

THE EFFECT OF NUCLEATION CATALYSTS ON CRYSTALLIZATION CHARACTERISTICS OF ALUMINOSILICATE GLASSES

SAMIA N. SALAMA, SAAD M. SALMAN, HUSSEIN DARWISH

*Glass Research Dept.,
National Research Centre,
Dokki, Cairo, Egypt*

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The effects of compositional variation, nucleation catalyst and thermal treatment on the nature, type and stability field of crystallizing phases and microstructure formed in CaO and/or MgO aluminosilicate glasses are described using differential thermal analysis (DTA), X-ray powder diffractometry (XRD) and scanning electron microscopy (SEM). Wollastonite solid solution was formed in calcium aluminosilicate glass-ceramics, however, with MgO replacing CaO, pyroxene solid solution was developed. The addition of the nucleants brings varieties of aluminosilicate phases e.g., plagioclase, melilite and spodumene developed together with fluorite, fluorosilicate and/or TiO₂-bearing phases. Intense uniform bulk crystallization with fine-grained microstructure was achieved by an addition of TiO₂ or CaF₂ rather than LiF. The role of the nucleating agents during the formation of the crystal phases and the microstructure of the resultant glass-ceramics are discussed.

Keywords: Crystallization, Aluminosilicate glasses

INTRODUCTION

Glass-ceramics are polycrystalline solids produced by the controlled crystallization of glass. Glass-ceramic structure is characterized by fine-grained, randomly oriented crystals with some residual glass, without voids, microcracks or other porosity. The basis of controlled crystallization lies in efficient nucleation [1]. Different varieties of nucleating agents greatly promote the crystallization process of the glass and enhance the formation of fine-grained microstructure [1]. The mechanism of the process is greatly related to the type of catalysts and chemical systems of the base glass-composition. The properties of glass-ceramics are determined both by the inherent characteristics of the constituent phases and by the form of the microstructure resulting from the nucleation and growth sequence [2]. The use of efficient nucleating agent has allowed the development of highly crystalline material of wide industrial application [3]. Pyroxenes are most desirable mineral phases, crystallized in CaO-MgO-Al₂O₃-SiO₂ glasses due to their interesting properties [4]. The formation of glass-ceramic material based on such glass constituents catalyzed by different nucleating agents like CaF₂, LiF or TiO₂ is the object of the present work. The study aims to establish the crystallization characteristics and microstructure of the resulting material in relation to the base glass composition and the nucleant added.

EXPERIMENTAL

Glass composition and preparation

The glass compositions based on the multi-component system, Na₂O-CaO-MgO-Al₂O₃-SiO₂ were selected for the present study. The composition of the glasses studied are (32-x)CaO-xMgO-5Na₂O-7Al₂O₃-56SiO₂, where x = 0 in G₁ and x = 16 in G₂. Similar glass compositions-containing nucleation catalysts were also prepared. The nucleant additions were 6 g CaF₂, 6 g LiF or 10 g TiO₂ to 100 g of the base glass oxides.

Purified silica sand, analytical grade of CaCO₃, MgCO₃, Na₂CO₃ and calcined alumina, with additions of high purity CaF₂, LiF or TiO₂ as nucleating agents were used as starting material for batch preparation. The weighed batch materials, after thorough mixing were melted in platinum crucibles in an electric furnace with SiC heating elements at 1350 - 1450°C for 3 hours depending upon the type of nucleation catalyst added. The melt-containing TiO₂ were relatively more viscous than those containing fluorides. The sample containing LiF melts more easily than those containing TiO₂ or CaF₂. The homogeneity of the melt was achieved by frequent swirling the melt-containing crucible several times at about 20 min. intervals. After complete melting and refining, the glass melt was cast into rods, which were then properly annealed in a muffle furnace to minimize the residual stresses.

Differential thermal analysis

The thermal behaviour of the glasses was followed by the DTA technique. The DTA thermograms were carried out using Seiko 2200 thermal analyzer with 50 mg of the fine powdered glass against Al_2O_3 powder as reference material. A heating rate of $20^\circ\text{C}/\text{min}$ and sensitivity setting $20 \mu\text{V}/\text{inch}$ were maintained.

Thermal treatment

The glass samples were heated in a muffle furnace to the required heat-treatment temperature, in the nucleation and crystallization range, determined according to the DTA results. Therefore, double stage heat-treatment were used where the glass sample was kept for 5 h at the first DTA endothermic peak temperature and then thermally treated for 10 h at a temperature around the DTA exothermic effects.

Material investigation

Identification of crystal phases precipitating due to the course of crystallization was conducted by the X-ray diffraction analysis of the powdered samples. The X-ray diffraction patterns were obtained by using a Philips-type diffraction (P.W. 1730) with Ni-filtered Cu-K α radiation. Tube voltage of 40 kV and current of 25 mA were applied for the radiation. Scanning speed $2^\circ 2\theta/\text{min}$, paper speed 1 cm/min and pulse/sec. 2×10^3 were used in these analysis. The reference data for the interpretation of the X-ray diffraction patterns were obtained from ASTM X-ray diffraction card file.

The crystallization characteristics and internal microstructures of the resultant materials were examined on the fractured surfaces of the samples by scanning electron microscopy (SEM), where representative electron micrographs were obtained using a Senco Nanolab 7 scanning electron microscope.

RESULTS

The DTA thermograms of the glasses are presented by figure 1. The results of the X-ray diffraction analysis of the crystallized glasses are shown in figures 2 and 3. Table 1 gives a summary of the crystalline phases developed in the crystallizing glasses.

