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Crystallization characteristics and physico-chemical properties of the glasses based on Li_2O–CaO–SiO_2 eutectic (954 °C) system containing magnesium oxide

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Abstract

The crystallization process of glasses in the Li_2O–CaO–SiO_2 (954 °C) eutectic system containing MgO at the expense of Li_2O and/or CaO were investigated by means of DTA, XRD, and SEM. Minor additives of CaF_2 or TiO_2 were added on the batch of the eutectic glass as nucleating agents. The relationship between the crystalline phases formed, heat-treatment applied and their effect on the properties were discussed. The crystallization of the glasses was greatly enhanced by modification processes, thus fine fibrous and prismatic-like growths were obtained therefrom. The dilatometric thermal expansion of the glasses and their corresponding glass-ceramics were determined. The thermal expansion properties of the glasses depend on the glass compositions. The addition of CaF_2 or TiO_2 as nucleating agent to the eutectic glass led to increase the α-values of the glasses. However, both the T_g and T_s values decreased. The α-values of the glasses were decreased with the increase of MgO at the expense of Li_2O and/or CaO, while both the transformation (T_g) and softening (T_s) temperatures increased. The thermal expansion coefficients of the crystalline materials exhibited a wide range depending upon the type and relative proportions of the crystalline phases formed. The chemical durability test, using acid solution, of the glass-ceramics was determined. The data obtained depend on the nature and concentration of crystalline phases present and microstructure.

Keywords: C. Thermal expansion; D. Glass; Crystallization; Chemical durability

1. Introduction

Crystallization of glasses can lead to a wide range of glass-ceramics having unusual microstructures and properties. From a more fundamental point of view, the vitreous state is only attainable when crystallization can be avoided during synthesis. Hence, the scientific and technological importance of understanding and controlling the crystallization mechanisms of glass is crucial [1].

The crystallization and sintering behaviour, as well as the final properties of glass-ceramic parts, are affected by the composition of the parent glass, the nucleating system and the crystallization conditions [2].

West [3] studied the phase relations in the system Li_2O–CaO–SiO_2 by the quenching method. Four stable ternary compounds were found $Li_2Ca_3Si_6O_{16}$, $Li_2Ca_4Si_4O_{13}$, $Li_2Ca_2Si_2O_7$ and Li_2CaSiO_4 as well as phase Y, which is probably, fairly close to Ca_2SiO_4 in composition.

The invariant point $Li_2Si_2O_5 + Li_2Ca_3Si_6O_{16} + SiO_2$ + liquid is probably an eutectic although it has been given the same temperature as the thermal maximum on the join $Li_2Si_2O_5$–$Li_2Ca_3Si_6O_{16}$ (954 ± 4 °C) [3].

Shelby and Shelby [4], revealed that Li_2O–CaO–SiO_2 system is of interest because most of the glass-forming region lies within the immiscibility region. They indicated that, many properties of Li_2O–CaO–SiO_2 glasses are strongly affected by the morphology of the samples. The properties considered include density, refractive index and thermal expansion coefficient, which are not sensitive to the presence of phase separation, whereas electrical conductivity, glass transformation temperature, are strongly affected by phase separation.

Pyroxene is a group of minerals of variable compositions, which crystallize fairly readily. They are closely related in crystallographic and other physical properties as well as in

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chemical composition, though they crystallized in two crystal systems; orthorhombic and monoclinic [5]. A large number of the monoclinic pyroxenes can be considered as members of the four components system $CaMgSi_2O_6$–$CaFeSi_2O_6$–$MgSiO_3$–$FeSiO_3$. Diopside-$CaMgSi_2O_6$ is one of the most important mineral phases of the pyroxene family [5]. Diopside showed high mechanical properties and characteristic thermal properties [6].

The purpose of this work is to study the crystallization characteristics of glasses based on lithia calcia silica system modified by adding MgO at the expense of Li_2O and/or CaO. The study aimed also to obtain some varieties of glasses and glass-ceramics that have wide range of thermal expansion coefficients and high chemical durability.

2. Experimental

2.1. Batch composition and glass preparation

In the present work, a systematic study of the crystallization characteristics of lithia calcia silica eutectic (954 ± 4 °C) glass, modified by adding MgO at the expense of Li_2O, CaO or (Li_2O + CaO). Minor additives of CaF_2 or TiO_2 were added, as nucleating agents, to the eutectic batch in amounts of 3.0 or 1.0 g, respectively over 100 g oxide constitutions of the glass batch composition. The glass batches were prepared from reagent grade powders of Li_2CO_3, $CaCO_3$, $MgCO_3$, quartz (SiO_2), CaF_2 and TiO_2. The components of the batch after being accurately weighed were thoroughly mixed in agate mortar for about 15 min to ensure complete homogeneity. The weighed batches were melted in Pt–2% Rh crucibles, covered with platinum cap to minimize the evaporation, in an electric furnace with SiC heating elements at 1250–1450 °C for 3 h. The homogeneity of the melts was achieved by stirring the crucible containing melt several times at about 30 min intervals, the melt was cast into rods, squares and buttons which were then properly annealed in a muffle furnace at 550 °C for 30 min to minimize the strain.

2.2. Differential thermal analysis (DTA)

The thermal behaviour of the finely powdered (45–75 μm) glass samples was examined using a SETARAM Labsys^{TM} TG-DSC16. The powdered glass was heated in Pt-holder against another Pt-holder containing Al_2O_3 as a reference material. A uniform heating rate of 10 °C/min was adopted. Data were recorded using a computer-driven data acquisition system. The results obtained were used as a guide for determining the required heat-treatment temperatures applied to induce crystallization of the glasses. The progress of crystallization in the glasses was followed by double stage heat-treatment regimes. The glasses were first heated according to the DTA results at the endothermic peak temperature for 5 h, which was followed by another thermal treatment at the exothermic peak temperature for 10 h.

