.3. Effect of LiF

Thin section examinations of samples BCL indicated that the use of LiF, even at such low deliberately concentrations used (3%), greatly enhances the crystallization process. In comparison to those nucleated by the fluorides of Al and Mg (BCA and BCM, respectively), LiF shows a remarkable effect on lowering the temperature of beginning crystallization. It also enhances crystallizability and degree of crystallinity, as well as fining the microcrystalline structure.

The BCL samples, which isothermally treated at 850 °C for 3 h, displayed relatively much more finer grained textures in comparison with the preceding glasses (BCA and BCM). Also, the DTA exotherm peaks of the BCL glass (Fig. 1) appeared with higher intensities and more pronunciation than those of BCA and BCM glasses indicating a higher crystallizability. The XRD pattern of sample heat-treated at 850 °C/3 h revealed a significant triplet reflections at 3.58 and 3.70 which may indicate a petalite-

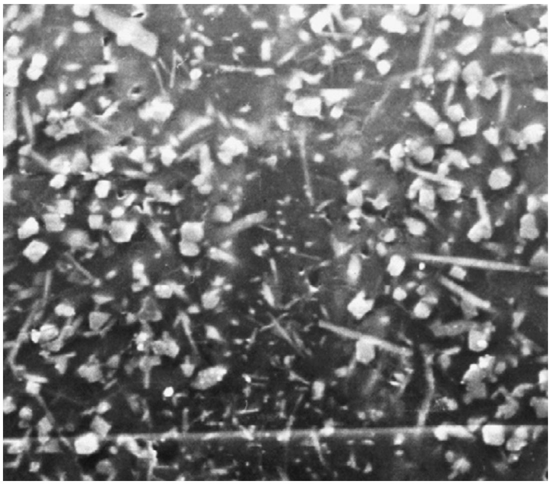

Fig. 4. SEM micrograph of BCM glass heat-treated for 6 h at 950 °C and 1100 °C/14 h showing the marked effect of MgF_2 through double stage crystallization treatment on enhancing the formation of uniform fine-grained microcrystalline structure embedded in crystalline base of μ-cordierites, pseudo-brookite, spinal and CaF_2. (X = 500, polars+).

like phase in accordance to Schryrer and Schairer.[9] Besides this phase, the premature phases of β-quartz ss (Li and Mg-bearings), spinel, pseudo-brookite, and fluorite were detected. A largely residual glassy phase could be also indicated by the high intensity of X-ray background.

Increasing the temperature of the BCL samples to only 900 °C, for the same soaking time, results in a uniform bulk crystallization of large amounts of very minute acicular of β-quartz ss, anorthite, spinel, pseudo-brookite ss and fluorite (Fig. 5). The XRD pattern of this sample showed that the crystallizing β-quartz ss are of Li- and Mg-bearings as indicated by the slight of splitting of its main peak at 3.42. The preceding uncontained minor petalite-like phase was still detected. At higher temperature as 1050 °C, no great variation occurs except the predominance crystallization of anorthite over the β-quartz ss phases. At this temperature the Mg-petalite-like phase and the residual glassy phase were completely vanished and α-cordierite, in very small amounts began to develop. For soaking durations as long as 30 h, at 1050 °C, no great changes were noticed except the slight increase of the α-cordierite as revealed by the detectable increase of their d-spacing at 8.45, 3.20 and 3.03 and the slight decrease of spinel (note diffraction lines 2.44).