Crystallization characteristics of the catalyst-free glasses

Sluggish crystallization characteristics were observed for the catalyst-free glasses (G_1 and G_2). The crystallization began essentially at about 900°C from the surface of glass 1 and through the bulk of glass 2 and continued inwards as the temperature increased. Crystallization of the glasses around the exothermic peak temperature (1000 – 1020°C) for 10 hours duration generally developed a holocrystalline non-deformed mass of a coarse microstructure of fibrous growths in G_1

and an interlocked aggregates or rounded-like growths in G_2 glass (figures 4a and 5a).

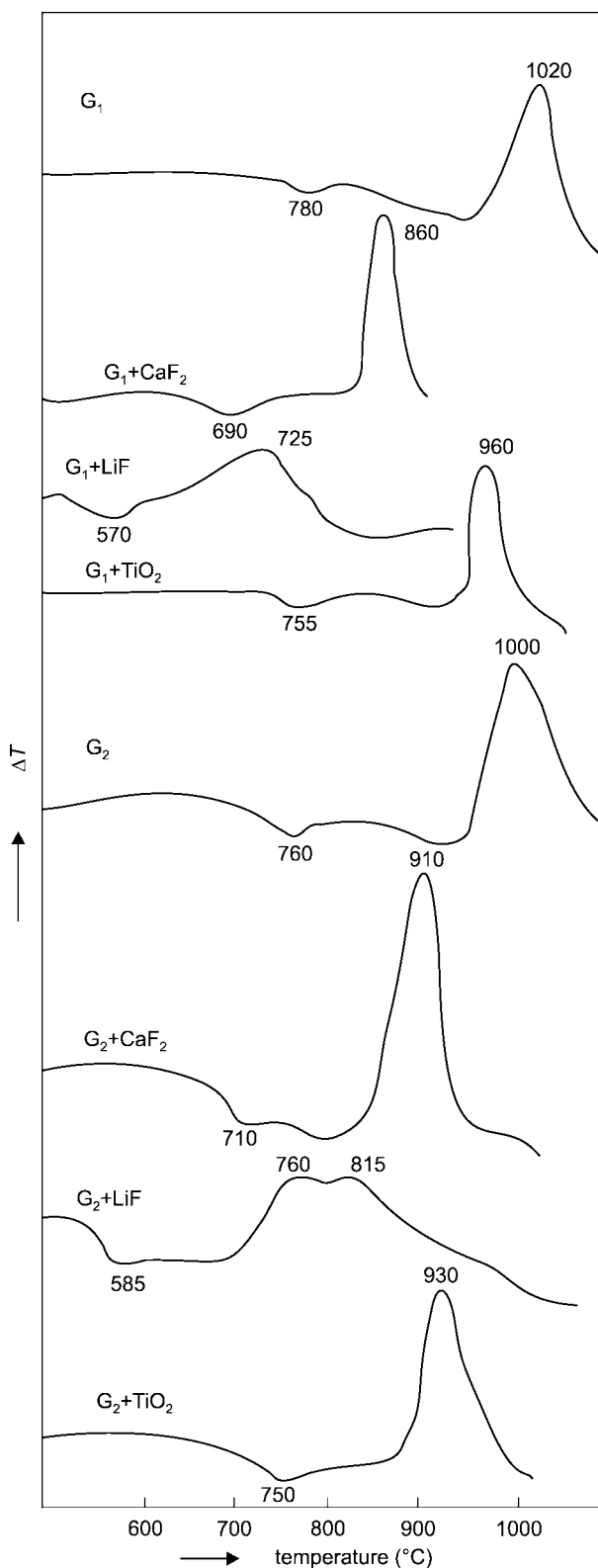


Figure 1. DTA thermograms of the studied glasses.

Table 1. A summary of the crystal phases developed in the glasses after heat-treatment.

glass no.	nucleation agent	heat-treatment (°C/h)	crystalline phases developed
G ₁	-	780/5-1020/10	wollastonite solid solution
G _{1-CF}	CaF ₂	690/5-860/10	anorthitic plagioclase, Ca ₂ SiO ₂ F ₄ , gehlenite, wollastonite
G _{1-LF}	LiF	570/5-725/10	wollastonite, spodumene, gehlenite, CaF ₂
G _{1-T}	TiO ₂	760/5-960/10	wollastonite, titanite, anorthitic plagioclase
G ₂	-	760/5-1000/10	pyroxene solid solution
G _{2-CF}	CaF ₂	710/5-910/10	diopsidic pyroxene, anorthite, plagioclase, CaF ₂
G _{2-LF}	LiF	580/5-820/10	diopsidic pyroxene, Li-phlogopite
G _{2-T}	TiO ₂	750/5-930/10	pyroxene solid solution, titanite, MgTiO ₃

The sole crystalline phase developed in the heat-treated G₁ glasses was wollastonite solid solution. The XRD analysis (figure 2, pattern I) clearly indicated the diffraction lines (7.63, 3.81, 3.50, 3.30, 3.07 and 2.96), which are greatly identical, with a slight shift, to those of wollastonite (card No. 29-372). On partial replacement of CaO by MgO (i.e. G₂) clinopyroxene solid solution was formed where its d-spacing lines (figure 3, pattern I, lines 3.3, 3.21, 2.98, 2.93, 2.88, 2.547, 2.52 and 2.49) were very similar to those of diopside (card No. 17-318).