2.3. Material investigation

Identification of the crystal phases precipitating due to the course of crystallization was conducted by X-ray diffraction (XRD) analysis of the powdered samples. The X-ray diffraction patterns were obtained by using XSPEX, X-ray diffractometer with search/match option, version 5.45, Diano Corporation, Woburn Massachusetts 01801, USA. The reference data for the interpretation of the X-ray diffraction patterns were obtained from ASTM X-ray diffraction card files. The crystallization characteristics and internal microstructures of fractured surfaces of the crystalline samples, coated with gold spray, were examined by using scanning electron microscopy (SEM). Representative electron micrographs were obtained by using Jeol, JXA-840 on Electron Probe Microanalyzer.

2.4. Thermal expansion

The measurements of the linear thermal expansion coefficients were carried out on 1.5–2.0 cm long rods using (Linseis L76/1250) automatic recording multiplier dilatometer. The measurements were first carried out on different glass samples previously annealed at 550 °C. The samples were heated at rate 5 °C/min. The thermal expansion coefficients of the glass specimens were measured from room temperature up to 300 °C and the glass-ceramics were measured from room temperature up to 700 °C. The linear thermal expansion coefficient was automatically calculated using the general equation:

$$\alpha = \left(\frac{\Delta L}{L}\right)\cdot\left(\frac{1}{\Delta T}\right)$$

Table 1
Chemical composition of the glasses

Glass no.	Oxide constitutions (mol%)					Additives in g over 100 g glass oxide
	Li_2O	CaO	MgO	SiO_2	CaF_2	TiO_2
G_1	23.50	11.50	–	65.00	–	–
G_{1F}	23.50	11.50	–	65.00	3.00	–
G_{1T}	23.50	11.50	–	65.00	–	1.00
G	19.50	11.50	4.00	65.00		
G_3	15.50	11.50	8.00	65.00		
G_4	11.50	11.50	12.00	65.00		
G_5	23.50	5.50	6.00	65.00		
G_6	23.50	–	11.50	65.00		
G_7	18.00	5.50	11.50	65.00		

where ΔL is the change in the original length (L) of the rod. ΔT is the temperature interval over which the samples were heated to give the elongation ΔL.

2.5. Chemical durability

The powder method was applied to assess the chemical durability of the obtained glass-ceramic. The selected samples were crushed in an agate mortar and then sieved using B.S. sieves to obtain particles with diameters ranging between 0.63 and 0.32 mm. The grains were washed by decantation in ethyl alcohol and then with pure dry ether three times and then dried. The dried sample was accurately weighed (1.0 g) in a sintered glass crucible (#4), which was then placed in 400 ml polyethylene beaker.

The samples were tested in 0.1N HCl solutions, 200 ml of the acid solution in a the polyethylene beaker. This quantity was sufficient to cover sintered glass crucible. The polyethylene beaker with its contents was covered by the polyethylene cover to reduce evaporation. The chemical durability was expressed as the weight loss percent. The experiment was carried out at 95 °C for 1 h. The effect of time on leaching for 1, 3 and 7 h duration were tested for most of the glass-ceramic samples (Table 1).

3. Results

3.1. Differential thermal analysis

The DTA curves of glasses are shown in Figs. 1 and 2. Endothermic effects were recorded in the 463–618 °C temperature range which probably corresponds to the pre-crystallization processes in the glasses. Various exothermic effects in the 571–877 °C temperature range, which referred to the crystallization reaction characteristics of the glasses, are also detected.

The DTA data (Figs. 1 and 2) revealed that, the addition of MgO instead of Li_2O, CaO or (Li_2O + CaO) led to shift the endothermic dips to higher temperatures, i.e. a higher temperature is needed to start the nucleation process in the glasses.

3.2. Crystallization characteristics

The X-ray diffraction analysis of the eutectic glass (Fig. 3, Pattern I), showed that lithium disilicate-$Li_2Si_2O_5$ (major lines 7.29, 5.39, 3.73, 3.64 and 3.57, Card No. 17-447) was crystallized as a major phase together with lithium calcium silicate phase-$Li_2Ca_3Si_6O_{16}$ (lines 9.51, 5.97, 3.16, 2.99 and 2.88, Card No. 31-713) and α-quartz phase (lines 4.26, 3.34 and 1.96, Card No. 5-490).

Experimentally, the addition of minor amounts of CaF_2 as a nucleating agent facilitated the melting process and enhanced the crystallization of the glass. The XRD analysis (Fig. 3), indicated that, the crystallization of the base glass with CaF_2, G_{1F}, led to the development of fluorite-CaF_2 phase (lines 3.16, 1.93 and 1.64, Card No. 4-864) in addition to lithium disilicate, lithium calcium silicate and α-quartz phases (Fig. 3, Pattern II). While the addition of TiO_2 to the eutectic base glass, i.e. (G_{1T}) heat-treated at 470 °C/5 h–750 °C/10 h, resulted into the enhancement of crystallization of lithium disilicate, lithium calcium silicate and α-quartz phases, however, no TiO_2-containing phase could be detected (Fig. 3, Pattern III).

