Original Paper

Effect of Cr_2O_3, ZrO_2 and LiF on nucleation and crystallization of nepheline syenite-dolomite glass-ceramic compositions

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Inexpensive nepheline-pyroxene glass-ceramics of superior mechanical, and thermal properties could be easily prepared from nepheline syenite and dolomite rock mixture by using the conventional glass preparation and heat treatment methods. The parent glass composition, to yield ≈35 % nepheline ss (solid solution) and 65 % diopside ss, was formulated by a modified chemico-mineralogical calculation method after CIPW norm. The effect of the nucleating agents Cr_2O_3, ZrO_2 and LiF on the mechanisms of nucleation and crystallization of these phases were determined by DTA, XRD, as well as optical and electron microscopy.

In the absence of these nucleators, crystallization was difficult and semi-crystalline coarse microstructure of diopsidic ss was obtained. LiF showed maximum effect on crystal growth rates, while sufficient nucleation density for glass-ceramic of good quality was achieved by adding Cr_2O_3 even in the amount as small as 0.5 wt%. Both Cr_2O_3- and ZrO_2-containing samples hindered the crystallization of nepheline but greatly stimulated the epitactic formation of diopside ss of holocrystalline microstructures. LiF-containing samples stimulated the crystallization of the framework silicates, nepheline ss and carnegieite, which progressively increased with the LiF concentration. The thermal expansion coefficient and Vickers hardness of the obtained glass-ceramic reached values of 9.0×10^{-6} K^{-1} (20 to 300 °C) and ($950 \times 10^7 \pm 25$) N/m^2, respectively.

Wirkung von Cr_2O_3, ZrO_2 und LiF auf die Keimbildung und Kristallisation von Glaskeramik-Zusammensetzungen aus Nephelinsyenit-Dolomit

Kostengünstige Nephelin-Pyroxen-Glaskeramiken mit sehr guten mechanischen und thermischen Eigenschaften konnten aus einer Nephelinsyenit/Dolomit-Gesteinsmischung auf einfache Weise unter Verwendung konventioneller Glasherstellungs- und Wärmebehandlungsmethoden hergestellt werden. Die Zusammensetzung des Ausgangsglases, die ungefähr 35% Nephelin- und 65% Diopsid-Mischkristall ergeben sollte, wurde durch eine modifizierte chemisch-mineralogische Berechnungsmethode nach dem CIPW-Verfahren ermittelt. Die Wirkung der Keimbildner Cr_2O_3, ZrO_2 und LiF auf die Mechanismen der Keimbildung und Kristallisation dieser Phasen wurde durch DTA, XRD sowie durch optische und Elektronenmikroskopie ermittelt.

Ohne diese Keimbildner erwies sich die Kristallisation als schwierig, und es wurde eine teilkristalline grobe Mikrostruktur mit diopsidischen Mischkristallen erhalten. Die Zugabe von LiF zeigte die größte Wirkung auf die Kristallwachstumsgeschwindigkeiten, während die Zugabe von Cr_2O_3 sogar bei nur geringen Mengen von 0.5 Gew.% eine ausreichende Keimdichte für Glaskeramiken von guter Qualität ergab. Sowohl in Cr_2O_3- als auch in ZrO_2-enthaltenden Proben wird die Kristallisation von Nephelin behindert, die Zugaben haben jedoch eine sehr günstige Auswirkung auf die epitaktische Bildung von Diopsid-Mischkristallen und die Ausbildung einer hochkristallinen Mikrostruktur. LiF-enthaltende Proben stimulieren die Kristallisation der Gerüstsilikate, des Nephelin-Mischkristalls und des Carnegieits, die mit zunehmender LiF-Konzentration progressiv ansteigt. Der Wärmeausdehnungskoeffizient und die Vickers-Härte der erhaltenen Glaskeramiken erreichen Werte von $9{,}0 \times 10^{-6}$ K^{-1} (20 bis 300 °C) bzw. ($950 \times 10^7 \pm 25$) N/m^2.