Crystallization characteristics of the nucleated glasses

a) Effect of CaF₂

The results showed that the addition of 6 wt.% CaF₂ into G₁ and G₂ composition decreased the glass melting temperature by about 100°C. The addition also decreased the temperature at which the crystallization started, and increased crystallizability (figure 1). The presence of CaF₂ greatly increased the rate of nucleation in the glass during heating. It showed a powerful catalytic effect on crystallization of the present glasses to the extent that almost holocrystalline material was obtained at about 900–925°C. The crystallization proceeded readily with the two-step heat-treatment by internal (bulk) nucleation rather than surface nucleation mode of tiny aggregates of prismatic, dendritic and/or numerous spherulite-like growths as indicated by SEM of the fractured surface of nucleated samples (figure 5b), providing in most cases non-deformed ceramic materials.

The presence of CaF₂ in the glasses facilitated the crystallization of anorthitic type plagioclase and gehlenite. It enhanced the disintegration of the wollastonite solid solution into anorthite, gehlenite and wollastonite. Alkali aluminous wollastonite solid solution was detected only in the crystallization of G₁ (figure 2, pattern I), while the d-spacing reflections of anorthite (lines 3.75, 3.64, 3.46, 3.36, 3.24, 3.2, 3.17, 3.05...), gehlenite (lines 3.75, 3.07, 2.86, 2.44, 2.406 and 1.93) and wollastonite together with Ca₂SiO₂F₄ (lines 7.37, 3.24, 3.07, 2.947 and 2.86) were detected in

the diffraction patterns of the fluoride sample G_{1-CF} (figure 2, pattern II).

The presence of CaF₂ helps also in disintegration of the clinopyroxene solid solution (i.e., alkali-aluminous pyroxene solid solution) formed in G₂ glass (figure 3, pattern I) into anorthite (pattern II) and diopside in the sample nucleated by CaF₂. Fluorite (lines 3.14, 1.92 and 1.62) was also encountered among the crystallization products of the glass.

b) Effect of LiF

The addition of LiF to the glass batch decreased the melting temperature (by about 100–150°C) of the glass as compared with that free of catalyst. It greatly lowered the temperature at which the crystallization begins by about 200°C, and enhanced the crystallizability of the glass. The DTA thermograms (e.g., G₁, G_{1-LF} and G₂, G_{2-LF} in figure 1), showed that the span of exothermic crystallization peaks of the glass were enlarged and shifted to lower temperature by LiF addition.

From the microstructure, standpoint, SEM of the fractured surface of the glass-ceramics (figure 4b) showed the main effect of LiF on the crystal growth with almost slight effect on the nucleation process. This is illustrated by the higher crystallizability and the relatively coarser microstructure developed.

The presence of LiF in the glasses greatly facilitated the formation of gehlenite, spodumene and Li-phlogopite as indicated by the X-ray analysis (figures 2 and 3). Gehlenite, lithia aluminosilicate as β-spodumene phase (figure 2, pattern III, lines 4.62, 3.90, 3.47, 3.15, 1.92 and 1.87) were crystallized in the glass of G₁ (with CaO) nucleated by LiF, while Li-phlogopite (figure 3, pattern III, lines 9.73, 3.14 and 1.92) together with diopsidic pyroxene, were detected in G₂ (with CaO and MgO).

c) Effect of TiO₂

It was found practically that the addition of 10 wt.% TiO₂ to the base glasses (G₁ or G₂) improved the batch melting and the crystallizability of the glass through its bulk. The presence of TiO₂ resulted in a decrease in the temperatures of melting by about 100°C,