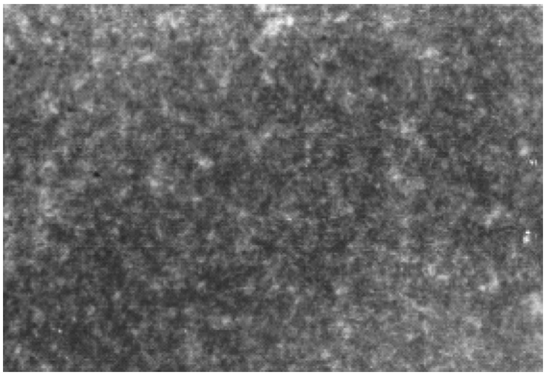

Fig. 5. SEM micrograph of BCL glass, 900 °C/3 h. Uniform volume crystallization. Essentially of very minute aciculars of μ-cordierite crystallites showing a homogeneous fine-grain microstructure. (X = 350 polars+).

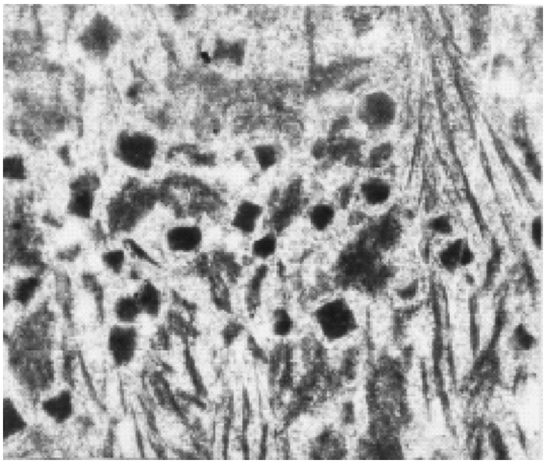

Fig. 6. SEM micrograph of BCL glass heat-treated at 1050 °C/50 h + 1100 °C/14 h showing almost a holocrystalline material of anorthitic and well developed α-cordierite crystals embedded in crystalline base of μ-cordierites, pseudo-brookite, spinel and CaF_2 (X = 150, polars+).

The XRD pattern of sample thermally cured at 1050 °C for 50 h and then at 1100 °C for 14 h showed a similar pattern to the above sample (1050 °C/30 h) but with somewhat higher intensities, more sharpness and resolution of their peaks. This may indicate an advanced state of progression of development and maturity of the resultant crystals. Its thin section exhibits almost a holocrystalline material of anorthitic microlites and well-developed α-cordierite as equate and six-sided crystals indicating its hexagonal symmetry, all of which are embedded in a fine-grained crystalline base of β-quartz ss, spinel, pseudo-brookite ss and fluorite (Fig. 6).

4. Discussion

4.1. *Effects of Ca, Ti and F ions on meltability and crystallizability*

The relatively low melting temperatures and viscosity, and consequently the good meltability and workability traits, as well as the high crystallizability throughout the entire volume upon heat treatments of the present modified basaltic glasses could be ascribed to the role played by the foreign ions. These foreign ions may be the CaO, which precursory present in basalt and constitutes ∼6.5 wt% of the glass, TiO_2 which added to promote melting, and, fluorine ions which brought in as the said crystallization catalysts. These ions are the most essential ones responsible for reducing the temperature of melting, transition (Tg) and softening (Ts) and hence the viscosity of the present glasses; compared to ternary cordierite glasses cited in literature.[1,8–10] The effect of CaO in cordierite glasses can find its explanation in the work of deVeky and Majumdar[11] who have also shown that by adding a small amount of about 5 wt% CaO to a ternary magnesium aluminium silicate (MAS) cordierite glass nucleated by 11% TiO_2 resulted in a substantial reduction of the viscosity and the temperature of melting and beginning of crystallization. These two authors also showed that the additions of TiO_2 have a similar effect to that of CaO. However, these effects were ascribed to their weakening effects on the network structure of glass, due to the lesser field strength of Ca^{2+} cations than Mg^{2+} cations[12] and consequently the weaker bond character of Ca–O than that of Mg–O bonds, which results in lower viscosity values and increasing in the mobility of the glass structural elements.