1. Introduction

Nepheline($NaAlSiO_4$)-based glass-ceramic is characterized by superior technical properties, e.g. high mechanical strength and chemical durability. The majority of the nepheline-containing glass ceramics are normally prepared from $Na_2O-Al_2O_3-SiO_2$ glasses using high-purity proportions of pure chemicals [1 to 5]. TiO_2 alone, or in combination with other oxides, is effective in catalyzing the crystallization of nepheline in these sodium aluminosilicate glasses [2, 3 and 6]. Duke et al. [6] found a solid solution of CaO in the nepheline and up to 6 wt% of this oxide was added before anorthite could be detected. Russak and Kivlighn [1] obtained a very fine-grained dense body by rapid heat treatment above the softening point of glasses in the system $Na_2O-Al_2O_3-SiO_2$ with 4 % MgO and 4.5 % TiO_2 in excess and As_2O_3 as a fining agent. The hexagonal nepheline and minor amount of magnesium dititanate were the only crystalline phases detected. MacDowell [2] examined the microwave heating characteristics of nepheline glass-ceramics containing K_2O, CaO, and Li_2O

Received 3 August 2000, revised manuscript 17 August 2001.

Table 1. Chemical composition of quenched (unmodified) nepheline syenite glass frits and dolomite rock

raw material	oxide in wt%									
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	LOI[1]
glass frits	55.75	0.13	23.20	2.41	1.18	0.92	2.70	10.99	2.72	–
dolomite	0.54	0.04	0.50	0.18	–	20.95	30.90	–	–	47.1

[1] LOI = Loss on ignition.

Table 2. Chemical composition of glass batches

glass no.	oxide in wt%											
	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	FeO	CaO	MgO	Na_2O	K_2O	Cr_2O_3[2]	LiF[2]	ZrO_2[2]
G1	49.73	20.70	0.12	2.15	1.50	8.83	5.19	9.80	2.43	–	–	–
GCr										0.50	–	–
G1.5F										–	1.50	–
G3F										–	3.00	–
GZ										–	–	1.00

[2] Weight exceeds 100 % glass batch.

substitution for Na_2O in the nepheline structure. The molar ratio of the whole composition is 1.00 Na_2O (or substituents): 1.05 Al_2O_3: 2.50 SiO_2, with 6 wt% TiO_2 added as a nucleating agent and 0.5 wt% As_2O_3 added as a fining agent.

The processing of the naturally occurring rocks into glass-ceramic materials may represent a great theoretical and practical interest since these glass-ceramics possess outstanding physical properties. The purpose of the present investigation was to study the crystallization processes of several glasses derived essentially from some Egyptian nepheline syenite and dolomite rocks using Cr_2O_3, LiF and ZrO_2 as nucleation catalysts to find out the possibility of obtaining valuable and inexpensive glass-ceramic materials. Some physical properties such as thermal expansion, hardness and density of the resultant glass-ceramics were also studied.

2. Materials and experimental procedure

Representative samples from high alumina- containing nepheline syenite (Abu-Khruq, Eastern Desert) and dolomite (Ataqa, Gulf of Suez) were the starting materials employed in preparing the glass batches. The prepared batches were melted in Pt crucibles at temperatures ranging from 1300 to 1400 °C, depending upon nucleant added, and kept at this temperature for 2.5 h. The homogeneous melts were then cast into rods and discs and transferred to a preheated muffle furnace (550 °C). The ratio of FeO and Fe_2O_3 was determined from quenched glass frits of nepheline syenite rock. Chemical analyses of the quenched nepheline syenite glass frits and original dolomite rock are given in table 1.

Normative calculation of nepheline syenite glass composition divides into nepheline ss (solid solution) (≈36 %) and pyroxene ss molecules (≈51 %) with ≈ 13 % free silica. Accordingly, 23.34 g dolomite is needed for each 100 g nepheline syenite glass (corresponding to 102 g of the original rock) to compensate the excess SiO_2, and to give diopsidic pyroxene molecules $CaMgSi_2O_6$. Table 2 depicts the chemical composition of each batch in oxide percentages.

The obtained glasses were subjected to single-stage heat treatment at 700 to 1100 °C for 4, 20, or 40 h. Double- or multistage heat treatments were also carried out at 700 to 1100 °C for 4 h at each temperature.