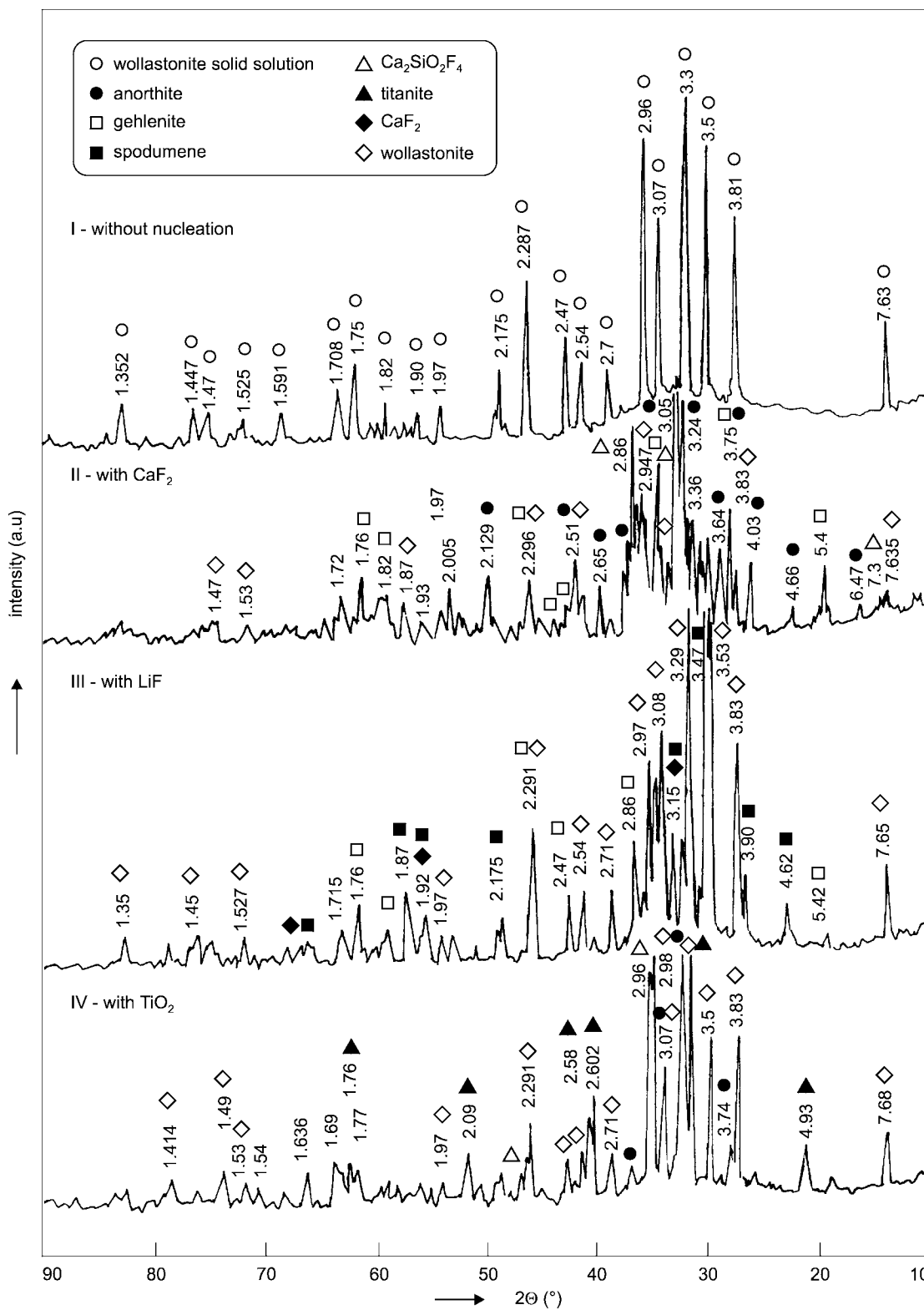


Figure 2. XRD patterns of crystallized glass 1 with and without nucleation catalyst.

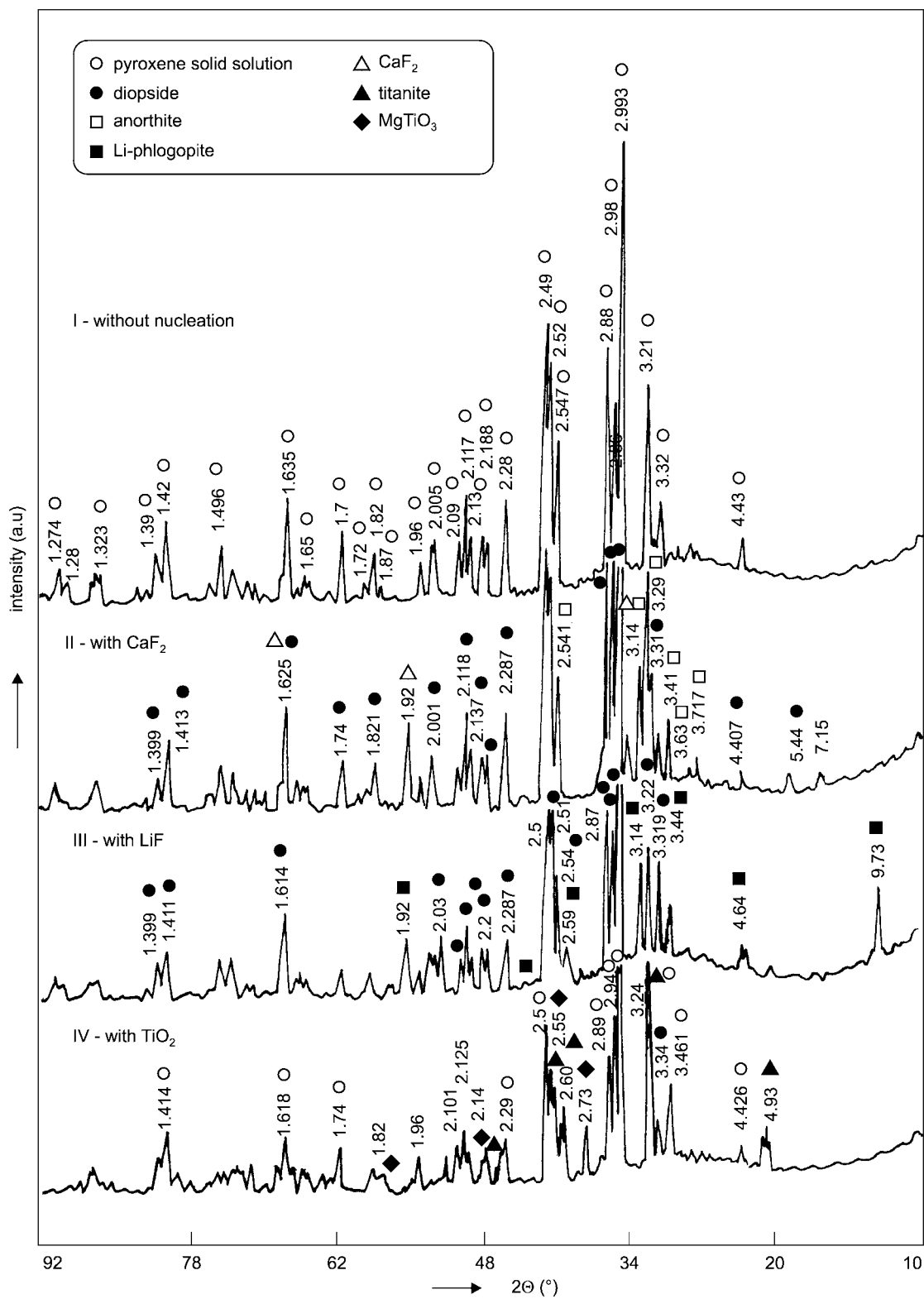


Figure 3. XRD patterns of crystallized glass 2 with and without nucleation catalyst.

and noticeably modified its crystallization kinetics. The DTA results indicated that introduction of TiO_2 in the glass resulted in a decrease in the temperature of onset of crystallization by about 50°C . However, its effect on the beginning of crystallization by the glasses is less than that occurred by CaF_2 or LiF .