An explanation for the relatively low viscosity and high volume crystallizability exhibited by the present titania- and fluoride-containing glasses may be also related to the weakening effect of either Ti or F ions on the network structure of the glass.[13–17] According to those authors, Ti^{4+} ions can act as network former and exist in Si-equivalent four-fold coordinated sites. However, Ti^{4+} has a field strength of 1.04 considerably, above that of the four-fold coordinated Al^{3+} (0.96) which is known to enter the network structure but below that of the major glass network-forming Si^{4+} (1.56).[18] Therefore, introduction of weaker Ti–O bonds will thus weaken the network structure, which in turn, is reflected in lowering the viscosity of melts or glasses and consequently leads to more mobilization of the glass-forming elements, i.e., conducive to crystallization.

The X-ray diffractometry has revealed that of psudo-brookite (titanate phase), fluorite, spinel and Mg-petalite-like phase are cocrystallized as accessories at the initial stages of crystallization besides the relatively major μ-cordierite.

4.2. *Effect of F ions on inducing volume crystallization*

Several researchers used fluorine as a bulk nucleating agent in many systems.[19–24] Incorporation or substitution of fluorine ions in silicate melts is known to lower their viscosity by disrupting the Si–O–Si bonds. Dingwell et al.,[17] also found that fluorine reduces the viscosities and activation energies of the melts. These authors inferred that reduction in viscosity of polymerized melts occurs due to substitution of fluorine for bridging oxygens, with consequent depolymerization of these melts by replacement of Si–O–(Si,Al) bridges with = Si–F bonds. In other words, the incorporation of fluorine ions in the glass structure occurs in the $[SiO_4]^{4-}$ tetrahedral in place of O^{2-} ion with formation of $[SiO_3F]^{3-}$ groups and in such case the network is only anchored through bridging oxygen. This substitution leads to weakening of the glass structure. This weakening effect of fluorine on the glass structure results in easier atomic rearrangements upon reheating the glass and consequently crystalline fluorine nuclei may be formed.[13]

However, it was also suggested[25,26] that crystallization may be initiated by the formation of crystalline nuclei consisting of a simple binary fluoride. These fluorite nuclei then act as heterogeneous centers for the growth of the first crystalline silicate phase, and consequently responsible for the great fineness of the obtained homogeneous microstructures. These findings explain the formation of the CaF_2 phase (fluorite) separated out at the initial stages of crystallization.

4.3. *Sequence of crystallization*

The crystallization of a wide range of compositions in the $MgO-Al_2O_3-SiO_2$ system, has been studied.[8–10,27,28] These studies have shown that μ-cordierite is the first crystal phase formed metastably and is then rearranged at higher temperature to form α-or hexagonal-cordierite. This high temperature α-form can be readily obtained by the crystallization of glass at temperatures greater than 1050 °C. These findings became complicated by the presence of minor constituents and nucleating agents which significantly affect the sequence of crystallization of cordierite-based glasses.[19]

In the present complex basaltic glasses, which are deviated largely from the pure cordierite stoichiometry, the sequence and proportions of the crystallizing phases strongly depend on the heat treatment parameters of crystallization (temperature and time) and to some extent on the type of the fluorides which were added.

Heating above 1050 °C resulted in complete transformation of the metastable Mg petalite-like phase (if present) into β-quartz ss.[29]

