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Crystallization of some aluminosilicate glasses

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Abstract

The crystallization behaviour of some glasses within the spodumene-willemite-diopside system is described. DTA, XRD and polarizing microscopy were used for this investigation. Increase of the calculated spodumene and/or willemite contents enhanced batch melting, internal nucleation, and lowered the temperatures of crystallization onset in the glass. Stable β-spodumene, willemite, and diopside phases were directly developed from the melts, whereas, metastable β-eucryptite ss and β-Zn_2SiO_4 ss phases initially crystallized out from the glass. These latter phases were transformed into the stable β-spodumene ss and willemite forms above 900°C and around 840°C respectively. Diopside was generally difficult to crystallize out from the glasses. Some crystalline glasses exhibited very low thermal expansion coefficients (-8 to 16×10^{-7}/°C); this was discussed in terms of the type and relative proportions of the constituent phases. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: Crystallization; Aluminosilicate glasses

1. Introduction

Since the discovery of glass–ceramics intensive proliferation of glass compositions for many technical diverse application have been exploited [1]. The choice of composition for a glass–ceramic must depend not only on the ease with which the glass can be prepared and nucleated, but also on the properties expected for the subsequent crystalline phases developed [2]. As the number of possible phases increases, the probability of formation of fine-grained microstructures increases as well because the complex nature of the chemical composition hinders the diffusion of ions over large distances.

In addition, compositions crystallizing to give solid solutions (ss) are of great importance from the physical properties point of view. The more complex the composition of the glass is, the greater will be the diversity of the expected crystalline phases, and the higher the probability of a successful combination of properties in the resultant glass–ceramic [3].

The present work is concerned with the study of the crystallization processes of complex polycomponent aluminosilicate glasses containing Li_2O, MgO, CaO and ZnO, which may yield one or more of the most promising glass–ceramic-forming phases i.e spodumene ss, willemite ss and diopside ss [4–7]. The effect of glass composition and heat-treatment parameters on the crystallization behaviour and thermal expansion characteristics as well as hardness and density of the resultant products are the main object of this paper.

2. Experimental

2.1. Glass preparation

The glasses (Table 1) were prepared from acid washed quartz sand and chemical reagents of high purity Li_2CO_3, $CaCO_3$, $MgCO_3$, ZnO, and Al_2O_3. The calculated proportions were thoroughly mixed and melted in platinum crucibles in an electrical furnace at about 1450°C for 2.5–3.5 h; depending on glass composition. The homogeneity of the melt was achieved through swirling of the melt-containing crucible several times at about 20 min intervals, and was checked by the uniformity of the refraction index of glass grains under a microscope. Specimens for heat-treatments were prepared in the form of buttons and rods. Crystallization of the glass was achieved through single, double and multi-stage (successive) heat-treatment schedules.

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The thermal behavior of the prepared glasses was determined using differential thermal analysis. All the glass samples were crushed to a grain size of 90–250 μ m. The DTA scans were performed on a computerized system (Perkin-Elmer Model DTA-7/Unix system, Norwalk, CT) in dynamic pure nitrogen atmosphere flow (50 cm^3/min). Approximately 70 mg of the powdered sample, a heating rate of 10°C/min and corundum as reference material, was applied in all the DTA runs. Heating scans were conducted from ambient temperature to 1100°C.

Powder X-ray diffraction analyses of the heat-treated glasses were performed using a Philips PW 1390 diffractometer.

The mineralogical composition and microstructures of heat-treated samples were determined whenever possible in thin sections. Fresh fractured surfaces of some samples also were examined via scanning electron microscopy (SEM) (model JSM-T20, Jeol, Tokyo, Japan); these surface were etched by a 5% HF solution for 10 s before scanning.

The linear thermal expansion of the crystalline products was determined up to 900°C using a fused silica dilatometer of Malkin type and the specimen dimension was 5–7×1×1cm at a heating 5°C/min. The microhardness values were measured with a Shimadzu Microhardness Tester type-M under indentor load of 50 g and a time of 15 s.

3. Results and discussion

The DTA traces of the studied glasses (Fig. 1) exhibit a shallow endothermic effect in the temperature range 532–554°C and an exothermic peak in the temperature range 710–813°C. Occasionally minor but significant exotherms were observed at higher temperatures, especially in glasses G4 and G5.