The DTA runs were made on a Shimadzu DT-30 microdifferential thermoanalyzer using 80 mg of the powdered glass sample (−0.60 and +0.25 mm grain size), a heating rate of 20 K/min, a sensitivity setting of 0.254 µV/m and Al_2O_3 as standard.

X-ray diffraction analysis was carried out using a Philips PW 1390 X-ray diffractometer, adopting nickel-filtered copper radiation for some of the samples and iron-filtered cobalt radiation for some others. The mineralogical constitution, as well as the microstructure developed in these specimens were optically examined using a polarizing Carl-Zeiss research microscope. With a JOEL (T-20) mini-scanning electron microscope, some samples were investigated also for their microstructure.

Measurements of the linear thermal expansion coefficient (C.T.E.) were made by a Netzsch dilatometer of the 402 EP type using a fused silica tube bar and a heating rate of 5 K/min. The diamond pyramid hardness (D.P.H) measurements were performed with a Shimadzu

Table 3. Crystallization of glasses at different temperatures

Heat treatment in °C/h	glass no.				
	G1	GCr	G1.5F	G3F	GZ
700/4	–	–	–	–	–
750/4	–	–	–	Ne+Aug	–
800/4	–	–	–	Ne+Aug	–
850/4	–	Aug	Aug+Ne	Ne+Aug	–
900/4	Aug	Aug	Aug+Ne	Ne+Aug+He(m)	–
1000/4	Aug	Aug	Aug+Ne	Ne+Aug+Car(m)+He	Aug
1100/4	Aug	Aug	Aug+Ne	–	Aug
1100/40	Aug	Aug	Aug+Ne(t)	–	Aug

Note: Aug = augite, Ne = nepheline, Car = carnegieite, He = hematite, m = minor, t = trace.

microhardness tester on a polished sample surface. The load used was 100 g in 15 s. About seven different indentations were made and the average readings were obtained.

3. Results

3.1 Thermal behavior

Figure 1 depicts the DTA traces of the base (nucleant-free) and the nucleated glasses. The DTA trace of the dark amber transparent parent glass shows a minor endothermic effect maximized at about 700 °C, a weak broad exothermic effect at about 860 °C, and another relatively stronger exothermic peak at about 1100 °C. The low intensities of these exothermic effects may indicate a somewhat low propensity towards crystallization. The incorporation of LiF displaces both the endothermic and exothermic peaks to lower temperatures. ZrO_2-nucleated glass shows a similar DTA curve to the parent glass but the exothermic peak is shifted to a higher one by about 40 K; i.e. it appears at about 1120 °C. Addition of very low percentage (0.5 wt%) of Cr_2O_3 dramatically affects the crystallization kinetics, peak temperatures and span of DTA effects, which indicates the great effect of Cr_2O_3 in enhancing the crystallizability of the glass.

