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Preparation and properties of Li_2O-BaO-Al_2O_3-SiO_2 glass-ceramic materials

Gamal A. Khater[1,*], Maher H. Idris[2]

[1] *National Research Center, Glass Research Department, Dokki, Cairo, Egypt*
[2] *Saudi Geological Survey-Jeddah, Saudi Arabia*

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Abstract

The crystallization of some glasses, based on celsian-spodumene glass-ceramics, was investigated by different techniques including differential thermal analysis, optical microscope, X-ray diffraction, indentation, micro-hardness, bending strengths, water absorption and density measurement. The batches were melted and then cast into glasses, which were subjected to heat treatment to induce controlled crystallization. The resulting crystalline materials were mainly composed of β-eucryptite solid solution, β-spodumene solid solution, hexa-celsian and monoclinic celsian, exhibiting fine grains and uniform texture. It has been found that an increasing content of celsian phase in the glasses results in increased bulk crystallization. The obtained glass-ceramic materials are characterized by high values of hardness ranging between 953 and 1013 kg/mm^2, zero water absorption and bending strengths values ranging between 88 and 126 MPa, which makes them suitable for many applications under aggressive mechanical conditions.

Keywords: *crystallization, celsian-spodumene glass-ceramics, characterization, mechanical properties*

I. Introduction

Glass-ceramics are polycrystalline solids produced by controlled devitrification of glass. Starting materials are first melted, casted into glass, shaped and finally converted to a ceramics by a specific heat treatment. The glass-ceramic structure is characterized by fine-grained randomly oriented crystals with some residual glass, but with no voids or micro cracks. Glass-ceramics is characterized by a wide variety of unique properties, which are determined by the inherent characteristics of their constituent phases, and by the form of microstructure resulting in crystal nucleation and growth process.

The use of different natural rocks for the production of glass-ceramic materials is an ever widening field of technology. Economic considerations may dictate the use of cheap starting materials. Sedimentary rocks cover the greatest part of the Saudi territories, and the study of their use in the production of glass-ceramic materials may be of special scientific, technological and economic importance. Some local raw materials, such as kaolin clay and some quartz sands were used, together with barium and lithium carbonates, as starting materials for the preparation of glass-ceramics based on celsian $BaAl_2Si_2O_8$ and spodumene $LiAlSi_2O_6$ crystal phases. Such types of glass-ceramics were extensively investigated by many authors [1–4].

Glass-ceramics are used in a wide range of technical applications, for example, in construction, domestic purposes, and in the microelectronics industry [5]. Khater [6] managed to obtain a glass-ceramic material characterized by low thermal expansion coefficient from glasses based on clay, sand, $BaCO_3$ and Li_2CO_3, with some additions of catalysts. Idris [7] studied the effect of different nucleating agents on crystallizing phases and microstracture in Li, Ba aluminosilicate glasses. He conducted that TiO_2 and LiF facilitate the crystallization process and favour the transformation of β-eucryptite solid solution (β-eucryptite ss) to β-spodumene solid solution (β-spodumene ss), and hexacelsian to monoclinic celsian (m-celsian). Khater and Idris [8,9] studied the expansion characteristics of some Li_2O-BaO-Al_2O_3-SiO_2 glasses and glass-ceramics. They conducted tests to obtain glass-ceramic materials characterized by low thermal expansion coefficient. El-Shennawi *et al.* [10] studied the crystallization of celsian polymorphs in some alkaline earth aluminosilicate glasses.

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[*] Corresponding author: tel: +2 01099291305
fax: +2 0233370931, e-mail: *j.khater@yahoo.com*

The nature and character of the crystalline phases and the microstructure of the materials are the most important factors affecting the technical properties of glass-ceramics [11,12]. The aim of this paper is to study the crystallization process of some glass compositions based on the celsian-spodumene with successive additions of celsian component and an evaluation of glass-ceramic products, depending on phases, microstructures and hardness.