Intense uniform bulk crystallization with fine-grained microstructures was achieved on addition of TiO_2 to the glass G_1 or G_2 . The SEM (figures 4c and 5c) revealed that the addition of TiO_2 led to the development of volume crystallization of tiny aggregate-like growths to provide a non-deformed ceramic material.

The X-ray diffraction analysis (figure 2, Pattern IV) revealed that the presence of TiO_2 in the CaO glass (G_1) has a catalytic effect on the crystallization of anorthitic plagioclase phase. It also favoured the formation of titanite phase- CaTiSiO_5 (lines 4.93, 3.24, 2.986, 2.602 and 2.58), among the crystallization products of glass G_1 . However, the addition of TiO_2 to the CaO , MgO -silicate glass i.e., G_2 , was found to be preferentially nucleates the formation of titanite- CaTiSiO_5 and MgTiO_3 (lines 2.73, 2.55, 2.21 and 1.85), beside the pyroxene solid solution, as indicated by the X-ray diffraction analysis (figure 3, pattern IV).

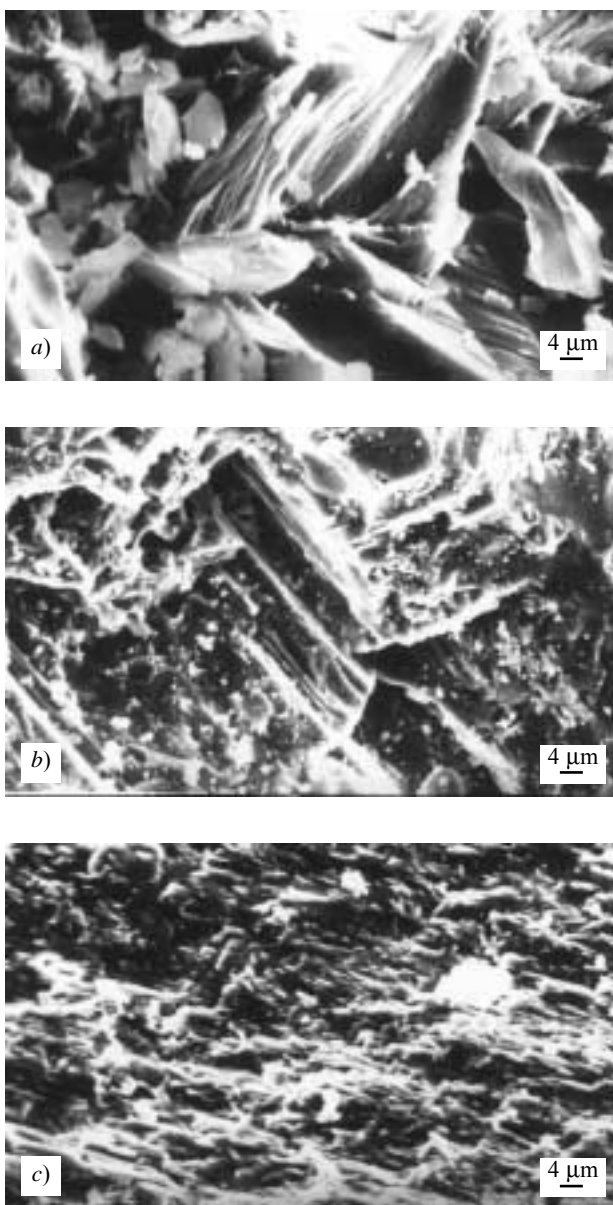


Figure 4. SEM micrographs of fractured surface of CaO -glass-ceramics showing the effect of nucleation on the microstructure.