As was mentioned by El-Shennawi et al. [8], this endotherm indicates the glass transition temperature (T_g), which is believed to have been caused by an increase in heat capacity that was attributed to the transformation of the glass structure [9]. The major exotherms (in the 710–813°C range) are attributed, in general, to the cocrystallization of β-eucryptite ss and β-Zn_2SiO_4 phase (as in G2 and G4). At slightly higher temperatures, diopside ss appears (G1). In G3 and G5 both β-Zn_2SiO_4, in significant amounts and diopside ss, in much lesser amounts, form together with the major β-eucryptite ss during the temperature span of the exotherms. The minor exotherms observed at 840 and 860°C in G5 and G4 are ascribed to the β→α transformation of the zinc orthosilicate phase.

By comparing of the DTA exothermic peaks of G2 with that of G4 and G1 with G3, it becomes evident that these glasses, which maintain a constant nominal willemite/diopside molar ratio, have a similar crystallization behaviour, however, the exothermic peaks representing crystallization are displaced to slightly higher temperatures as the nominal spodumene content

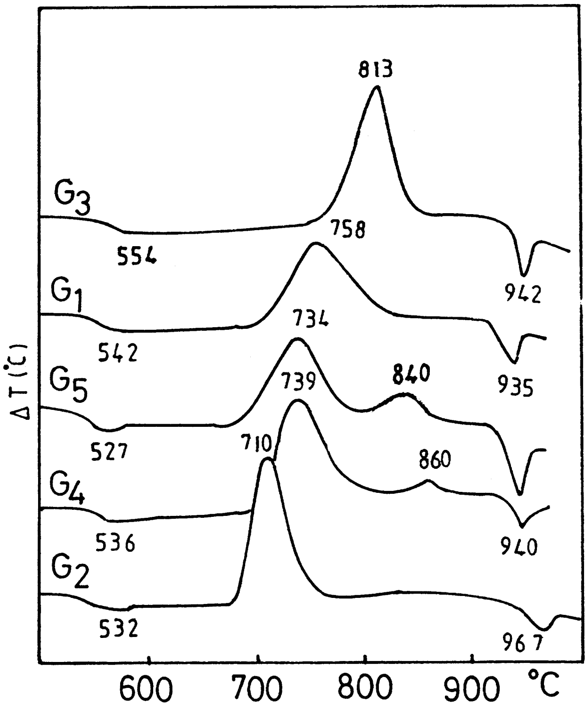


Fig. 1. DTA traces of the studied glasses.

Table 1
Composition of the investigated glasses

Glass No.	Constituent oxides (wt.%)			Nominal phase composition (mol%)					
	Li_2O	CaO	MgO	ZnO	Al_2O_3	SiO_2	Spod[a]	Will.[a]	Diop[a]
G1	4.98	6.89	4.95	8.33	16.98	57.87	62.0	11.4	26.6
G2	4.98	2.95	2.12	19.3	16.98	53.54	62.0	26.6	11.4
G3	3.31	10.67	7.67	12.5	11.29	54.21	41.2	17.6	41.2
G4	3.31	4.56	3.27	30.9	11.29	47.48	41.2	41.2	17.6
G5	4.34	5.96	4.28	16.0	14.79	53.83	54.0	23.0	23.0

[a] Spodumene, willemite and diopsid.

decreases (from both G1 and G2 to both G3 and G4 respectively, Table 1). The substitution of willemite for diopside, in glasses G2 and G1 or G4 and G3, which have the same nominal spodumene content, caused a decrease in the temperature of the exothermic peak from 758 to 710°C for G1 and G2 and from 813 to 739°C for G3 and G4. In other words, as the nominal spodumene and willemite contents in the glass increase, the crystallization temperature decreases and, simultaneously, the crystallization range becomes wider. On the other hand, the crystallization range is reduced as the spodumene and willemite contents decrease, and the glasses crystallize within a narrow temperature range.

3.1. Effect of heat-treatment on crystallization

The progressive development of the crystalline phases in the heat-treated glasses was followed microscopically and by XRD (Table 2 and Fig. 2). In general, the increase of spodumene/diopside ratio (G3: 1.00, G1: 2.33, G5: 2.34, G4: 2.34, G2: 5.43) causes the crystallization to begin at lower temperatures (Fig. 1).