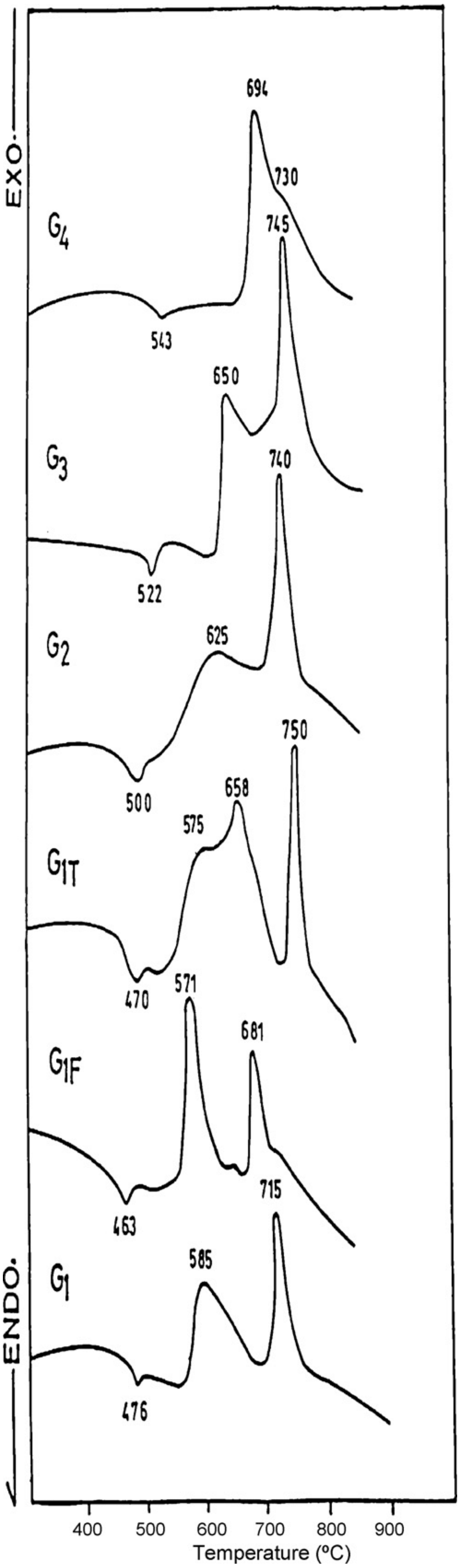

Fig. 1. DTA data of the glasses G_1, G_{1F}, G_{1T}, G_2–G_4.

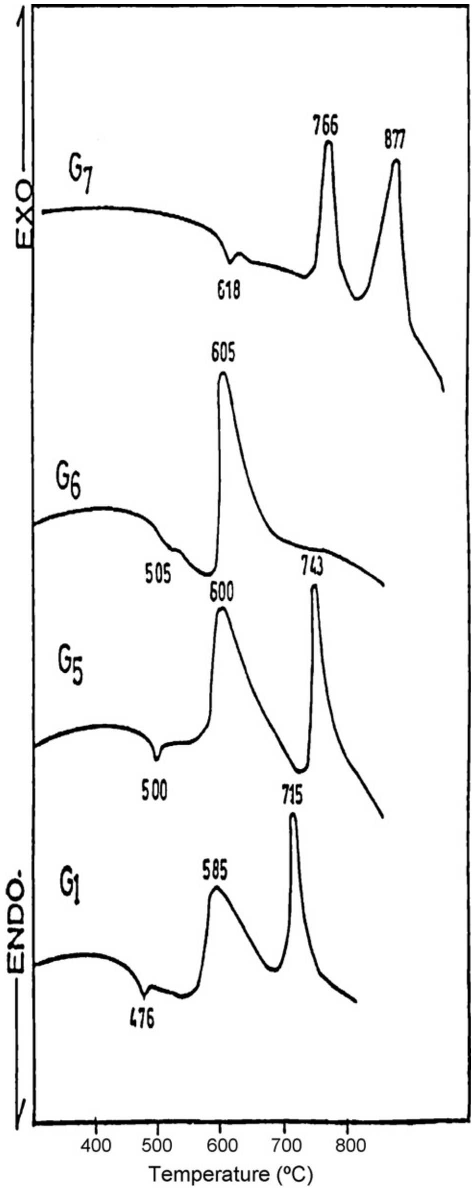

Fig. 2. DTA data of the glasses G_1, G_5–G_7.

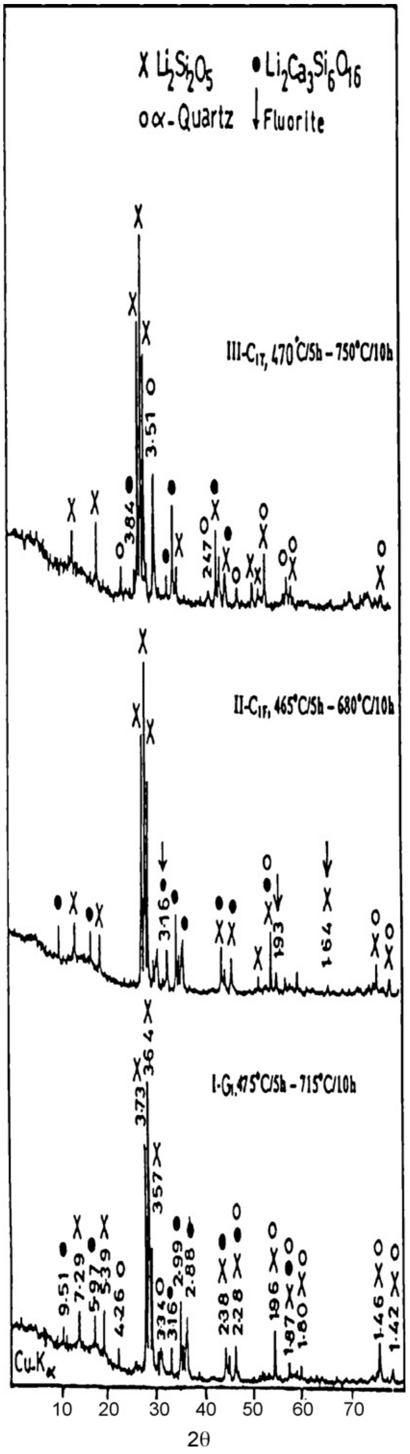

Fig. 3. XRD analyses of crystallized glasses G_1, G_{1F} and G_{1T}.

3.2.1. *Effect of substitution of Li_2O by MgO (G_1–G_4)*

The effect of substitution of MgO as 4.00, 8.00 and 12.00 mol%, instead of Li_2O of the eutectic base glass, on cation per cation basis was investigated.

At low MgO addition, e.g. G_2, lithium disilicate was crystallized as a major phase in addition to diopside-$CaMgSi_2O_6$ phase (lines 3.35, 2.97 and 2.51, Card No. 11-654), α-quartz and minor amounts of lithium calcium silicate, $Li_2Ca_4Si_4O_{13}$ (lines 6.95, 3.08 and 2.62, Card No. 31-714), phases as proved by the X-ray diffraction analysis (Fig. 4, Pattern II).

For the crystalline glass of G_3 the XRD analysis (Fig. 4, Pattern III), indicated that the lithium disilicate (major), diopside, α-quartz and traces of lithium calcium silicate-$Li_2Ca_4Si_4O_{13}$ phases were crystallized. At higher MgO/Li_2O replacement, e.g. G_4, lithium disilicate, diopside and α-quartz phases were developed as indicated by the XRD analysis (Fig. 4, Pattern IV). However, no lithium calcium silicate-$Li_2Ca_4Si_4O_{13}$ phase could be detected among the crystallization of the glass.