II. Experimental

2.1. Glass compositions and batch preparation

The choice of a suitable base glass composition for conversion into glass-ceramic depends not only on the preparation and crystallization conditions, but also on the crystalline phase properties. Kaolin clay and silica sand were used as starting materials for batch preparation of technical glass-ceramics. The chemical analyses data of these materials are listed in Table 1. Five glass compositions within the celsian ($BaAl_2Si_2O_8$) - spodumene ($LiAlSi_2O_6$) system were selected for the present paper. These compositions are based on the spodumene with successive addition of celsian, up to 50 wt.%, and are designated as G10, G20, G30, G40 and G50 (Table 2), where the number indicates the weight percentage of the celsian component, and the rest being the spodumene component. The batches corresponding to these compositions were prepared by calculating the appropriate proportions of local Saudi kaolin clay and silica sand. In addition to these local raw materials, some technical chemical reagents such as Li_2CO_3 and $BaCO_3$ were used as sources of Li_2O and BaO and corresponding compositions of prepared batches are given in Table 2.

After being thoroughly mixed, the weighted powdered batch materials were melted in Pt crucibles in a Globar furnace at temperatures ranging from 1450 °C to 1550 °C for 2–3 h, depending on composition. Homogeneity of the melts was achieved by swirling the crucible several times at about 20 min intervals. After melting and refining, the bubble-free melt was cast onto a steel marver into buttons and rods, and transferred to a preheated muffle furnace for annealing.

2.2. Thermal treatment

The glass samples were heated in a muffle furnace from room temperature to the required temperature (which was 800 °C to 1050 °C at 50 °C intervals) and kept at the intended temperature for 1–40 h, after which the furnace was switched off and the samples were allowed to cool inside it to room temperature.

A double-stage heat-treatment schedule was also used to study its effect on the microstructure. Glass samples were first soaked at 700 °C for 1 h and then at 950 °C for 1 h.

2.3. Characterization

Differential thermal analysis (DTA) was carried out using a Perkin-Elmer (7 series) micro differential thermo analyser. Powdered glass sample (60 mg), having grain size less than 0.60 mm and larger than 0.2 mm, was used against Al_2O_3 powder, as a reference material. Heating rate of 20 K/min was maintained for all DTA runs.

Identification of crystals precipitating in the course of crystallization was conducted by X-ray diffraction analysis of the powdered samples, using a Philips type (BM 1710) and Ni-filtered CuK radiation. All the instrument settings were maintained for all the analysis, using a Si disk as an external standard. This was necessary to make the measurements more accurate, based on the peak height.

The mineralogical constitution and microstructure of almost all the heat treated specimens were examined optically in thin sections using a polarizing Carl Zeiss research microscope.

Indentation micro-hardness of the investigated samples was measured by using Vicker's micro-hardness indenter (Shimadzu, Type-M, Japan). Testing was made using a load of 100 g and loading time of 15 s. The Vicker's micro-hardness value was calculated using the

Table 1. Chemical analyses of the raw materials used

Raw material	SiO_2 [wt.%]	Al_2O_3 [wt.%]	Fe_2O_3 [wt.%]	TiO_2 [wt.%]	MgO [wt.%]	CaO [wt.%]	Na_2O [wt.%]	K_2O [wt.%]	L.O.I. [wt.%]
Silica sand	99.5	0.52	0.04	—	<0.05	<0.05	<0.05	<0.05	—
Kaolin clay	42.9	36	1.1	2.8	0.2	0.63	0.99	0.09	15.1

Table 2. Compositions of the investigated glasses

Glass No.	Nominal phase composition		Calculated oxide constituents				Batch ingredient			
	Celsian [wt.%]	Spodumene [wt.%]	SiO_2 [wt.%]	Al_2O_3 [wt.%]	Li_2O [wt.%]	BaO [wt.%]	Kaolin clay [wt.%]	Silica sand [wt.%]	Li_2CO_3 [wt.%]	$BaCO_3$ [wt.%]
G10	10	90	61.42	27.38	7.23	4.08	59.45	22.50	13.94	4.11
G20	20	80	58.08	27.35	6.42	8.17	59.44	19.94	12.40	8.22
G30	30	70	54.81	27.33	5.62	12.25	59.36	17.47	10.85	12.32
G40	40	60	51.55	27.30	4.82	16.34	59.29	14.98	9.30	16.43
G50	50	50	48.29	27.27	4.02	20.42	59.24	12.49	7.75	20.52

