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 compositions 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 \((32-x)\text{CaO-}x\text{MgO-}5\text{Na}_{2}\text{O-}7\text{Al}_{2}\text{O}_{3-}56\text{SiO}_{2}\), 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 Al₂O₃ powder as reference material. A heating rate of 20°C/min and sensitivity setting 20 µV/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-Kα radiation. Tube voltage of 40 kV and current of 25 mA were applied for the radiation. Scanning speed 2° 2θ/min., paper speed 1 cm/min and pulse/sec. 2 × 10³ 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 Semco 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 (G₁ and G₂). 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 G₁ and an interlocked aggregates or rounded-like growths in G₂ glass (figures 4a and 5a).

![Figure 1. DTA thermograms of the studied glasses.](image)
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).

Crystalization 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 anorthetic type plagioclase and gehlenite. It enhanced the disintegration of the wollastonite solid solution into anorthite, gehlenite and wollastonite. Alkali aluminous wollastone 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 Ca3SiO2F4 (lines 7.37, 3.24, 3.07, 2.947 and 2.86) were detected in the diffraction patterns of the fluoride sample G1-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, G1-LF and G2, G2-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 diopside 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,

<table>
<thead>
<tr>
<th>Glass no.</th>
<th>Nucleation agent</th>
<th>Heat-treatment (°C/h)</th>
<th>Crystalline phases developed</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>-</td>
<td>780/5-1020/10</td>
<td>Wollastonite solid solution</td>
</tr>
<tr>
<td>G1-CF</td>
<td>CaF2</td>
<td>690/5-860/10</td>
<td>Anorthite plagioclase, Ca3SiO2F4, gehlenite, wollastonite</td>
</tr>
<tr>
<td>G1-LF</td>
<td>LiF</td>
<td>570/5-725/10</td>
<td>Wollastonite, spodumene, gehlenite, CaF2</td>
</tr>
<tr>
<td>G1-T</td>
<td>TiO2</td>
<td>760/5-960/10</td>
<td>Wollastonite, titanite, anorthite plagioclase</td>
</tr>
<tr>
<td>G2</td>
<td>-</td>
<td>760/5-1000/10</td>
<td>Pyroxene solid solution</td>
</tr>
<tr>
<td>G2-CF</td>
<td>CaF2</td>
<td>710/5-910/10</td>
<td>Diopside pyroxene, anorthite, plagioclase, CaF2</td>
</tr>
<tr>
<td>G2-LF</td>
<td>LiF</td>
<td>580/5-820/10</td>
<td>Diopside pyroxene, Li-phlogopite</td>
</tr>
<tr>
<td>G2-T</td>
<td>TiO2</td>
<td>750/5-930/10</td>
<td>Pyroxene solid solution, titanite, MgTiO3</td>
</tr>
</tbody>
</table>
Figure 2. XRD patterns of crystallized glass 1 with and without nucleation catalyst.
The effect of nucleation catalysts on crystallization characteristics of aluminosilicate glasses

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 aggregates-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 anorthic 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 SiO₂ and AlO₄ 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 Al₂O₃ in silicate glass causes an accumulation of different groups as clusters, which may explain the observed increase in 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 holocristalline state below 1000–1020°C for 10 hours duration.

Although wollastonite has been reported to be composed mainly of CaSiO₃ [6], the wollastonite structure can accept considerable amount of Mn, Fe and Mg [6]. There is a solid solution between wollastonite and diopside - CaMgSi₂O₆ [7]. Only solid solution of akermanite-CaMgSi₂O₆ and/or gehlenite-Ca₂Al₂SiO₇ 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 (G₁) 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 metastable solid solution towards higher 2θ values may support the suggestion that both Al³⁺ and Na⁺ ions were incorporated in the wollastonite structure under favourable conditions of crystallization [8], an alkali aluminous wollastonite solid solution variety of the probable formula, (Na₀.₃₈, Ca₀.₆₂)(Mg₀.₆₂, Al₀.₃₈)(Si₁.₈₆, Al₀.₁₄)₂O₆. The maximum solubility of NaAlSi₂O₆ 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 NaAlSi₂O₆) only in small quantities. The maximum solubility of NaAlSi₂O₆ molecule in diopside is about 10 wt.%, which corresponds to about 2.5 wt.% Na₂O. Therefore, in glass G₂, it seems that both CaAl₂SiO₆ and NaAlSi₂O₆ components could be present but accommodated in the pyroxene (diopsidic)-base structure under favourable conditions of crystallization and the crystallizing glass yields monomineralic pyroxene products of complex alkali aluminous diopsidic composition. Based on the normative calculation, the pyroxene solid solution formed may have the probable formula, (Na₀.₃₈, Ca₀.₆₂)(Mg₀.₆₂, Al₀.₃₈)(Si₁.₈₆, Al₀.₁₄)₂O₆.