3.2.2. *Effect of substitution of CaO by MgO (G_5 and G_6)*

The effect of MgO/CaO replacements on the crystallization characteristics of the Li_2O–CaO–SiO_2 (954 ± 4 °C) eutectic glass was studied.

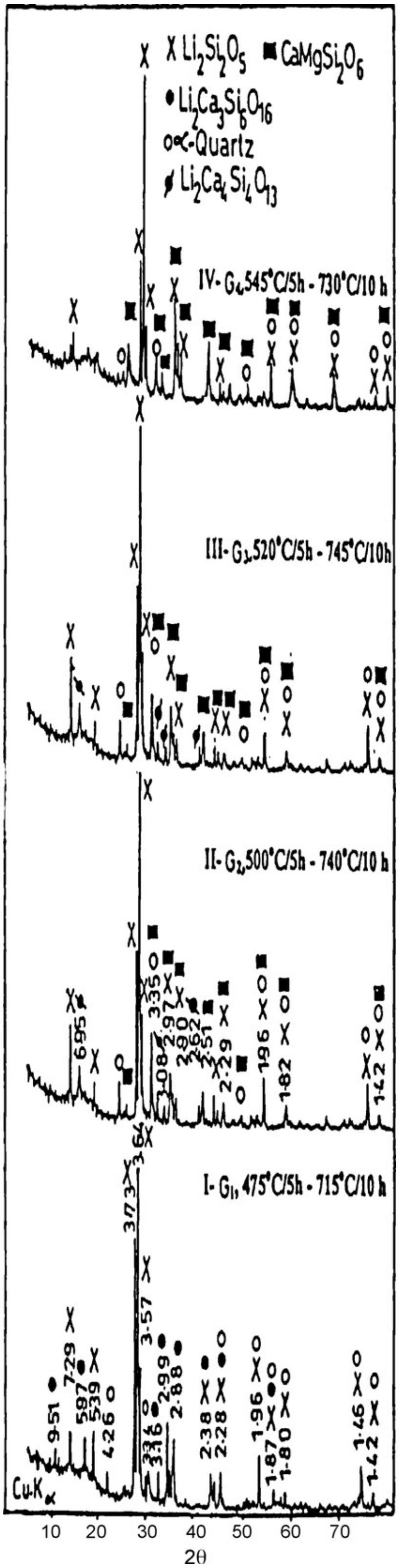

Fig. 4. XRD analyses of crystallized glasses G_1–G_4.

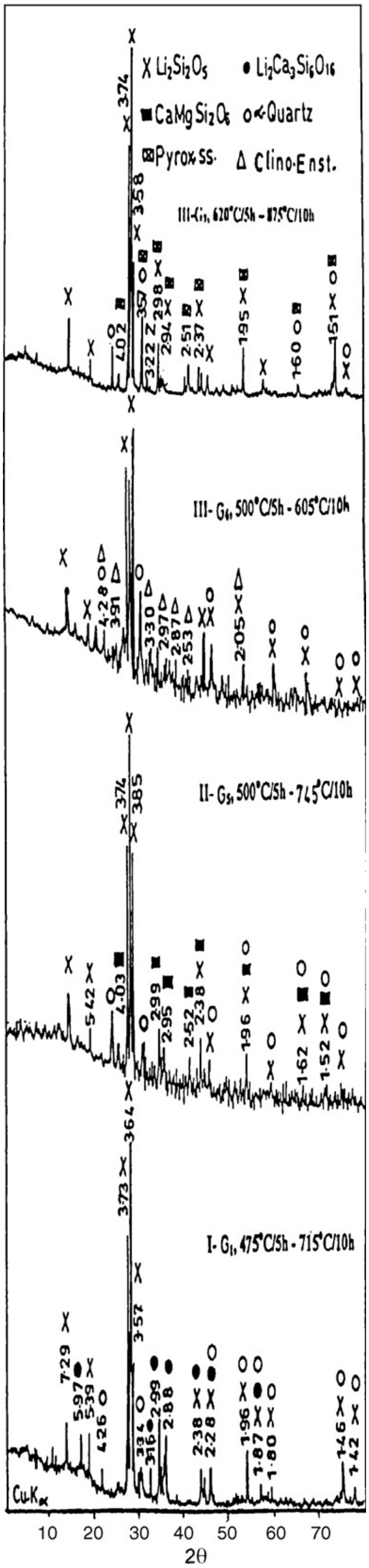

Fig. 5. XRD analyses of crystallized glasses G_1, G_5–G_7.

The X-ray diffraction analysis (Fig. 5, Pattern II) of crystalline glass, G_5, revealed that lithium disilicate, diopside and α-quartz were crystallized. While, the crystallization of G_6 led to the formation of clinoenstatite-$MgSiO_3$ phase (lines 4.40, 3.91, 3.30, 2.97, 2.87 and 2.53, Card No. 35-610), which was formed instead of diopside phase, together with lithium disilicate (major) and α-quartz phases as indicated from the XRD analysis (Fig. 5, Pattern III).

Table 2
Crystalline phases developed in the studied glasses

Glass no.	Heat treatment (°C/h)	Crystal phases developed
G_1	475/5–715/10	$Li_2Si_2O_5$, α-quartz, $Li_2Ca_3Si_6O_{16}$
G_{1F}	465/5–680/10	$Li_2Si_2O_5$, α-quartz, $Li_2Ca_3Si_6O_{16}$, CaF_2
G_{1T}	470/5–750/10	$Li_2Si_2O_5$, α-quartz, $Li_2Ca_3Si_6O_{16}$
G_2	500/5–740/10	$Li_2Si_2O_5$, diopside, α-quartz, $Li_2Ca_4Si_4O_{13}$ (minor)
G_3	520/5–745/10	$Li_2Si_2O_5$, diopside, α-quartz, $Li_2Ca_4Si_4O_{13}$ (traces)
G_4	545/5–730/10	$Li_2Si_2O_5$, diopside, α-quartz
G_5	500/5–745/10	$Li_2Si_2O_5$, diopside, α-quartz
G_6	500/5–605/10	$Li_2Si_2O_5$, clinoenstatite, α-quartz
G_7	620/5–875/10	$Li_2Si_2O_5$, pyroxene ss, α-quartz

3.2.3. Effect of substitution of (Li_2O + CaO) by MgO (G_1 and G_7)

The substitution effect of (Li_2O + CaO) by MgO on the crystallization characteristics of Li_2O–CaO–SiO_2 eutectic glass (G_1) was studied.