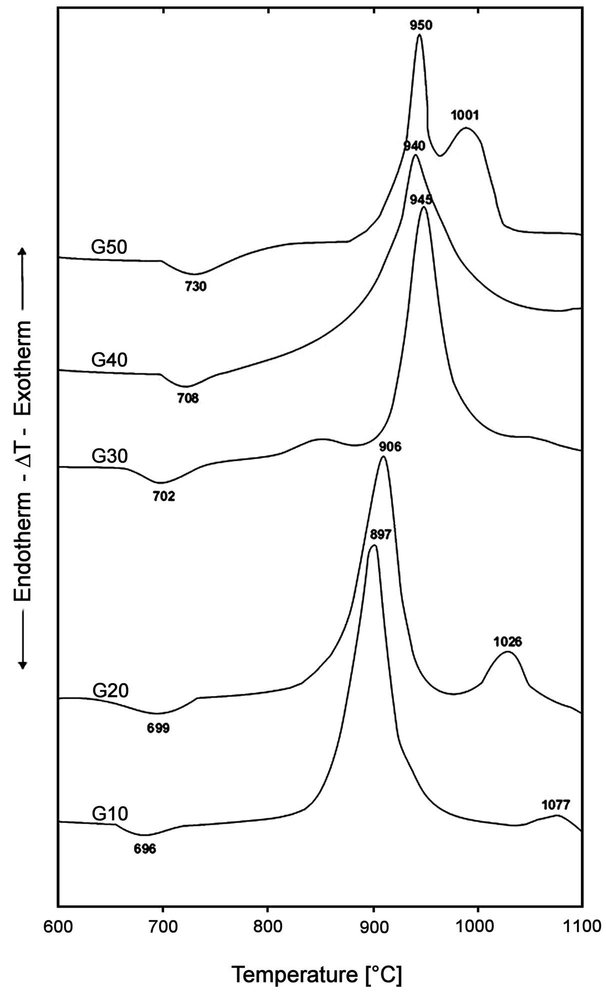

Figure 1. DTA traces of the investigated glasses

following equation: $H_v = A \cdot p/d^2$ (kg/mm^2), where A is a constant equal to 1854.5, p is the applied load (g) and d is the average diagonal length (µm).

Bending strength was evaluated by four point bending strength of the as-prepared glass-ceramics (1000 °C for 3 h), measured on unpolished as-produced test pieces using a universal testing machine (Shimadzu Autograph DCS-R-10TS, Shimadzu) at a crosshead speed of 0.5 mm/min. The reason for using unpolished test pieces is to obtain the strength data from the as-produced samples such as the actually used in building materials and also to avoid chipping of glassy-phase-containing samples by polishing.

Water absorption was also determined. A sample was dried until the weight remains constant, cooled in desiccators and weighed (W_1). Then, the sample was placed in a metal pot (filled with water) and heated until boiling for two hours. Finally, the sample was removed from the pot and excess water was removed from each side of a sample with damp cloth and recorded as (W_2). The percentage of water absorption (W_{abs}) was calculated according the following equation:

$$W_{abs} = \frac{W_2 - W_1}{W_1} \cdot 100 \tag{1}$$

Density was measured by the Archimedes method. Samples were weighed using calibrated four decimal point scales, once in air then again with the sample suspended in distilled water. This allowed the calculation of glass density using the following equation:

$$D = \frac{W_A}{W_A - W_w} \cdot \delta_w \tag{2}$$

where W_A is the weight in air, W_w is the weight in distilled water, and δ_w is the correction factor for the density of water at the measurement temperature, available from standard chemistry data.

III. Results

Differential thermal analysis results of the investigated glasses are presented in Fig. 1. The endothermic peak that appears in the interval 696–730 °C is common to correspond to the glass transition effect. In addition, it is common that T_g is donated as glass transition temperature. It is widely known that if viscosity is higher, the glass transition temperature T_g is higher. These small heat absorptions may indicate the molecular rearrangement preceding the glass crystallization, i.e. pre-crystallization stage [13]. Exothermic peaks indicating crystallization reaction are also recorded. As the celsian content in the glass composition was increased the peak temperature of the crystallization exotherms increased, and the endothermic effects mentioned above slightly displaced towards high temperatures. These effects may be ascribed to the viscosity temperature relations of the glass since the upward shift of the endotherms may indicate higher viscosities.