The mineralogical constitution of the crystalline products (Table 2) was found to be largely dependent on the degree of equilibria which could be attained during the course of heat-treatment. In this concern, the metastable β-eucryptite ss and β-Zn_2SiO_4 phases, developed in the glasses and then transformed after longer periods of heat-treatment to the stable phases β-spodumene, willemite.

It is worthy to mention that the obtained X-ray diffraction peaks characteristic of both β-eucryptite ss and β-spodumene ss (e.g. Fig. 2) showed considerable shift to higher 2θ values than those given in the literature. This is due to the presence of silica in solid solution. The XRD patterns of the formed lithia-bearing phase, on low temperature heat-treatments, are almost similar to those of high quartz ss and fit between the diffraction lines of the limiting solid solutions obtained by Roy [10]. The β-eucryptite ss was verified by the characteristic 4.49, 1.87 and 1.62 Å lines besides its strongest 3.47 Å peak which is the same for β-spodumene ss. The latter is characterized by a substantial increase in the intensities of the 4.56, 3.89, 3.14 and 1.92 Å diffraction lines which are accompanied by a concomitant decrease in the intensities of the of the β-eucryptite ss diffraction lines. The presence of β-Zn_2SiO_4 was confirmed by the diffraction lines.4.09, 2.84, 2.52 and 2.48 Å.

The crystallization of the glasses generally began at low temperatures up to 750°C, by the formation of

Table 2
Crystalline phases, thermal expansion, hardness, and density of some selected glasses

Glass no.	Heat-treatment °C/h	Expansion coefficient ($\times10^{-7}$/°C) /(20–500°C)	Hardness kg/cm^2	Density g/cm^3	Phases developed[a]
G1	None	56.1	–	2.641	Amorphous
	660	–	–	–	Amorphous
	660/4 + 780/4	10.1	633	–	Euc,diop(m),g(m)
	660/4 + 900/3	14.4	593	2.665	Euc,diop,wil,spod(tr)
	660/4 + 1000/3	16.7	633	2.678	Spod,diop,wil,euc(tr)
	1000/15	–	–	–	Spod,diop,wil
G2	None	50.7	–	2.767	Amorphous
	650/4	–	–	–	Amorphous
	650/4 + 780/3	−8.2	766	–	Euc,zn-sil(m)
	650/4 + 900/3	−0.4	836	2.729	Euc,wil,spod,zn-sil(tr)
	650/4 + 1000/3	−0.2	801	2.720	Spod,wil,diop(tr)
	1000/15	–	–	–	Spod,wil,diop(tr)
G3	None	–	–	–	Amorphous
	750/3 + 780/3	–	–	–	Amorphous
	900/3	–	–	–	Euc,diop,wil
	1000/3	–	–	–	Spod,diop,wil,euc(m)
	1000/15	–	–	–	Spod,diop,wil
G4	None	45.4	–	2.989	Amorphous
	660/4	–	–	–	Amorphous
	660/4 + 780/3	5.7	618	–	Euc,zn-sil
	660/4 + 900/3	3.4	695	2.950	Spod,wil,euc
	660/4 + 1000/3	5.7	733	2.948	Spod,wil
	1000/15	–	–	–	Spod,wil
G5	None	49.2	–	2.693	Amorphous
	660/4	–	–	–	Amorphous
	660/4 + 780/3	3.6	750	–	Euc,zn-sil,diop(m)
	660/4 + 900/3	6.5	790	2.737	Euc,wil,diop,zn-sil
	660/4 + 1000/3	10.2	795	2.780	Spod,wil,diop
	1000/15	–	–	–	Spod,wil,diop

[a] euc: β-eucryptite ss; spod: β-spodumene ss; zn-sil: :β-Zn_2SiO_4; wil: wilemite; diop: diopside, tr: trace, m: minor.

β-Zn_2SiO_4 phase especially in ZnO-rich glasses (G2, G4 and G5). A concomitant development of β-eucryptite ss, as star-like, skeletal, feathery growths and hexagonal markings (Fig. 3), took place. Diopside, when crystallized, was usually developed in minor amounts at much higher temperatures (around 1000°C).