5. Conclusions

1. In the AlF_3-nucleated glasses, the onset of crystallization in bulk glass samples are considerably at higher temperatures than in powdered samples, e.g., as those subjected to DTA, indicating the effectiveness of the sintered route. AlF_3 greatly encouraged the formation of anorthite and has an opposite effect on spinel crystallization. It also greatly enhances the α-cordierite. AlF_3 has no significant effect on the fineness of the resultant microstructure except those nucleated by double stage heat treatment.
2. In the MgF_2-nucleated glasses, the presence of MgF_2 decreases the onest of crystallization temperature and enhances the formation of anorthite and cordierite polymorphs (μ- and α-cordierites) as well as the maturity of the former phase. The outstanding effect of MgF_2 as a nucleating agent is its effectiveness on the microstructure, i.e., it stimulates the formation of the unique uniform fine-grained microcrystalline structure characterizing glass-ceramic; especially on appropriate heat-treating through double-stage schedule.
3. In the LiF-nucleated glasses, the use of LiF greatly enhanced the crystallizability and consequently the degree of crystallinity of the glass, and widening the crystallization temperature span by lowering the crystallization temperature onset. It is very effectual on promoting fine-grained microcrystalline structure especially at the appropriate heat treatments (950 °C + 1100 °C for 16 h each). From the mineralogical standpoint, LiF stimulates the crystallization of the major phases anorthite and β-quartz ss, as well as the minor spinel. The crystallized β-quartz ss are of Li and Mg-bearing varieties. It inhibits the formation of the α-cordierite, relative to the other fluorides of (Mg and Al) used. The α-cordierite normally formed at high temperatures in glasses BCM and BCA as a result of the interaction of the residual non-crystallized glass with the components of spinel. Therefore, the inhibi-

tion effect of LiF on the formation of α-cordierite may be due to its great stimulating effect on crystallizability which leads to completeness of crystallization process at lower temperature and thus depriving α-cordierite from one of its main component, i.e., residual siliceous glass.

LiF also encourages the formation of the metastable Mg-petalite-like phase at low temperatures (850–950 °C).

4. The sequence and proportions of the crystallizing phases depend strongly on the heat treatment parameters of crystallization (temperature and time) and to some extent on the type of the fluorides which were added.