The positions of both exothermic and endothermic peaks (Fig. 1) were slightly shifted to higher temperatures for glasses in the order from G10 to G50, respectively. In other words the temperatures corresponding to either T_g or pre-crystallization endothermic peaks of the glasses emerged slightly towards higher temperature values with the increase of celsian content in the glasses.

The broad nature of the exothermic peaks (Fig. 1) indicates the wide temperature range through which crystallization of the investigated glasses may take place. Accordingly, the glass samples (G10-G50) were treated at a temperature in the middle and extreme crystallization range, i.e. from 800 to 1050 °C. However, the low peak height indicates that relatively long heating time is necessity to form considerable volume fraction of the crystalline phases. Thus, heating for about 1 h was found to be the minimum time required to initiate the crystallization process in these glasses. The heat treatment process in temperature range from 800 to 1050 °C for 1 h covers most of the thermal variations appearing on their DTA curves (Fig. 1). Table 3 summarizes the DTA peak temperatures, thermal effects and corresponding structural changes.

Another two pertinent features related to the crystallization process could be noticed on the DTA curves. The first feature is the broad endothermic

Table 3. Thermal behaviour of the investigated glasses

Glass No.	Peak temperature (°C)	Thermal effect
G10	680	Minor shallow dip
	696	Little explicit endothermic peak
	897	Sharp exothermic peaks
	1077	Broad exothermic peaks
G20	683	Minor shallow dip
	699	Little explicit endothermic peak
	906	Sharp exothermic peaks
	1026	Moderate exothermic peaks
G30	689	Minor shallow dip
	702	Little explicit endothermic peak
	945	Sharp exothermic peaks
G40	691	Minor shallow dip
	708	Little explicit endothermic peak
	940	Sharp exothermic peaks
G50	695	Minor shallow dip
	730	Little explicit endothermic peak
	950	Sharp exothermic peaks
	1001	Moderate exothermic peaks

peaks appearing in the temperature range 696–730 °C. These endothermic peaks approximately correspond to phenomenon preceding glass crystallization (pre-crystallization processes), where the glass forming elements begin to arrange themselves in preliminary structural groups suitable for subsequent crystallization [14]. However, it is possible that small amount of nuclei already exist in glass matrix prior to the thermal treatment. The second feature is the major exothermic peaks appearing in the temperature range 864–907 °C immediately following the major endothermic peaks. These exothermic peaks are due to glass devitrification and release of corresponding thermal energy.

X-ray diffraction (Fig. 2) showed that β-eucryptite ss, β-spodumene ss, hexacelsian and the monoclinic celsian were the main crystalline phases developed in the glasses after treated at 950 °C for 1 h. Their amount depended largely on base composition and on crystallization parameters. In the sample G10 β-spodumene ss and monoclinic celsian were formed, and in the sample G20 β-spodumene ss and hexacelsian ss as a major crystalline phase together with traces of β-eucryptite ss and monoclinic celsian. In the samples G30, G40 and G50, β-eucryptite ss and hexacelsian were formed together.

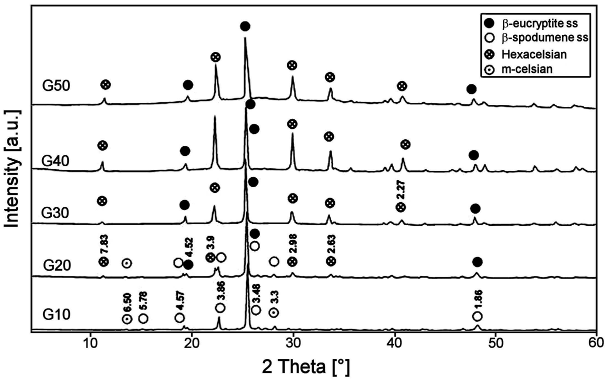

Figure 2. X-ray diffraction patterns of glass samples G10 - G50 heat-treated at 950 °C for 1 hour