The crystallization of G_7 led to the formation of pyroxene solid solution (ss) of diopsidic type (lines: 3.34 3.23, 2.98, 2.94, 2.37, Card No. 19-239) in addition to lithium disilicate (major) and α-quartz phases as indicated from the XRD analysis (Fig. 5, Pattern IV) (Table 2).

SEM micrograph of the fractured surface (Fig. 6) of crystalline base glass C_1 revealed that, volume crystallization of prismatic-like growths were developed. In the C_2 (with 4 mol% MgO/Li_2O replacement), volume crystallization of fine fibrous-like growths were formed (Fig. 7). The addition of MgO instead of (Li_2O + CaO), i.e., C_7 prismatic-like growths were also developed (Fig. 8).

3.3. Thermal expansion

The obtained data (Table 3) clearly indicated that the addition of CaF_2 in the eutectic glass (954 ± 4 °C) (i.e. G_{1F},) increased the α-values of the glasses, and decreased their transformation (T_g) and softening (T_s) temperatures. The expansion coefficient of the eutectic glass, i.e. G_1, was decreased by MgO/Li_2O replacements, and increased their T_g and T_s values (e.g. G_2, G_3 and G_4 with 4.00, 8.00 and 12.00 mol% of MgO, respectively).

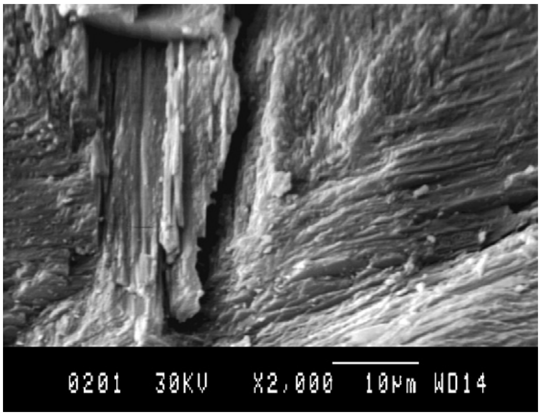

Fig. 7. SEM micrograph of fracture surface of G_2 crystallized at 500 °C/5 h–740 °C/10 h showing volume crystallization of fine-fibrous like growths.

The replacement of MgO instead of CaO in the eutectic glass, decreased the α-values of the glasses, and increased their T_g and T_s values. Table 3 revealed also that glasses G_5 and G_6 exhibited lower α-values than that of the eutectic glass G_1.

The experimental results (Table 3) revealed that the replacements of (CaO + Li_2O) by MgO, i.e. G_7, decreased the expansion coefficient and increased their T_g and T_s values. Table 3 clearly indicates that the α-value of G_7 exhibited lower value than that of glass G_5 (with MgO/CaO replacement, only).

The expansion coefficients of the crystalline products were generally lower than those of the corresponding glasses. The addition of CaF_2 in the Li_2O–CaO–SiO_2 eutectic crystalline glass increased the α-values of the crystalline materials. TiO_2 has a very low effect on the glass and glass-ceramic properties (Table 3).

The partial replacements of Li_2O by MgO in the eutectic crystalline glass decreased the α-values of the crystalline materials. The addition of MgO at the expense of CaO in the eutectic glass led to decrease the α-values of the glass-ceramics. Table 3 indicated that the α-values of sample C_5 were lower than those of the eutectic glass-ceramic (C_1, free of MgO). While on increasing the MgO content, instead of CaO, Table 3

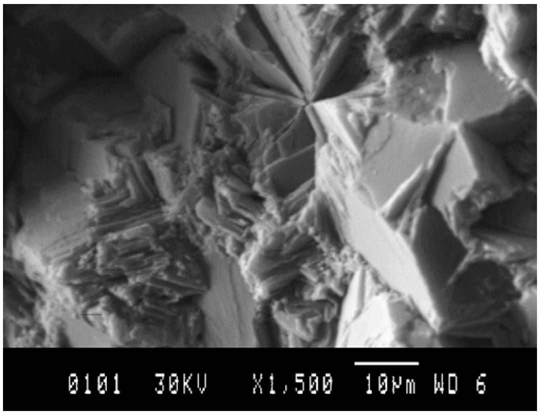

Fig. 6. SEM micrograph of fracture surface of G_1 crystallized at 475 °C/5 h–715 °C/10 h showing volume crystallization of prismatic-like growths.

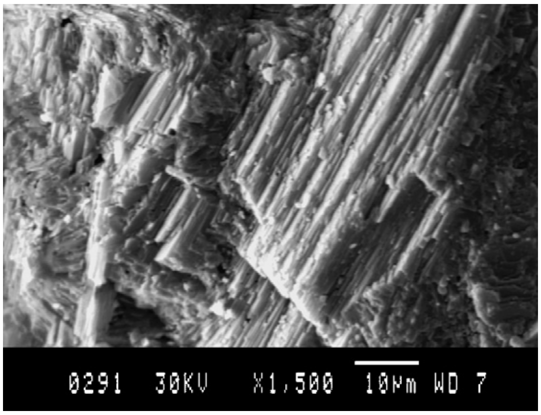

Fig. 8. SEM micrograph of fracture surface of G_7 crystallized at 620 °C/5 h–875 °C/10 h showing prismatic-like growths.