a) without nucleation, b) with LiF , c) with TiO_2

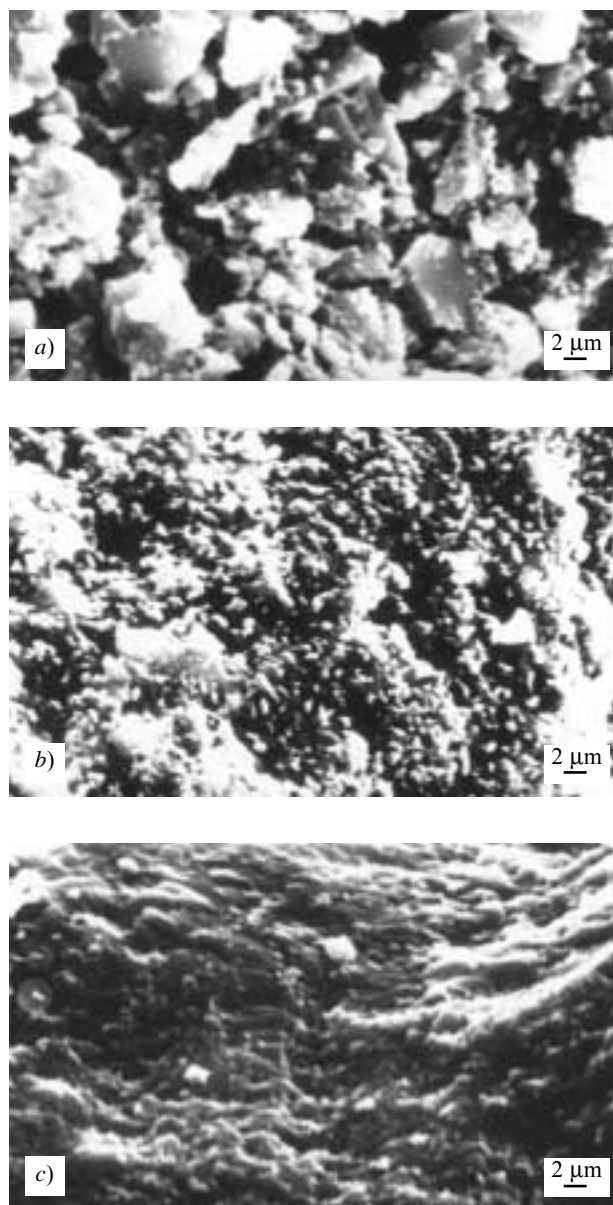


Figure 5. SEM micrographs of fractured surfaces of CaO - MgO -glass - ceramics showing the effect of nucleation on the microstructure.

a) without nucleation, b) with CaF_2 , c) with TiO_2

DISCUSSION

Crystallization characteristics of the base glasses

It is a well-known fact that alumina and silica are effective in increasing the viscosity of the glass due to the formation of polymorph units like SiO_4 and AlO_4 groups, which had an effect on the strength of the network of the obtained glasses structure. It was considered that the trivalent ions would form highly stable triangular or tetrahedral structure building units and the viscosity of the glass would depend on the strength of the oxygen linkages at the corners of adjoining units. The presence of Al_2O_3 in silicate glass causes an accumulation of different groups as clusters, which may explain the observed increase of viscosity in the present glass [5]. A sluggish crystallization nature of the base glasses was, therefore, observed although both CaO and MgO are effective in lowering viscosity of such melts and glasses [5]. The glasses did not attain the holocrystalline state below 1000–1020°C for 10 hours duration.

Although wollastonite has been reported to be composed mainly of CaSiO_3 [6], the wollastonite structure can accept considerable amount of Mn, Fe and Mg [6]. There is a solid solution between wollastonite and diopside - $\text{CaMgSi}_2\text{O}_6$ [7]. Only limited solid solution of akermanite- $\text{CaMgSi}_2\text{O}_6$ and/or gehlenite- $\text{Ca}_2\text{Al}_2\text{SiO}_7$ in wollastonite was detected [6]. It was shown that wollastonite and pseudo-wollastonite could acquire considerable amounts of aluminium, sodium and potassium oxides in their structure and Ca-Tschermak's may accommodate in the wollastonite.

X-ray analysis revealed that the base glass (G_1) crystallized into a new variety of monomineralic wollastonite solid solution phase. The d-spacing reflections of the solid solution are greatly similar to those of wollastonite. The displacement of the major characteristic d-spacing reflections of this metasilicate solid solution towards higher 2θ values may support the suggestion that both Al^{3+} and Na^+ ions were incorporated in the wollastonite structure and based on the petrochemical calculations [8], an alkali aluminous wollastonite solid solution variety of the probable formula $(\text{Ca}_{0.76}\text{Na}_{0.24})(\text{Si}_{0.8}\text{Al}_{0.2})\text{O}_3$ could be obtained. In the base glass G_2 , in which the CaO was partially replaced by MgO, pyroxene solid solution of diopside type was only crystallized as indicated by X-ray diffraction analysis. Glass G_2 has CaO/MgO molar ratio equal to unity, therefore, the CaO is present in just enough amounts to combine with the MgO in such silicate glass to form pyroxene phase of diopside type as follows:



Pyroxene consists of a group of minerals of variable composition, which crystallized fairly readily. They are closely related in crystallographic and other physical properties as well as in chemical compo-

sition [6]. A wide variety of ionic substitutions occur in the members of the pyroxene group. The complexity of this group is exhibited by the wide isomorphism of the various elements in the expandable pyroxene formula [9] $\text{W}_{1-p}(\text{X}, \text{Y})_{1+p}\text{Z}_2\text{O}_6$, where $\text{W} = \text{Ca}, \text{Na}$; $\text{X} = \text{Mg}, \text{Fe}^{2+}, \text{Mn}, \text{Zn}, \text{Li}$; $\text{Y} = \text{Al}, \text{Fe}^{3+}, \text{Cr}, \text{Ti}$; $\text{Z} = \text{Si}, \text{Al}, \text{Fe}^{3+}$ and $P =$ number of ions.

The development of d-spacing reflections (e.g., 2.98, 2.93, 2.547, 2.52, 2.49...) in the XRD of G_2 and displacement of the major characteristics d-spacing lines of the pyroxene variety towards higher 2θ values may support the suggestion that both Al^{3+} and Na^+ were accommodated in the diopside pyroxene solid solution phase. Diopside, $\text{CaMgSi}_2\text{O}_6$ is a proper pyroxene in which there are several series of solid solutions with a coupled substitution of ions for Mg and Si.

The isomorphous incorporation of the $\text{CaAl}_2\text{SiO}_6$ and $\text{NaAlSi}_2\text{O}_6$ component in the diopside structure is well known [10, 11]. In the presence of diopside structure phase as a host structure, Na^+ and Al^{3+} may be incorporated in the 8 and 6 fold coordinations in replacing Ca^{2+} and Mg^{2+} , respectively. It was shown that diopside can accommodate up to 48 % of the $\text{CaAl}_2\text{SiO}_6$ molecule in its structure, crystallizing under non-equilibrium conditions, to form a complex pyroxene solid solution phase [10,12]. In the presence of Al, sodium can also enter in diopside [6] (as $\text{NaAlSi}_2\text{O}_6$) only in small quantities. The maximum solubility of $\text{NaAlSi}_2\text{O}_6$ molecule in diopside is about 10 wt.%, which corresponds to about 2.5 wt.% Na_2O .