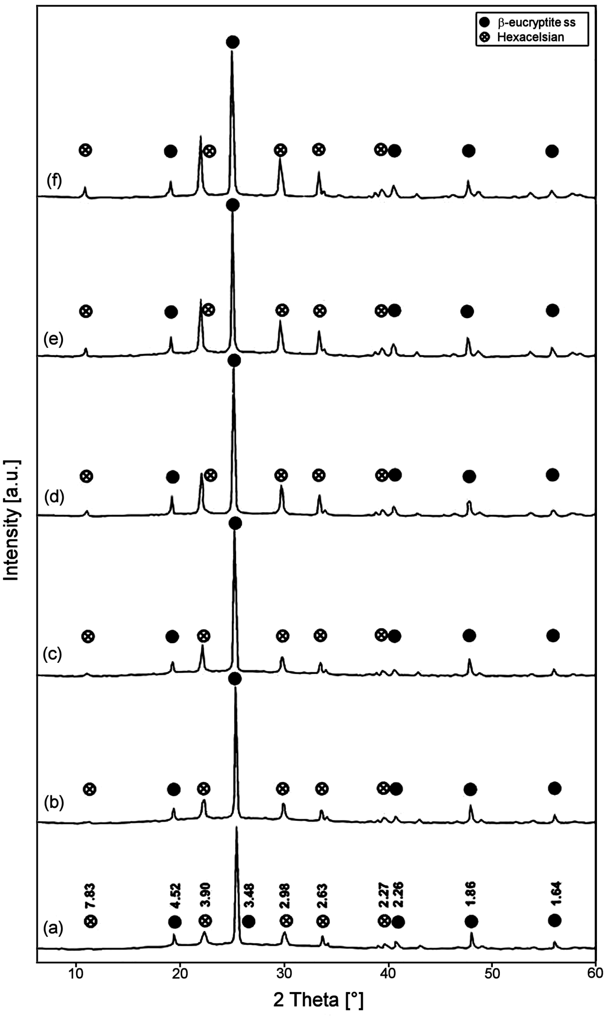

Figure 3. X-ray diffraction patterns of G30 glasses heat-treated for 1 h at: a) 800 °C, b) 850 °C, c) 900 °C, d) 950 °C, e) 1000 °C and f) 1050 °C

Figure 3 depicts the X-ray diffraction patterns of the sample G30 subjected to different heat-treatments schedule (800–1050 °C at 50 °C steps) for 1 h. At 800 °C to 1050 °C β-eucryptite ss and hexacelsian were formed together (Fig. 3 patterns a-f). The amount of these two phases increased progressively with temperature, the β-eucryptite ss and hexacelsian showed a maximum amount at around 1050 °C. The strong intensities of both β-eucryptite ss and hexacelsian diffraction lines and their slight shift to higher 2θ values indicate a solid solution character of the obtained phases. Although this sample was almost completely crystallized, β-spodumene ss or monoclinic celsian were not formed at these stages.

Figure 4 shows a comparison between the X-ray diffraction patterns of the sample G30 treated at 1050 °C for different times (5 h, 20 h, 30 h and 40 h). After the

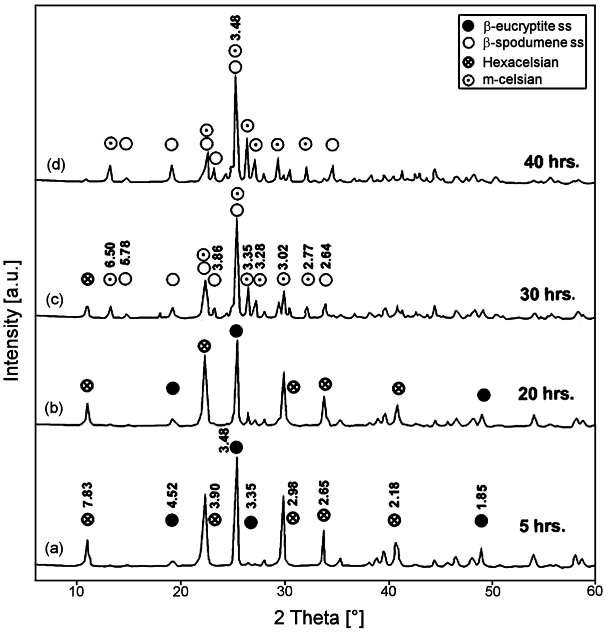

Figure 4. X-ray diffraction patterns of G30 glasses heat-treated at 1050 °C for: a) 5, b) 20, c) 30 and d) 40 hours