Table 3
Thermal expansion and chemical durability data of the investigated glasses and their corresponding crystalline solids

Sample no.	Thermal expansion coefficients, α ($\times 10^{-7}$ K)					T_g (°C)	T_s (°C)	Weight loss (%)		
	25–300	25–400	25–500	25–600	25–700			1 h	3 h	7 h
G_1	108	–	–	–	–	424	445	–	–	–
C_1	90	93	97	100	105	–	–	0.90	1.50	1.90
G_{1F}	123	–	–	–	–	386	409	–	–	–
C_{1F}	105	107	110	112	114	–	–	2.70	–	–
G_{1T}	109	–	–	–	–	422	441	–	–	–
C_{1T}	92	94	98	105	106	–	–	0.92	–	–
G_2	88	–	–	–	–	440	460	–	–	–
C_2	87	89	91	92	94	–	–	0.70	–	–
G_3	75	–	–	–	–	456	476	–	–	–
C_3	85	87	88	90	92	–	–	0.65	0.85	1.10
G_4	55	–	–	–	–	474	486	–	–	–
C_4	84	86	87	89	91	–	–	0.55	0.60	0.80
G_5	100	–	–	–	–	428	450	–	–	–
C_5	82	89	96	97	100	–	–	0.75	0.85	1.10
G_6	88	–	–	–	–	439	460	–	–	–
C_6	102	107	111	116	117	–	–	1.00	1.20	1.50
G_7	96	–	–	–	–	436	460	–	–	–
C_7	80	85	90	95	100	–	–	0.65	0.80	1.00

showed that sample C_6 has higher α-values than those of samples C_5 and C_1. The present results indicated also that the addition of MgO instead of (Li_2O + CaO), i.e. C_7, showed a decrease in the α-values than that of C_5 (Table 3).

3.4. Chemical durability

The chemical stability data of the investigated glass-ceramics are given in Table 3. The chemical durability of the eutectic glass-ceramic (i.e. C_1) was decreased by the addition of CaF_2 or TiO_2, in the eutectic glass-ceramic. The leaching values of the investigated glass-ceramics were generally decreased by the addition of MgO at the expense of Li_2O. The chemical stability given by samples C_3 and C_4, in acid media, for 1, 3 and 7 h was increased by the addition of MgO instead of Li_2O. C_5 (with MgO instead of CaO) was more durable than that of sample C_6. However, on applying the long-term action on samples C_1, C_5 and C_6, the chemical durability values of sample C_5 exhibit the best.

The present results indicated also, that the addition of MgO at the expense of (Li_2O + CaO) led to decrease the leaching values of the crystalline glass C_7 as compared with those of sample C_5 (with 6.00% MgO/CaO replacements, only), and sample C_1 (free of MgO) (Table 3). On applying the long-term action, it was found that the chemical stability of sample C_7 was better than that of sample C_5 (Table 3).

4. Discussion

4.1. Crystallization characteristics of the studied glasses

Experimentally, the Li_2O–CaO–SiO_2 eutectic (954 ± 4 °C) glass had high crystallization tendency upon heat-treatment and the crystallization was proceeded due to the phase separation formed [4,7,8] to form bulky crystallization mass.

West [3] revealed that the triangle bounded by SiO_2, Li_2SiO_3 and $CaSiO_3$ contains one ternary phase, $Li_2Ca_3Si_6O_{16}$, and all compositions containing above 50 mol% SiO_2 contain this phase at subsolidus temperatures.

The invariant point $Li_2Si_2O_5 + Li_2Ca_3Si_6O_{16} + SiO_2$ + liquid is an eutectic although it has been given the same temperature as the thermal maximum on the join $Li_2Si_2O_5 + Li_2Ca_3Si_6O_{16}$ (954 ± 4 °C).

The sequence of the phase development during crystallization of the present eutectic glass revealed that, lithium disilicate was formed as a major phase together with secondary phases; lithium calcium silicate-$Li_2Ca_3Si_6O_{16}$ and α-quartz.

The petrochemical calculation of the glass composition (G_1) into normative mineral molecules [9] revealed that lithium disilicate can be formed as a major constituent, while lithium calcium silicate and α-quartz are crystallized as secondary phases. However, there is no lithium metasilicate phase could be detected.

According to the differential thermal analysis (DTA) of the present eutectic glass (954 ± 4 °C), the first exothermic peaks appeared at 585 °C was attributed to the crystallization of lithium disilicate phase. The second exothermic peak observed at higher temperature (715 °C) was attributed to the formation of lithium calcium silicate and α-quartz as secondary crystalline phases. After the formation of lithium disilicate and lithium calcium silicate phases, the remaining silica crystallized out as a minor constituent in the form of α-quartz. $Li_2Ca_3Si_6O_{16}$ which has a triclinic structure melts incongruently at (982 ± 4 °C) to yield $CaSiO_3$ and liquid [3].

The addition of CaF_2 as a nucleating agent, in the eutectic glass (954 ± 4 °C) had a marked effect on the nucleation processes. Thus the presence of CaF_2 in glasses, greatly, lowered the temperature at which the crystallization begins. The effect of F^- ion on the structure of silicate glass embodies how it plays a role in the structure of the glass. 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 weakening the glass structure and facilitating the glass crystallization [10].

On one hand, in the eutectic glass, it was found that the presence of fluoride led to enhance the crystallization of lithium disilicate (major), lithium calcium silicate and α-quartz phases. Also, it favoured the formation of fluorite-CaF_2 phase, which could be identified. Our results are in agreement with those found by Liang [11], who mentioned that fluoride crystals are the first precipitated during the crystallization. These fluorite crystals can serve as nucleation sites for the growth of silicate crystals. On the other hand, TiO_2 has a very low effect on the crystallization characteristics of the eutectic glass G_1.

To discuss the effect of replacement of MgO at the expense of Li_2O on the $Li_2O–CaO–SiO_2$ (954 ± 4 °C) eutectic glass, the role of such oxide in the geometrical arrangement of the building units of the glassy network must be considered. MgO seems to be incorporated in the present glass in fourfold coordination (i.e. MgO_4) and an increase of the SiO_2 chain length of the glass structure could be expected. It could be concluded, therefore, that MgO/Li_2O replacement would increase the coherency of the network in the glass structure. Thus the diffusion of different ions and ionic complexes decreased the rate of crystal growth [12]. Therefore, a higher crystallization temperature of the glasses could be expected and the conversion of the glass into crystalline material becomes more difficult by MgO/Li_2O replacement.