Therefore, in glass G_2 , it seems that both $\text{CaAl}_2\text{SiO}_6$ and $\text{NaAlSi}_2\text{O}_6$ components could be present but accommodated in the pyroxene (diopside)-base structure under favourable conditions of crystallization and the crystallizing glass yields monomineralic pyroxene products of complex alkali aluminous diopside composition. Based on the normative calculation, the pyroxene solid solution formed may have the probable formula, $(\text{Na}_{0.38}, \text{Ca}_{0.62})(\text{Mg}_{0.62}, \text{Al}_{0.38})(\text{Si}_{1.86}, \text{Al}_{0.14})_2\text{O}_6$.

Crystallization characteristics of nucleated glasses

a) Effect of CaF_2

In silicate glasses fluorine makes nonbridging bond of Si-F, resulting in the decrease of viscosity and in some silicate glasses fluorine promotes probably the phase separation leading to a decrease in the energy barrier necessary for crystallization. In many cases, phase separation alone is not, however, sufficient to induce bulk crystallization in the glass. This is greatly dependent on both the actual chemical compositions of the glass and the fluoride content [13].

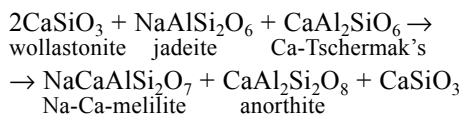
Fluor-substituted layer silicate of the mica type may separate from fluorine-containing glass [14]. It was suggested that [15] the crystallization is initiated by the formation of crystalline nuclei consisting of a simple binary fluoride. These nuclei then act as heterogeneous centers for the growth of the first crystalline silicate

phase. Lyng [15] and Lyng et. al.[16] pointed out that, in the fluorine -containing aluminosilicate glasses of more than 5 wt.% MgO, the first crystalline phase developed seems to be a layer type silicate, while below 5 wt.% MgO, CaF₂ could be identified.

The presence of the fluorine in the studied glass favours the formation of fluorite, calcium fluorosilicate Ca₂SiO₂F₄ or Li-phlogopite (LiAlMg₃Si₃O₁₀F₂). This was found to be dependent on the overall chemical composition of the parent glass and the type of fluorine added rather than on the MgO content present in the glass. In G_{1-CF}, CaF₂ was combined with some of SiO₂ to form calcium fluorosilicate-Ca₂SiO₂F₄, while fluorite-CaF₂ phase was identified in G_{2-CF}. Actually both of the MgO and CaO content are the same in this glass composition, which are just enough to combine in such silicate glass to form the high stable diopsidic pyroxene phase (as proved by XRD). Therefore, there is no remaining MgO molecule present to combine with the CaF₂ to form a more complex fluoride phase.

The enhancement effect of CaF₂ on the formation of gehlenite in G₁ and anorthite in both the glasses of G₁ and G₂ is mainly due to the reducing effect of fluorine on the glass viscosity, which subsequently increases the mobility and diffusion of complex ions. Also the reduction of viscosity by the addition of calcium fluoride to the composition will enhance the kinetics of formation of crystals, but the composition of the crystalline phases produced will be dependent on the composition of the glass. Addition of CaF₂ will increase the calcium content as well as the fluorine content, and will thus affect the final phase assemblage for both reasons.

The petrochemical calculation of G₁ into normative mineral molecules revealed that, both NaAlSi₂O₆ and CaAl₂SiO₆ molecules could be formulated and may be accommodated in the wollastonite structure to form the alkali-aluminous wollastonite solid solution phase i.e., (Ca, Na)(Si, Al)O₃ as proved by X-ray analysis. However, in the presence of CaF₂, it seemed that a redistribution of the element may take place and both anorthite and melilite phases, beside wollastonite, were encountered as follows:



The effectiveness of CaF₂ in facilitating the migration of ions and ionic complex in glass of G₂ may also caused the decomposition of the complex alkali aluminium pyroxene solid solution phase (Na, Ca)(Mg, Al)₂O₆ formed in the base glass ceramic into diopsidic pyroxene CaMgSi₂O₆ and anorthitic plagioclase phase in CaF₂-containing variety.

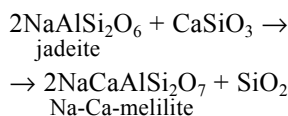
b) Effect of LiF

The results showed that introduction of 6 wt.% LiF into the glasses markedly decreases the temperatures of

both melting and beginning of crystallization. The DTA results (figure 1) showed that the addition of LiF enlarge the span of the crystallization temperature range of the glass. This will allow the heat evolved during crystallization to disperse over a wider temperature span and thus facilitate the glass-ceramic formation. Relative to the other nucleators used, LiF showed a powerful catalytic effect on crystallizing the present glasses to the extent that almost holocrystalline materials were obtained, while they partially crystalline with the others. This was greatly correlated with the role played by fluorine ions which act as network breaker in the glass structure due to their ability to remove bridging oxygen resulted into weaken the glass structure and facilitate the glass crystallization. Li⁺ ions have also a tendency to weaken the glass structure and to reduce the viscosity of the glass [3] and thus aid in crystallization of the glass. The crystallization of LiF-nucleated glasses, however, produced readily by internal nucleation giving rise to coarser-grained microstructure.