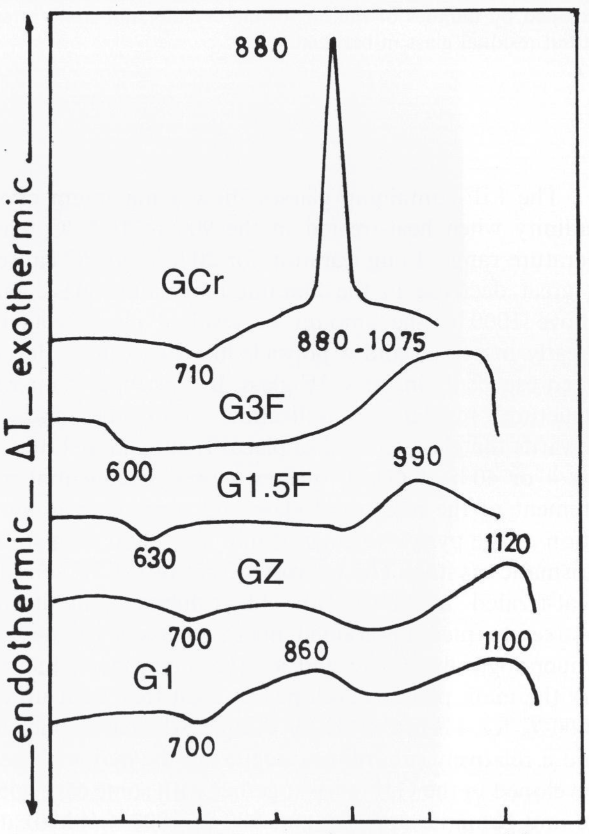

Figure 1. DTA traces of the investigated glasses; G1: base glass, GZ: 1.0 wt% ZrO_2, G1.5F: 1.5 wt% LiF, G3F: 3.0 wt% LiF, GCr: 0.5 wt% Cr_2O_3.

3.2 Effect of heat treatment on crystallization

Microscopic and XRD studies of the heat-treated base glass samples show that crystallization begins at 900 °C by surface nucleation mode. After 4 h treatment at 900 or 1000 °C weakly crystalline materials are obtained exhibiting some internal stellate-like crystals jacketed with a feathery crystalline surface. Long needles and fair-sized prismatic crystals are developed at 1100 °C. A large amount of residual glass is present, which relatively decreases after long duration heat treatment (for 40 h at 1100 °C). The sample consecutively heat-treated for 4 h at 700, 800 and 1100 °C does not show considerable difference from that heat-treated for 4 h at 1100 °C indicating the ineffectiveness of such precrystallization treatments in inducing nucleation and crystallinity. XRD analysis of these hemicrystalline samples reveals a single pyroxene phase of augite composition (table 3).

Figure 2. Photomicrograph of 1.5 wt% LiF-containing glasses heat-treated at 900 °C for 4 h: fair-sized fibriller spherulites enveloped by bundles of fine nepheline crystals and some interstitial residual glass in-between.

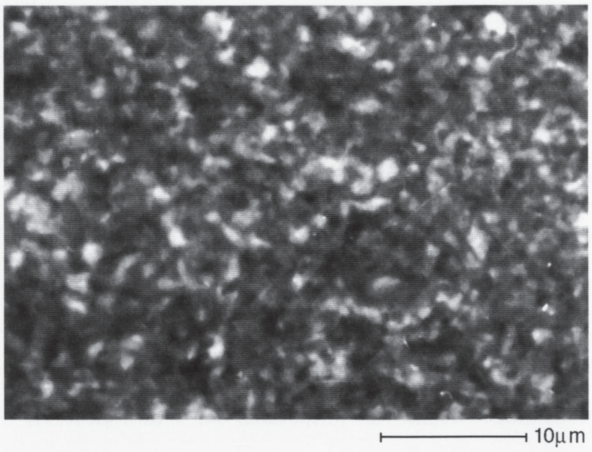

Figure 3. Photomicrograph of 1 wt% ZrO_2-containing glasses heat-treated at 700 °C/4 h, 850 °C/4 h and 1100 °C/4 h: moderately fine-grained microstructure.

The LiF-containing glasses show a maximum crystallinity when heat-treated in the 900 to 1000 °C temperature range. Long duration for 20 h at 900 °C causes a great decrease in the amount of residual glass, but above 1000 °C the amount of residual glass is again greatly increased and a popsicle-like structure is developed especially in the G3F glass. In this type of microstructure regular crystallization from the surface towards the glass core takes place. Treatment at 1100 °C for 4 or 40 h of G1.5F glasses causes a sequential increment of the interstitial glass and more individualization of the pyroxene growths into short and long stout prismatic crystals. The microstructure of G1.5F sample heat-treated at 900 °C for 4 h exhibits nonuniform coarse- to medium-grained microstructures (figure 2). Mineralogically, augite and a subordinate nepheline ss are the main phases developed on heat treatment up to 1000 °C for 4 h in the G1.5F sample, whereas nepheline and a relatively subordinate augite are the major phases developed in the G3F glass together with some carnegieite and hematite appearing at 900 to 1000 °C/4 h treatment (table 3). On increasing the crystallization parameters, up to 1100 °C for 4 h or 40 h, a considerable decrease and ultimate disappearance of nepheline with a relative decrease of augite takes place.