References

1. Gregory, A. G. and Veasey, T. J., Review: the crystallization of cordierite glass. *J. Mater. Sci.*, 1971, **6**(10), 1312–1321.
2. Schulz, H., Hoffman, W. and Machan, G. M., The average structure of Mg (Al_2 Si_3O_{10}), a stuffed derivative of the high-quartz structure. *Z. Kristallogr.*, 1971, **134**, 1–27.
3. Zdaniewski, W., Crystallization and structure of a MgO-Al_2O_3-SiO_2-TiO_2 glass-ceramic. *J. Mater. Sci.*, 1973, **8**, 192–202.
4. Morell, R., The mineralogy and properties of sintered cordierite glass-ceramics. *Proc. Br. Ceram. Soc.*, 1979, **28**, 53–71.
5. Barry, T. I., Cox, J. M. and Morell, R., Cordierite glass-ceramics-effect of TiO_2 and ZrO_2 content on phase sequence during heat treatment. *J. Mater. Sci.*, 1978, **13**(3), 594–610.
6. Nesse, D. Introduction to optical mineralogy, 2nd ed., Oxford Univ. Neutron Scattering Measurements and Simulations; Phys. Chem. Glasses 1991; 62 (4): 113–8.
7. Deer, W. A., Howie, R. A. and Zussman, J., *Rock forming minerals V1, ortho- and ring silicates*. John Wiley and Sons Inc, NY, 1962.
8. Zdaniewski, W., Microstructure and kinetics of crystallization of MgO-Al_2O_3-SiO_2 glass-ceramics. *J. Am. Ceram. Soc.*, 1978, **61**(5–6), 199–204.
9. Schryrer, W. and Schairer, J. F., Anhydrous alkali-free cordierites. *Carnegie Inst. Washington, Ann. Rep. Dir. Geophys. Lab.*, 1961, **58**, 197.
10. Watanabe, K., Giess, E. A. and Shafer, M. W., The crystallization mechanism of high-cordierite glass. *J. Mater. Sci.*, 1985, **20**, 508–515.
11. deVeky, R. C. and Majumdar, A. J., Nucleation and crystallization studies of some glasses in the CaO-MgO-NaO_2-SiO_2 system. *Min. Mag.*, 1970, **37**, 771–779.
12. Weyl, W. A. and Marboe, E. C., *The constitution of glasses* (*VII*). John Wiley and Sons, Inc., New York, 1962.
13. Uhlmann, D. R., In *Nucleation and crystallization in glasses*, ed. J. H. Simmons, D. R. Uhlmann and E. H. Beall. American Ceramic Society, Columbus, Ohio, 1982.
14. Weyl, A., *Coloured glass*. Society of Glass Tech, Shaffield, England, 1951.
15. Zdaniewski, W., DTA and X-ray analysis study of nucleation and crystallization of MgO-Al_2O_3-SiO_2 glasses containing ZrO_2, TiO_2 and CeO_2. *J. Am. Ceram. Soc.*, 1975, **58**(5–6), 163–169.
16. Barry, T. J., Clinton, D., Lay, L. A., Mercer, R. A. and Miller, R. P., The crystallization of glasses based on the eutectic composition in the system Li_2O-Al_2O_3-SiO_2; Part 2 lithium metasilicate eucryptite. *J. Mater. Sci.*, 1970, **5**(2), 117–126.
17. Dingwell, D. B., Scarfe, C. M. and Cronin, D. J., The effect of fluorine on viscosities in the system Na_2O-Al_2O_3-SiO_2: implications for phonolites, trachytes and rhyolites. *Am. Min.*, 1985, **70**, 80–87.
18. Uhlmann, D. R. and Kreidl, N. J., *Glass science and technology: Structure, microstructure, and properties* (*4A*). Acad Press Inc., New York, 1990.
19. Mukherjee, S. P. and Rogers, P. S., Nucleation and crystal growth in silicate glasses containing fluorides. *Phys. Chem. Glasses*, 1967, **8**(3), 81–87.
20. Omar, A. A., Mohmoud, M. Y. and Salman, S. M., Crystallization of some fluorine-containing glasses trans. *J. Br. Ceram. Soc.*, 1979, **78**(4), 81–86.
21. Kitaigorodskii, I. I. and Khodakovskaya, R. Ya., Some principles of the conversion of glass to pyroceram in the system SiO_2-Al_2O_3-MgO. *Inorg. Mater.*, 1965, **1**(5), 729–735.
22. Vogel, W. and Holand, W., *Advances in ceramics*, *Vol. 4*, ed. J. H. Simmons, D. R. Uhlmann and G. H. Beall. American Ceramic Society, Westerville, 1982, pp. 125–145.
23. Roginiskaya, Yu. F., Pavlushin, N. M., Surkisov, P. D., Matveev, T. S., Livorskaya, G. P. and Chernyak, N. S., Effect of flourine on crystallization of glasses in the CaO-Al_2O_3-SiO_2 alkali metal oxide system. *Inorg. Mater.*, 1975, **11**(1), 115–118.
24. Markis, J. H., Clemens, K. and Tomozawa, M., Effect of fluorine on the phase separation of sodium monoxide-silicon dioxide glasses. *J. Am. Ceram. Soc.*, 1981, **64**(1), C-20.
25. Lyung, S. N. and Popescu-Has, D., Porcelain from glass. *Glastech. Ber.*, 1958, **31**(9), 357.
26. Sil'Vestrovich, S. I. and Rabinovich, E. M., Opacifying particles in fluoride and phosphate opaque glasses. *Zh. Vses. Khim. Obshch.*, 1960, **5**, 186.
27. Stookey, S.D. US Patent 2,920,971. Singer, T.h.; 1946. Ceramic cordierite bodies. J. Can. Ceram. Soc. 15, 60; 1960.
28. Putnis, A. and Bish, D. L., The mechanism and kinetics of Al, Si ordering in Mg-cordierite. *Am. Mineral.*, 1983, **68**, 60–65.
29. Bozudzhiev, L., Crystallization properties of the basaltic fusions. *God Vissh. Khim-Tekhnal Inst, Burgos*, 1973, **9**, 47–53.