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 composition [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] W₁₋₄(X, Y)₁₋₄Z₂O₆, where W = Ca, Na; X = Mg, Fe³⁺, Mn, Zn, Li; Y = Al, Fe³⁺, Cr, Ti; Z = Si, Al, Fe³⁺ 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 G2 and displacement of the major characteristics d-spacing lines of the pyroxene variety towards higher 2θ values may support the suggestion that both Al³⁺ and Na⁺ were accommodated in the diopsidic pyroxene solid solution phase. Diopside, CaMgSi₂O₆, 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 CaAl₂SiO₆ and NaAlSi₂O₆ component in the diopsidic structure is well known [10, 11]. In the presence of diopsidic structure phase as a host structure, Na⁺ and Al³⁺ may be incorporated in the 8 and 6 fold coordinations in replacing Ca²⁺ and Mg²⁺, respectively. It was shown that diopsidic can accommodate up to 48% of the CaAl₂SiO₆ 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 NaAlSi₂O₆) only in small quantities. The maximum solubility of NaAlSi₂O₆ molecule in diopside is about 10 wt.%, which corresponds to about 2.5 wt.% Na₂O.

Therefore, in glass G₂, it seems that both CaAl₂SiO₆ and NaAlSi₂O₆ components could be present but accommodated in the pyroxene (diopsidic)-base structure under favourable conditions of crystallization and the crystallizing glass yields monomineralic pyroxene products of complex alkali aluminous diopsidic composition. Based on the normative calculation, the pyroxene solid solution formed may have the probable formula, (Na₀.₃₈, Ca₀.₆₂)(Mg₀.₆₂, Al₀.₃₈)(Si₁.₈₆, Al₀.₁₄)₂O₆.

Crystallization characteristics of nucleated glasses

a) Effect of CaF₂

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, CaF$_2$ could be identified.

The presence of the fluorine in the studied glass favours the formation of fluorite, calcium fluorosilicate Ca$_2$SiO$_2$F$_4$ or Li-phlogopite (LiAlMg$_3$Si$_3$O$_{10}$F$_2$). 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, CaF$_2$ was combined with some of SiO$_2$ to form calcium fluorosilicate-Ca$_2$SiO$_4$F$_2$, while fluoride-CaF$_2$ 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 diopside pyroxene phase (as proved by XRD). Therefore, there is no remaining MgO molecule present to combine with the CaF$_2$ to form a more complex fluoride phase.

The enhancement effect of CaF$_2$ on the formation of gehlenite in G$_1$ and anorthite in both the glasses of G$_1$ and G$_2$ 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 CaF$_2$ 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 G$_1$ into normative mineral molecules revealed that, both NaAlSi$_2$O$_6$ and CaAl$_2$SiO$_4$ 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)O$_3$ as proved by X-ray analysis. However, in the presence of CaF$_2$, it seemed that a redistribution of the element may take place and both anorthite and melilite phases, beside wollastonite, were encountered as follows:

$$2\text{CaSiO}_3 + \text{NaAlSi}_2\text{O}_6 + \text{CaAl}_2\text{Si}_2\text{O}_6 \rightarrow \text{wollastonite jadeite Ca}-\text{Tschermak’s}$$

$$\rightarrow \text{NaCaAlSi}_5\text{O}_8 + \text{CaSi}_3\text{O}_3$$

$$\text{Na-Ca-melilite anorthite}$$

The effectiveness of CaF$_2$ in facilitating the migration of ions and ionic complex in glass of G$_2$ may also caused the decomposition of the complex alkali aluminium pyroxene solid solution phase (Na, Ca)(Mg, Al)$_3$O$_5$ formed in the base glass ceramic into diopside pyroxene CaMgSi$_2$O$_6$ and anorthitic plagioclase phase in CaF$_2$-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 G$_1$. 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 Ca$^{2+}$ ions react with the F$^{-}$ ions giving rise to a CaF$_2$ phase, the presence of which was confirmed by XRD. The Na$^+$ ions present in the glass G$_2$ seemed to be combined with the residual alumina to form NaAlSi$_3$O$_8$ molecule (jadeite) which react with the proper amount of CaSiO$_3$ to form Na-Ca-melilite phase according to the following equation:

$$2\text{NaAlSi}_2\text{O}_6 + \text{CaSiO}_3 \rightarrow \text{jadeite}$$

$$\rightarrow 2\text{NaCaAlSi}_3\text{O}_8 + \text{SiO}_2$$

$$\text{Na-Ca-melilite}$$

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 G$_2$ favoured the formation of Li-phlogopite-LiMg$_3$AlSi$_3$O$_{10}$F$_2$. 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, $X_{0.1-1}Y_{2.3}(\text{Al, Si})_3\text{O}_{10}(\text{OH, F})_2$, 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 G$_2$, it is believed that most of Al$_2$O$_3$ 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-LiAlMg$_3$Si$_3$O$_{10}$F$_2$, is developed which is characterized by d-spacing 9.73 and 3.14 Å.
The effect of nucleation catalysts on crystallization characteristics of aluminosilicate glasses

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 fineness of the micro-structure. 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 G₁-T, titanite and MgTiO₃ (beside pyroxene solid solution) in G₂-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 G₁-T and G₂-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 G₂-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, (Ca₀.₇₆Na₀.₂₄)(Si₀.₈Al₀.₂)O₃ and (Na₀.₃₈, lastonite and pyroxene solid solution phases of the Na⁺ and Al ³⁺ in their structure to form aluminous wollastonite.

References


VLIV NUKLEAČNÍCH ČINIDEL NA KRYSŤALIZACI HLINITOKREMIČITÝCH SKEL

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