treatment at a higher temperature for long durations the X-ray patterns become more explicit, and nearly approaching the nominal phase constitution. At 1050 °C and heat treatment of 5 h and 20 h (Fig. 4 patterns a and b) β-eucryptite ss and hexacelsian phases were better developed. After 30 h at 1050 °C β-eucryptite ss completely transformed into β-spodumene ss and hexacelsian partially transformed into monoclinic celsian (pattern c). After 40 h at 1050 °C β-spodumene ss and monoclinic celsian were better developed and the X-ray patterns became more explicit and nearly approaching the nominal phase constitution. This is confirmed when the intensities of hexacelsian diffraction lines (7.83, 3.90 and 2.98 Å, Fig. 4 pattern a) disappeared and transformed into monoclinic celsian (characterized by the following XRD lines 6.50, 3.9 and 3.35 Å, Fig. 4 pattern d). Table 4 gives a summary of the crystalline phases developed after various heat treatment conditions as identified by XRD.

Visual and petrography investigations (Figs. 5 and 6) of the heat-treated glass showed that coarse grained textures contain rounded aggregates of β-eucryptite ss, β-spodumene ss, hexacelsian and monoclinic celsian in the samples G10 and G20. On the other hand, in the celsian rich glasses (G30, G40 and G50) the change in the texture of the glass-ceramic specimens from coarse grained to fine grained is noticed. Table 5 shows that the density of the glass-ceramics increases with the increase of celsian content. Table 5 also shows that densities of the glass-ceramics containing monoclinic celsian and β-spodumene ss are higher than densities of the glass-ceramics containing hexacelsian and β-eucryptite ss.

The various properties of the resultant glass-ceramics are also listed in Table 5. The bending strengths of 88 to 122 MPa were carried out in the glass ceramic samples heat treated at 950 °C for 1 h. The bending strength increases with the increase of celsian content and may

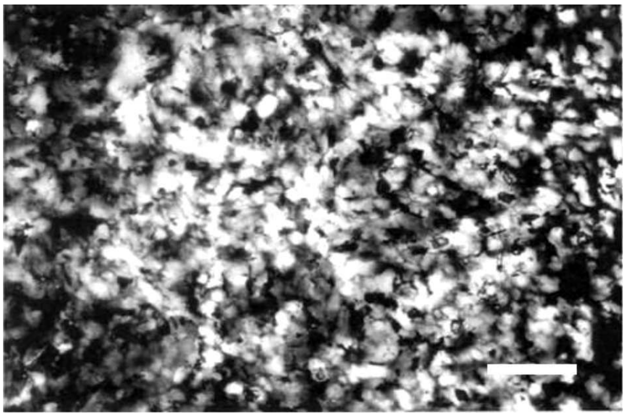

Figure 5. Micrograph of G10 glass heat treated at 700 °C, 1 hour and 950 °C, 1 hour (bar = 60 µm)

Table 4. X-ray identification of crystalline phases developed in the investigated glasses at selected heat-treatment temperatures