The occurrence of the various phases developed was a function of the MgO/Li_2O ratios in the glasses and the crystallization parameters used. At low MgO-content (e.g. G_2 and G_3), lithium disilicate, diopside, α-quartz and lithium calcium silicate phases were formed. The present results indicated that diopside-$CaMgSi_2O_6$ and lithium calcium silicate-$Li_2Ca_4Si_4O_{13}$ phases were developed at the expense of $Li_2Ca_3Si_6O_{16}$ phase. It seemed that a co-reaction can take place between $Li_2Ca_3Si_6O_{16}$ and proper amount of MgO resulting into the formation of the above mentioned phases as indicated by the following schematic equation:

$$2Li_2Ca_3Si_6O_{16} + 2MgO \\ \rightarrow Li_2Ca_4Si_4O_{13} + 2CaMgSi_2O_6 + Li_2Si_2O_5 + 2SiO_2$$

The silica resulting from the equation was assumed to be crystallized in the form of α-quartz phase.

At high MgO/Li_2O ratio (i.e. >1), G_4 was crystallized into lithium disilicate, diopside, and α-quartz phases. However, the amount of diopside phase was increased as indicated from the increase of their line intensities of the XRD analysis and no lithium calcium silicate phase could be detected. It seemed that a co-reaction can take place between $Li_2Ca_3Si_6O_{16}$ and proper amount of MgO and SiO_2 from the residual glass resulting into the formation of the above-mentioned phases as indicated by the following schematic equation:

$$2Li_2Ca_3Si_6O_{16} + 6MgO + 4SiO_2 \\ \rightarrow 6CaMgSi_2O_6 + 2Li_2Si_2O_5$$

Consequently, the crystallization of diopside phase in the present glasses was more apparent by MgO/Li_2O replacements.

The introduction of MgO at the expense of CaO in lithium calcium silicate eutectic (954 ± 4 °C) glass led to increase their nucleation temperature. To explain this, it was suggested that, the Mg^{2+} ions formed in these silicate glasses exhibited tetrahedral coordination state with oxygen. These tetrahedral Mg^{2+} groups possess a higher field strength (4.73) than that of Ca^{2+} (2.04) in octahedral coordination [13,14]. This may account for the increase of the coherency of glass structure. Therefore, the tendency of glass-crystalline conversion becomes more difficult by addition of MgO instead of CaO.

XRD pattern of glass ceramic (G_5) revealed that predominant lithium disilicate phase was developed together with diopside and α-quartz phases. While, on replacing all the CaO-content by equivalent amount of MgO (i.e. G_6), clinoenstatite-$MgSiO_3$ phase was crystallized at the expense of diopside phase.

The addition of MgO at the expense of (Li_2O + CaO) led to shift both the endothermic and exothermic peak temperatures to higher values. This could be attributed to the fact that Mg^{2+} preferably exhibits a tetrahedral coordination (MgO_4) which led to an increase in the viscosity of the glass which hinder the diffusion of different ions and ionic complexes [13,15]. The field strength of Mg^{2+} (4.73) is higher than those of Li^+ (2.78) or Ca^{2+} (2.04) [14]. It is expected, therefore, that the addition of MgO at the expense of (Li_2O + CaO) led to increase the nucleation temperature of these glasses.

The occurrence of the various phases formed in the present glasses was function of MgO/(Li_2O + CaO) ratios in the glasses and the crystallization parameters used. At low MgO content, i.e. G_5, diopside phase was formed together with lithium disilicate (major) and α-quartz phases. Theoretically, on the basis of petrochemical method [9], the recalculation of the resultant compositions into normative mineral molecules indicated that diopside could be formed from the glass composition. Thus, during the crystallization of glass G_5, it was assumed that MgO can combine with the equivalent amount of CaO together with proper amount of SiO_2 to form diopside phase.

However, on increasing MgO/(Li_2O + CaO) ratios in glass G_7, pyroxene solid solution of diopsidic type was developed instead of diopside phase, as indicated from the shift of d-spacing lines (XRD) of diopside phase towards higher 2θ values. It seemed, therefore that there is a preferential tendency for diopside to capture the excess of MgO in its structure [5] forming pyroxene ss of diopsidic type.

4.2. Thermal expansion

The thermal expansion is one of the properties, which are highly sensitive to structural cohesiveness. It was found that in silicate glasses, the expansion coefficient values increase with the decrease of the electrostatic bond strengths of the cations present in the glass structure [7,16].

The thermal expansion is a complex property connected with the magnitude and distribution of force acting in the system and reflects any change of the distribution of the forces with increasing thermal vibration [17].

The presence of CaF_2 in the eutectic glass (i.e. G_{1F}) led to increase the α-value of the studied glass and decrease both the T_g and T_s values. This may be due to the fact that CaF_2 causing a great disturbance in the arrangement of the glass-network. CaF_2 is more powerful in decreasing the coherency of the glass-network [18], due to the formation of non-bridging fluorine instead of the bridging oxygen. Therefore, fluorine served to disrupt the glass structure and this led to increase the α-values of the glass.

The addition of TiO_2 in the eutectic glass led to a very slight increase in the thermal expansion coefficient and decrease the T_g and T_s values. This may be related to a change in glass viscosity, since addition of TiO_2 to glass is known to reduce its viscosity [7] and, consequently, leads to more mobilization of the glass-forming elements. Therefore, an increase in α-value and a decrease in both of T_g and T_s values could be expected.

The addition of MgO at the expense of Li_2O, CaO or both of (Li_2O + CaO) (i.e. glass nos. G_2, G_3, G_4, G_5, G_6 and G_7) in the eutectic glasses resulted in a decrease in thermal expansion coefficients of the glass and increased their T_g and T_s values. This could be explained by assuming that, MgO can be housed in the glass structure, as MgO_4 group forming tetrahedral coordination [19]. This may be led to the increase in the coherency and the compactness of the glass structure [20], and so a decrease in thermal expansion coefficients and an increase in both of T_g and T_s temperature values, could be expected.

The variation of thermal expansion of crystalline materials with temperature is generally quite different from that of the original glass. The thermal expansion coefficient may increase, decrease or practically remain unchanged as a result of crystallization. This generally, depends upon the nature and concentration of the separating crystalline phases that almost have different expansion coefficients and may cover a wide range of α-values [21]. The crystallization process greatly altered the thermal expansion of the glasses. Therefore, the glass-ceramic materials may have high or low α-values depending on the expansion coefficients and elastic properties of the crystal phases formed including the residual glass matrix [12]. In most cases, the expansion coefficients of the crystalline materials generally increased with the increase of the glass phase content in the material.