Crystallization of glass containing 1 wt% ZrO_2 (GZ) in the 900 to 1100 °C temperature range produces partially crystalline materials. Microscopically, stellate-like growths are obtained at 1000 °C and fairly long prismatic crystals are developed at 1100 °C (for 4 or 40 h). Multistage heat treatment at 700, 850 and 1100 °C for 4 h significantly promotes the degree of crystallinity and to some extent the fineness of crystals which exhibit moderately fine-grained microstructures (figure 3). Augite is the only crystalline phase developed in all heat treatment regimes (table 3).

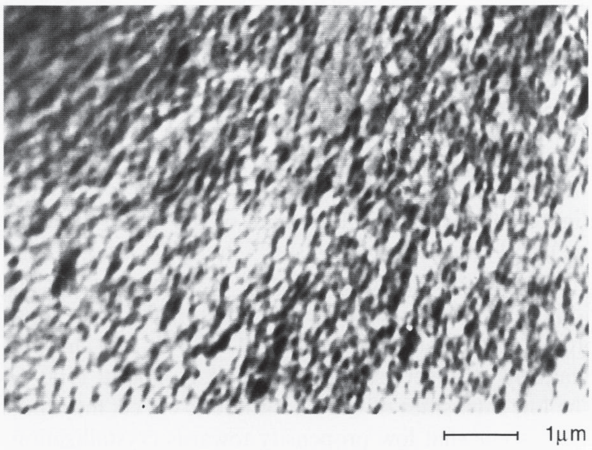

Figure 4. SEM micrograph of 0.5 wt% Cr_2O_3-containing glasses heat-treated at 900 °C for 4 h: ultrafine-grained microstructure.

In Cr_2O_3-containing amber glass (GCr) heat-treated at 800, 850 or 900 °C, translucent and largely cryptocrystalline materials are obtained. SEM shows them to be largely crystalline with ultrafine-grained microstructures (figure 4). However, the translucency of the original amber glass still exists up to 900 °C. On increasing the temperature up to 1100 °C, the opacity is increased and the samples attain a lighter grayish color indicating excessive progression of crystallization. The result for heat treatment for longer periods (40 h) at 1100 °C is almost similar to that at the same temperature for 4 h. Double-stage heat treatment at both endothermic and exothermic peak temperatures does not show any significant difference from the single-stage heat treatment at the exothermic peak temperature. Mineralogically, only a single pyroxene solid solution phase is formed under the influence of such very low percentage of Cr_2O_3 in the wide heat treatment temperature range investigated (table 3).

Table 4. Thermal expansion coefficient, density and Vickers hardness (VH) of some glasses and glass-ceramics

glass no.	heat treatment in °C/h	α x 10^{-7} in K^{-1}	density in g/cm^3	VH x 10^7 in N/m^2	phases present
G1	–	82.0		813	A
GCr	–	82.9	–	–	A
	800/4	90.2	2.713	808	Aug
	800/4+900/4	94.1	2.727	843	Aug
	800/4+900/4+1100/4	90.1	2.713	–	Aug
G1.5F	–	88.0	–	–	A
	900/4	95.0	2.744	–	Aug+Ne
	900/4+1000/4	103.0	2.788	889	Aug+Ne
	900/4+1000/4+1100/4	92.0	2.721	850	Aug+Ne
G3F	–	92.3	–	–	A
	900/4	110.1	2.776	950	Ne+Aug
	900/4+1000/4	96.0	2.741	844	Ne+Aug
GZ	–	81.8	–	–	A
	900/4	104.0	2.767	940	Aug

Note: A = amorphous, Aug = augite, Ne = nepheline.

3.3 Physical properties of glasses and crystalline glasses

The C.T.E. (α value) in the 20 to 300 °C range of all the glasses lies between 81.8 and 92.3 x 10^{-7} K^{-1}. The data show that the type of the nucleant used considerably affects the thermal expansion coefficient of the glass. Generally, the C.T.E. increases with additions of Cr_2O_3 or LiF, e.g. 0.5 wt% Cr_2O_3 slightly increase the C.T.E. The α value of G1.5F and G3F glasses is increased to 88.0 and 92.3 x 10^{-7} K^{-1}, respectively. In contrast, a slight decrease in the thermal expansion coefficient is noticed in GZ glass composition. The incorporation of these catalysts at the concentration level studied also affects the temperatures of T_g and T_s of the glasses.