Mineralogically, the presence of LiF catalyzed the formation of gehlenite in the glass of G₁. It also favoured the crystallization of lithium aluminosilicate as β-spodumene phase.

The presence of LiF provides sufficient Li⁺ ions to establish β-quartz solid solution-like phase, the Ca²⁺ ions react with the F⁻ ions giving rise to a CaF₂ phase, the presence of which was confirmed by XRD. The Na⁺ ions present in the glass G₁ seemed to be combined with the residual alumina to form NaAlSi₂O₆ molecule (jadeite) which react with the proper amount of CaSiO₃ to form Na-Ca-melilite phase according to the following equation:



The resulted silica can be incorporated in the β-quartz solid solution phase and at temperature as high as 900°C, β-quartz was transformed into keatite solid solution i.e., β-spodumene as proved by XRD. The presence of LiF in the glass of G₂ favoured the formation of Li-phlogopite-LiMg₃AlSi₃O₁₀F₂. The Li-phlogopite variety is related to the fluor-mica type in which the hydroxyl ions in the layer are replaced by fluorine ions. The general formula of mica may be written as, X₀₋₁Y₂₋₃(Al, Si)₄O₁₀(OH, F)₂, where X- could be K, Ca, Na, Rb, Sr and Y- could be Al, Mg, Fe, Mn, V, Ti and Li [17].

In the glass G₂, it is believed that most of Al₂O₃ together with MgO are incorporated in the β-quartz solid solution. Therefore, in the presence of LiF, the most probable explanation is that at the proper heat-treatment regime a layer type silicate, i.e., lithium phlogopite-LiAlMg₃Si₃O₁₀F₂ is developed which is characterized by d-spacing 9.73 and 3.14 Å.

c) Effect of TiO₂

Concerning the role of TiO₂ during the crystallization of the glasses, a number of pre-crystalline events, such as enhanced amorphous phase separation and/or appearance of trace nucleant phase [3], are probable and responsible for the uniformity and finess of the microstructure. It is well known also that Ti⁴⁺ can be accommodated in the glass structure either as network-former or as network-modifier [3]. The Ti⁴⁺ occupancy of Si⁴⁺ sites in the glass structure introduces a Ti-O bond that is weaker than the Si-O bond [18]. This leads to improve the batch melting and crystallizability of the glass.

The addition of TiO₂ in the glass enhances the crystallization of anorthite, plagioclase and titanite-CaTiSiO₅ (beside wollastonite) in G_{1-T}, titanite and MgTiO₃ (beside pyroxene solid solution) in G_{2-T}. The crystallization of plagioclase phase in G₁ could be related to the influence of TiO₂ in reducing the viscosity of the glass during crystallization [3] and consequently increasing the diffusion rate of ions and ionic complexes forming glass, thereby facilitating the formation of the structurally more complex phase like anorthitic plagioclase. On the other hand, the formation of titanite phase in both G_{1-T} and G_{2-T} is attributed to the accommodation of appreciable TiO₂ in the CaSiO₃ structure since Ti⁴⁺ can replace Si⁴⁺ in the tetrahedral positions of the wollastonite [19]. The formation of CaTiSiO₅ (i.e., CaSiO₃ + TiO₂) in G_{2-T} leaves behind the CaSiO₃-MgSiO₃ i.e., (diopside molecule) formed in G₂ rich in MgO content, i.e., the MgO content is more than that needed to form diopside. This excess of MgO can react with some of TiO₂ to form MgTiO₃.

CONCLUSION

Glass-ceramics materials nucleated by CaF₂, LiF or TiO₂ could be obtained by controlled crystallization of sodium calcia and/or magnesia aluminosilicate glasses.

Wollastonite or diopside phase can accommodate Na⁺ and Al³⁺ in their structure to form aluminous wollastonite and pyroxene solid solution phases of the probable formula, (Ca_{0.76}Na_{0.24})(Si_{0.8}Al_{0.2})O₃ and (Na_{0.38}, Ca_{0.62})(Mg_{0.62}, Al_{0.38})(Si_{1.86}, Al_{0.14})₂O₆, respectively. On addition of nucleation catalyst, decomposition of these phases was crystallized as well. The kinetics of phase transformation, the final phase assemblages and microstructure formed were greatly dependent on the type of the nucleant added. Fluorides are more effective in facilitating the formation of aluminosilicates than TiO₂. TiO₂ and CaF₂, however, had more influence to initiate intense uniform fine-grained microstructure than LiF.

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VLIV NUKLEAČNÍCH ČINIDEL
NA KRYSTALIZACI HLINITOKŘEMIČITÝCH SKEL

SAMIA N. SALAMA, S. M. SALMAN, H. DARWISH

*Glass Research Dept., National Research Centre,
Dokki, Cairo, Egypt*

Byly studovány účinky změn složení, nukleačních katalyzátorů a tepelného zpracování na povahu, typ a stabilitní pole krystalických fází a mikrostrukturu CaO/MgO aluminosilikátových skel pomocí diferenční termické analýzy (DTA), rentgenové práškové difraktometrie (XRD) a řádkovací elektronové mikroskopie (SEM). Tuhý roztok wollastonitu ve vápenaté aluminosilikátové sklokeramice se mění s nahrazením MgO za CaO na pyroxenový tuhý roztok. Přídavkem nukleačních činidel vznikaly různé aluminosilikátové fáze jako plagioklas, melilit a spodumen spolu s fluoritem, fluorosilikátem a/nebo TiO₂ obsahujícími fázemi. Byl diskutován mechanismus působení nukleačních činidel na tvorbu krystalických fází a mikrostrukturu výsledných sklokeramických materiálů.