Glass No.	Heat-treatment parameters	Phases developed after heat treatment
G10	950 °C, 1 h	β-spodumene ss + m-celsian (trace)
G20	950 °C, 1 h	β-eucryptite ss + β-spodumene ss + hexacelsian + m-celsian
G30	800 °C, 1 h	β-eucryptite ss + hexacelsian
	850 °C, 1 h	β-eucryptite ss + hexacelsian
	900 °C, 1 h	β-eucryptite ss + hexacelsian
	950 °C, 1 h	β-eucryptite ss + hexacelsian
	1000 °C, 1 h	β-eucryptite ss + hexacelsian
	1050 °C, 1 h	β-eucryptite ss + hexacelsian
	1050 °C, 5 h	β-eucryptite ss + hexacelsian
	1050 °C, 20 h	β-eucryptite ss + hexacelsian
	1050 °C, 30 h	β-spodumene ss + m-celsian + hexacelsian (trace)
	1050 °C, 40 h	β-spodumene ss + m-celsian
G40	950 °C, 1 h	β-eucryptite ss + hexacelsian
G50	950 °C, 1 h	β-eucryptite ss + hexacelsian

Table 5. Properties of the investigated glass-ceramic materials

Glass No.	Heat-treatment parameters	Hardness [kg/mm^2] (±3)	Bending strength [MPa] (±1)	Water absorption [%]	Density [g/cm^3] (±0.013)	Phases developed after heat treatment
G10	950 °C, 1 h	953	88	0.0	2.997	β-spodumene ss + m-celsian (trace)
G20	950 °C, 1 h	967	97	0.0	3.002	β-eucryptite ss + β-spodumene ss + hexacelsian + m-celsian
G30	950 °C, 1 h	983	110	0.0	3.014	β-eucryptite ss + hexacelsian
	1050 °C, 40 h	1008	126	0.0	3.352	β-spodumene ss + m-celsian
G40	950 °C, 1 h	992	118	0.0	3.148	β-eucryptite ss + hexacelsian
G50	950 °C, 1 h	1013	122	0.0	3.221	β-eucryptite ss + hexacelsian

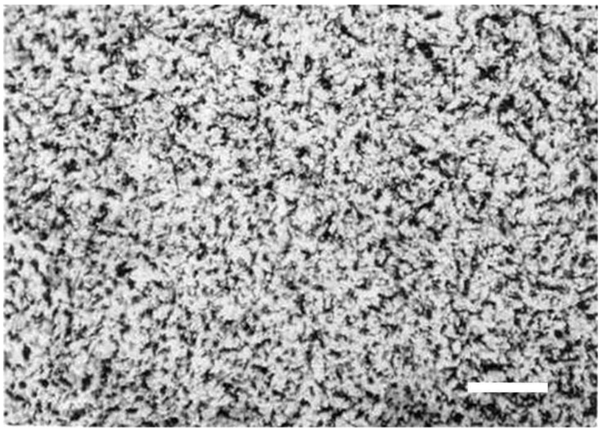

Figure 6. Micrograph of G40 heat treated at 700 °C, 1 hour and 950 °C, 1 hour (bar = 60 µm)

be attributed to the different major crystalline phases. Therefore, it is found that hexacelsian and monoclinic celsian are more preferable crystalline phases than β-eucryptite ss and β-spodumene ss from the viewpoint of the strength of these glass-ceramics.

Indentation microhardness measured for the obtained glass-ceramic materials heat treated at 950 °C for 1 h was found to lie in the range from 953 to 1013 kg/mm^2 (Table 5). The Vicker's hardness increases with the increase of celsian content and the hardness of the glass-ceramics containing monoclinic celsian and β-spodumene ss are higher than the glass-ceramics containing hexacelsian and β-eucryptite ss.

IV. Discussion

The crystallization process in the obtained glass-ceramics is carefully analysed. It is confirmed that crystallization starts in the glasses G10 and G20 at relatively lower temperature, and causes formation of coarse grained texture. In the glasses G30 to G50 crystallization starts at higher temperatures and throughout the entire volume of the samples fine grained texture is formed. Generally speaking, as spodumene content increases in the compositions and consequently celsian content decreases, the crystallization is easier (i.e. the glass is more crystallizable) and begins at lower temperatures, and vice versa. This is most probably due to the role played by Li$^+$ ions, which are known to reduce the viscosity of the melt, and consequently the mobility and diffusion of ions in the corresponding glasses are increased. Avramov [15] studied the properties of the basic oxides in lithium aluminosilicate glasses and attributed the efficiency of the Li$_2$O towards the homogeneous crystallization to the combination of the high mobility and high field strength of the Li$^+$ ion.