The C.T.E. (α value) of some nucleated glasses, subjected to accumulative heat treatments is depicted in table 4. In general, the thermal expansion coefficient of the crystallized glasses is higher than the corresponding one of the parent glasses. The thermal expansion coefficient α of crystalline glasses nucleated by 0.5 wt% Cr_2O_3 is slightly lower than that with 1.5 and 3 wt% LiF or ZrO_2.

In the present investigation, the C.T.E. of the glass-ceramics is particularly influenced by the type and concentration of nucleating agents used, which has a significant effect on the resulting crystalline phases. The observed decrease in the α value of almost all samples treated at the top heat treatment temperature (1000 or 1100 °C) is actually due to the increase in the amount of the glassy phase resulting from remelting of the crystalline phases at high temperatures.

The density of the crystalline materials is found to be in the range 2.767 to 2.795 g/cm^3. The Vickers hardness number of the glass-ceramics is considerably higher than that of the original glasses.

4. Discussion

The preferential formation of pyroxene and/or the lack of any crystalline nepheline in the parent glass and in the presence of the nucleating agents ZrO_2 or Cr_2O_3 upon heat treatment may be explained by one or more of the following reasons:

a) From the thermodynamic point of view, the crystalline phases that possess the lower values of activation energy would separate first and more readily than those with higher values during the crystallization of the glass. Therefore, the low activation energy of aluminous pyroxenes ($\approx 25 \times 10^3$ J/mol [7]) as compared with that of the nepheline ($\approx(38 \pm 0.3)$ J/mol [8]) is the main factor favoring the formation of pyroxene under the conditions of nonequilibrium crystallization. This is because of the simplicity of the "chain structure" of pyroxenes compared to the more complicated aluminosilicate "framework structure" of nepheline.

b) The solubility limit of aluminum or aluminous Tschermak's molecules (e.g. $CaAl_2SiO_6$) in diopside increases with nonequilibrium crystallization and reaches 48 mol% under highly nonequilibrium crystallization conditions [7]. Other molecules such as $NaFeSi_2O_6$ and $NaAlSi_2O_6$ can also share in the building of complex pyroxenes and this tendency may also increase under nonequilibrium conditions, thus leaving lesser amounts of the sodium and aluminum components for nepheline formation. Actually pyroxenes crystallized in the rectified nepheline syenite glasses are solid solutions as evidenced by minor displacement of x-ray diffraction lines towards higher two theta degrees.

c) The progressive formation of pyroxenes may lead to enrichment of the residual noncrystallized glass by the nepheline components. This leads to increase of its viscosity which hinders the mobilization and diffusion of the ions and ionic complexes to the extent that the crystallization of nepheline is delayed or even prevented.

On the other hand, LiF favors and enhances the formation of nepheline, which increases with the LiF content. The fluoride ions of the added LiF may act as network modifier in the anionic structure of the glass. The bridging oxygens can be replaced by fluoride ions due to their radius similarity (fluorine = 0.136 nm and oxygen = 0.140 nm). The replacement of the strong Si−O−Si linkage by a pair of the weak Si−F one results in weakening of the glass network structure. This is reflected in facilitating the melting process of the fluoride-containing charges as well as in decreasing the viscosity of the resultant melts and glasses [9 to 11]. This may result in subsequent ease of migration and diffusion of ions and ionic complexes present in the glass to such an extent that crystallization of such a structurally more complex aluminosilicate nepheline phase can take place. The possibility of Li^+ of entering interstitial positions in the nepheline structure [2] may add to such an enhancing effect on the formation of nepheline ss and its crystal growth.

The remarkable increase in the thermal expansion coefficients of nucleant-containing glasses, especially those containing LiF, which is directly proportional to their concentrations (table 4), is accordingly attributed to the introduction of weaker bonds. This results in a much less rigid or more loosely compacted nature of the glass structure.