The thermal expansion coefficients were markedly changed by the conversion of the glasses into glass-ceramic materials. In this case, the data were correlated to the nature, composition and concentration of all phases present [22].

An extremely wide range of the thermal expansion coefficients is covered by the different crystal types and the development of these phases in appropriate proportions. It has been reported that pyroxenes and lithium silicate phases have positive values of thermal expansion coefficients. Diopside and clinoenstatite, which are related to the pyroxene-type phases, have α-values of $78 \times 10^{-7}\,K^{-1}$ (23–1000 °C) [23,24], and $135 \times 10^{-7}\,K^{-1}$ (300–700 °C) [9], respectively. Lithium disilicate has α-value of $110 \times 10^{-7}\,K^{-1}$ (20–600 °C) [7] while α-quartz has α-value of $237 \times 10^{-7}\,K^{-1}$ (20–600 °C) [7]. Fluorite has α-value of $188.5 \times 10^{-7}\,K^{-1}$ (20–600 °C) [25].

According to the previous consideration it follows therefore, that the addition of CaF_2 in the eutectic glass led to increase the α-values of the glass-ceramic (e.g. C_{1F}). This may be due to the formation of high thermally expanding fluorite phase [25]. Also, the slight increase in the α-values of the crystalline solids caused by addition of TiO_2 to the eutectic glass (e.g. C_{1T}), may be attributed to the slight enhancement of the crystallization of relatively high thermally expanding lithium disilicate, lithium calcium silicate and α-quartz phases.

In the present investigation, the thermal expansion of the crystalline samples C_2–C_4 decreased with MgO/Li_2O replacement ratios. This may be due to the formation of moderately thermal expanding diopside phase [23,24], at the expense of the highly expanding lithium disilicate and lithium calcium silicate phases.

The addition of MgO at the expense of CaO (i.e. C_5) led to decrease their α-values as compared with that of the crystalline eutectic glass C_1 (free of MgO). This may be attributed to the development of relatively moderate low expanding diopside phase instead of the highly expanding lithium calcium silicate phase. Further addition of MgO instead of CaO, i.e. C_6 (free of CaO) led to increase their α-values. This may be attributed to the formation of clinoenstatite phase of higher expansion coefficient than that of diopside phase [9]. Also, the addition of MgO at the expense of (Li_2O + CaO), i.e. C_7, caused slight decrease in the thermal expansion values as compared with that of sample C_5 (with MgO/CaO replacement only). This may be due to the formation of pyroxene ss phase of diopsidic type (in C_7) of lower α-values than that of diopside phase (in C_5) [23,26].

4.3. Chemical durability of glass-ceramics

The chemical stability of glasses and glass-ceramics determines their applications in different environments and is therefore of considerable practical importance. The mechanisms of reactions occurring between glasses and aqueous solutions, and the factors affecting the chemical durability were studied. It is generally agreed that the chemical behaviour of silicate glasses is related to their composition [27].

The acid durability of glass-ceramics depends essentially on the nature and content of crystalline phases present and residual glassy phase [21]. Microstructure can be also taken into considerations. The non-porous microstructure of the glass-ceramics makes it possible to count on better chemical stability as compared with porous ceramics, which have a more extensive surface and greater penetrability to liquids and vapors [28].

Lithium meta- and disilicates on the other hand, are decomposed by acidic solution [7]. McMillan [7] showed that the presence of a large proportion of crystalline silica in the form of cristobalite or quartz gives a better chemical durability.

The present results revealed that, by adding CaF_2 in the eutectic glass, i.e. C_1, the leaching value of the investigated glass-ceramic was increased. This may be attributed to the formation of fluorite phase, among the crystallization products, which is slightly soluble in HCl [5]. Also, the presence of TiO_2 in the eutectic glass slightly decreased the chemical stability of the investigated glass-ceramic. This may be due to the slight enhancement of the crystallization of less durable lithium disilicate and lithium calcium silicate phases [5].

The gradual addition of MgO at the expense of Li_2O in the investigated glass, decreases the leachability of the crystalline samples (e.g. C_2, C_3 and C_4), i.e. the chemical durability was markedly improved. This may be due to the crystallization of more durable diopside phase instead of the less durable lithium calcium silicate phase ($Li_2Ca_4Si_4O_{13}$) [5].

However on increasing MgO/CaO replacement, e.g. C_6 (with high MgO content, i.e. free of CaO), the decrease in the chemical durability was detected, this may be attributed to the formation of the slightly attacked clinoenstatite phase [5] instead of insoluble diopside phase ($CaMgSi_2O_6$). The combined replacement of ($Li_2O + CaO$) by MgO, i.e. C_7, slightly improved the durability of the crystalline samples in acidic solution as compared with that of sample C_5. This may be ascribed to the crystallization of the more durable pyroxene ss of diopsidic type phases [5].

5. Conclusions

The crystallization process and the properties of the glasses based on the eutectic system $Li_2O–CaO–SiO_2$ modified by adding MgO at the expense of Li_2O and/or CaO were investigated. The addition of CaF_2 as a nucleating agent to the eutectic glass led to improve the rate of crystallization of the glasses. TiO_2 has a very low effect on glass and glass-ceramic properties. Fine microstructures of fibrous and prismatic growths were developed in magnesium-containing glass-ceramic.

Varieties of Mg-containing phases, $CaMgSi_2O_6$, $MgSiO_3$ and pyroxene solid solution could be obtained together with lithium disilicate, α-quartz and lithium calcium silicate phases. The types of the crystallized phases are discussed in relation to the compositional variation of the glasses and thermal treatment used.

The α-values of the studied glasses ranged between $(+18) \times 10^{-7}\,K^{-1}$ and $(+123) \times 10^{-7}\,K^{-1}$ (25–300 °C) temperature range and those of the crystalline materials ranged from $(-7) \times 10^{-7}\,K^{-1}$ to $(+115) \times 10^{-7}\,K^{-1}$ (25–700 °C) temperature range. The chemical durability of the glass-ceramics towards the attack of acid solution was markedly improved with addition of MgO at the expense of Li_2O and/or CaO.

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