The phases encountered during the crystallization of the studied glasses were β-eucryptite ss, β-spodumene ss, hexacelsian and monoclinic celsian. The relative abundance and the appearance or disappearance of some of the above mentioned phases depend greatly upon the composition of the crystallizing glass and the parameter of crystallization, namely temperature and time of heat-treatment.

Lithium aluminium silicate phases (β-eucryptite ss and/or β-spodumene ss) are the essential minerals that crystallized in the investigated glasses (G10 to G50). Hexacelsian and monoclinic celsian are also encountered. The crystallization in the spodumene-rich glasses begins at relatively lower temperature with the formation of solid solution. β-eucryptite ss was formed at 950 °C for 1 hour duration (G10 and G20). In cases of high barium oxide content (G30 to G50) the β-eucryptite ss → β-spodumene ss transformation needs long duration due to the presence of increasing Ba^{2+} ions in the structure of lithium aluminium silicate phases.

The present results are in accordance with those given in the literature concerning the nature of crystallization and the character of lithium aluminosilicate phases. β-eucryptite solid solutions have previously been known to be metastable along the joint Li$_2$O-Al$_2$O$_3$-SiO$_2$ [16], but it was not expected so far from its end members and the joint between them. However, the lithium-bearing phases formed on heat-treatment at low temperature gives X-ray diffraction patterns similar to those of high quartz and fits between the diffraction lines of the limiting solid solution obtained by Roy [17]. The first phase developed was β-eucryptite solid solution. This indicates a solid solution of Al^{3+} and Li^{+}, probably with the other suitable Mg^{2+} ions. The β-spodumene ss were apparently formed by recrystallization of the primarily formed β-eucryptite ss rather than by direct crystallization from glass.

The phase relations of celsian polymorphs have been the subjects of much controversy. The present results are, however, in fair agreement with most of the literature [18–20], relating to the stoichiometry of celsian only to the broad behaviour of the crystallizing $BaAl_2Si_2O_8$ phases despite the presence of fair amounts of β-eucryptite ss in the parent glass as well as the deviation of the crystallization conditions from true thermodynamic equilibrium. Hexacelsian is the only $BaAl_2Si_2O_8$ phase that crystallizes directly from the present glasses; the monoclinic celsian essentially originates from the reconstructive transformation of the hexacelsian formed initially and not through direct crystallization from the glass.

The fact that hexacelsian, rather than the monoclinic celsian, is formed in the glass could be explained on the basis that the phase most likely to be formed first is the one having the lowest thermodynamic potential barrier for the formation of nuclei of critical size. It may be assumed that short range hexagonal structural elements arise first in the glass and that the formation of nuclei of the hexagonal-like crystalline phase occurs most easily from the kinetic aspect, with the lowest barriers to be overcome [21].

The density of hexacelsian (3.303 g/cm^3) is closer to that of the stoichiometric $BaAl_2SiO_2O_8$ glass (3.025 g/cm^3) than the density of either the monoclinic (3.570 g/cm^3) or the orthorhombic phase (3.310 g/cm^3). This also makes the hexacelsian crystallize more readily than either the monoclinic or the orthorhombic varieties.

V. Conclusions

The crystallization of some glasses based on celsian-spodumene system, generally exhibit good melting ability, workability and crystallizability upon heat-treatment. As the celsian component in the glass increases, showed fine-grained texture and yielded satisfactory products, while as the spodumene component in the glass increases showed coarse grained texture. Increasing the celsian content is desirable for enhancing the crystallizability of the glasses and favours the formation of undeformed crystalline products. The crystallization sequence in the glass begins with the formation of metastable β-eucryptite ss and hexacelsian at 950 °C for 1 h. The β-eucryptite ss was transformed into stable β-spodumene ss and hexacelsian was transformed into stable monoclinic celsian at temperature up to 1050 °C for 40 h.

The obtained glass-ceramic materials are characterized by high values of hardness ranging between 953–1013 kg/mm^2, zero water absorption and bending strengths values ranged between 87 and 126 MPa, which makes them suitable for many applications under aggressive mechanical conditions.

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