Also, nepheline has a relatively higher thermal expansion coefficient (60 to 120 x 10^{-7} K^{-1} [6]) depending on the degree of substitution of Na_2O by K_2O, CaO and Li_2O [2]. The thermal expansion coefficient of diopside is reported to be 83.0 x 10^{-7} K^{-1} [11 and 12]. Therefore, in the present glass-ceramic samples, as the nepheline content increases, the thermal expansion coefficient is consequently increased.

The beneficial effect of Cr_2O_3 in favoring the formation of uniform fine-grained microstructures may be due to its rapid separation in the form of a minute chromium-containing crystalline spinel phase (Mg, Fe) (Al, Fe, $Cr)_2$ O_4 [11], or as chromium-rich amorphous droplets during heat treatment. These act as sites for the subsequent crystallization of the major phase. The chrome-spinel is responsible for the uniform bulk crystallization and the resulting fine-grained microstructure. The degree of fineness of the formed microstructures is dependent upon the number of crystallization spinellide centers developed in the glass, which is a function of the Cr_2O_3 content. Also it is found that Cr_2O_3 even in small quantities greatly stimulates the formation of pyroxenes while retarding the crystallization of the framework plagioclase structure [11].

In brief, the aforementioned data show that, at lower temperatures, both Cr_2O_3 and ZrO_2 tend to catalyze an early precipitation of heterogeneous centers either of chromium-containing spinel or zirconium-bearing nucleating phase. At higher temperatures, these phases act as nucleating centers on which the sole pyroxinic phase grows epitaxially, as well as bulk crystallization of homogenous fine-grained microstructures is developed. On the other side, fluorine does not induce the formation of nucleating centers, however it has a positive effect in lowering the viscosity of the glass, i.e. in increasing the mobility of ions in the glass, to arrange the complex aluminosilicate phase.

5. Conclusions

a) The base glass composition (nepheline syenite and dolomite) with or without nucleating agents is easily meltable and workable. Augite was the only phase developed upon heat treatment of the base glass.

b) 0.5 wt% Cr_2O_3 is greatly effective in inducing a very great number of crystallization centers leading to the formation of largely crystalline masses with extremely fine-grained microstructures.

c) LiF in amounts up to 3 wt% has a negligible effect on the nucleation process, but is very effective in increasing the crystal growth rate. Crystallization generally emanates from surface rather than internal nucleation mode resulting in the formation of nonuniform microstructure.

d) 1 wt% ZrO_2 does not promote volume crystallization, except by following a multistage heat treatment schedule.

e) The addition of Cr_2O_3 and ZrO_2 hinders the formation of nepheline, but greatly enhances the crystallization of augite. On the other hand, LiF (>1 wt%) greatly favors and stimulates the formation of nepheline, besides augite. This effect increases with LiF content. Other minor phases such as hematite are sometimes developed with carnegieite in the 1.5 and 3 wt% LiF-containing glasses.

f) The C.T.E. (α value) of the glass increases with addition of Cr_2O_3 and LiF. In contrast, a slight decrease in it is noticed when 1 wt% ZrO_2 is included in the glass.

g) The α value of the crystalline products was generally higher than that of the corresponding parent glasses. However, it is first increased as crystallization proceeds, and decreases thereafter upon further treatment at higher temperatures due to remelting of some of the crystalline phases.

h) The density of the crystalline materials is found to be in the range 2.706 to 2.795 g/cm^3.

i) The microindentation hardness considerably increases upon heat treatment, especially in samples containing nepheline. The Vickers hardness number amounts to 950 x 10^7 N/m^2, which is considerably higher than that of the parent glass.

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This work is based on the M.Sc. thesis of Esmat M. A. Hamzawy, Cairo University, Egypt (1992). The subject of that thesis was proposed by the late Prof. A. W. A. El-Shennawi. Also, the manuscript of this paper was completed, finally reviewed and approved by him before his sudden death. Dr. E. M. A. Hamzawy expresses his deep appreciation to Prof. A. W. A. El-Shennawi for the fruitful collaboration and discussions during his work at the National Research Centre. The author will miss him greatly, but his example will remain as an inspiration to himself and others.

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■ 11/1201P002

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