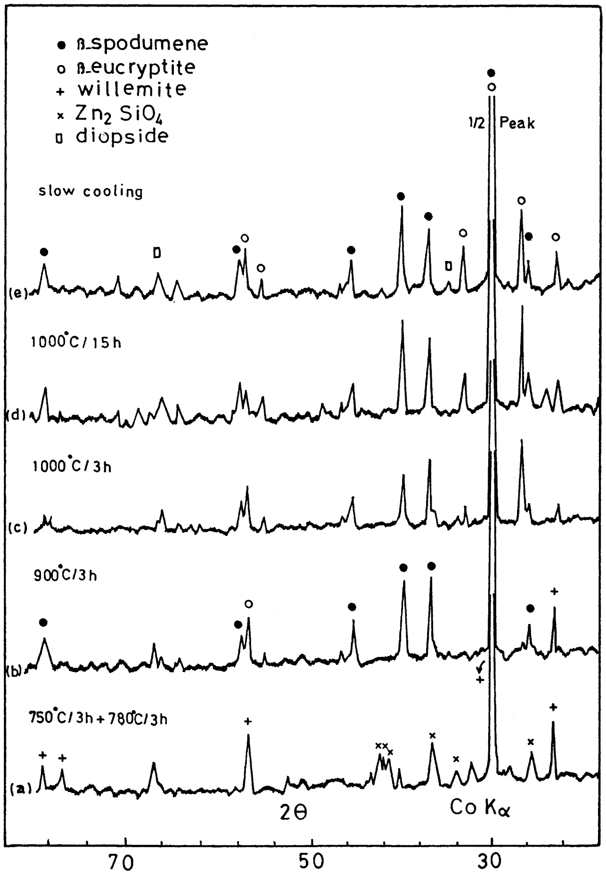


Fig. 2. XRD patterns of glasses G2 heat-treated at different temperatures.

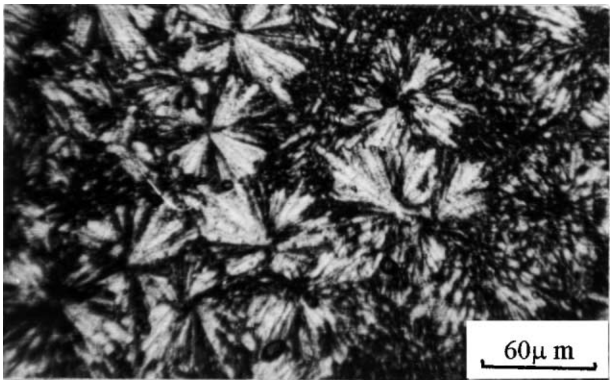


Fig. 3. Photomicrograph of glass G2 isothermally heat-treated at 780°C for 3 h shows, the development of β-eucryptite ss as star-like skeletal, feathery growths and hexagonal markings in cryptocrystalline Zn orthosilicate base.

The β-Zn_2SiO_4 ss rapidly developed in glasses G4, G2 and G5 after low temperature (750–840°C) heat-treatments, however, in amounts smaller than the calculated values, as qualitatively shown by the X-ray diffraction lines. This phase did not form in glasses G1 and G3 even those consecutively treated up to 750°C for long periods (15 h at 650, 10 h at 720, and 24 h at 750°C). When heating was extended for another 20 h at 780°C, traces of willemite were recorded in G3. The β-Zn_2SiO_4, developed in G2, G4 and G5, transformed readily into willemite at about 840°C. Above 840°C, even after short heat-treatment periods (2 h), willemite developed in all the investigated glasses. This is in agreement with Williamson and Glasser [11] who, reported that the β-Zn_2SiO_4 is thermodynamically metastable and converts to the stables α-phase (willemite) on prolonged heating and that at 1000°C the rate of conversion of the β-phase was very rapid, while below 600°C it was very slow.

Diopside was hardly crystallized, and detected in glasses G1, G3 and G5 after low temperature heat-treatments. It was either absent or uncertain in glasses G4 and G2. This was also the case even in long time-heated specimens either at the minimum (750°C) or at the maximum (1000°C) treatment temperatures.

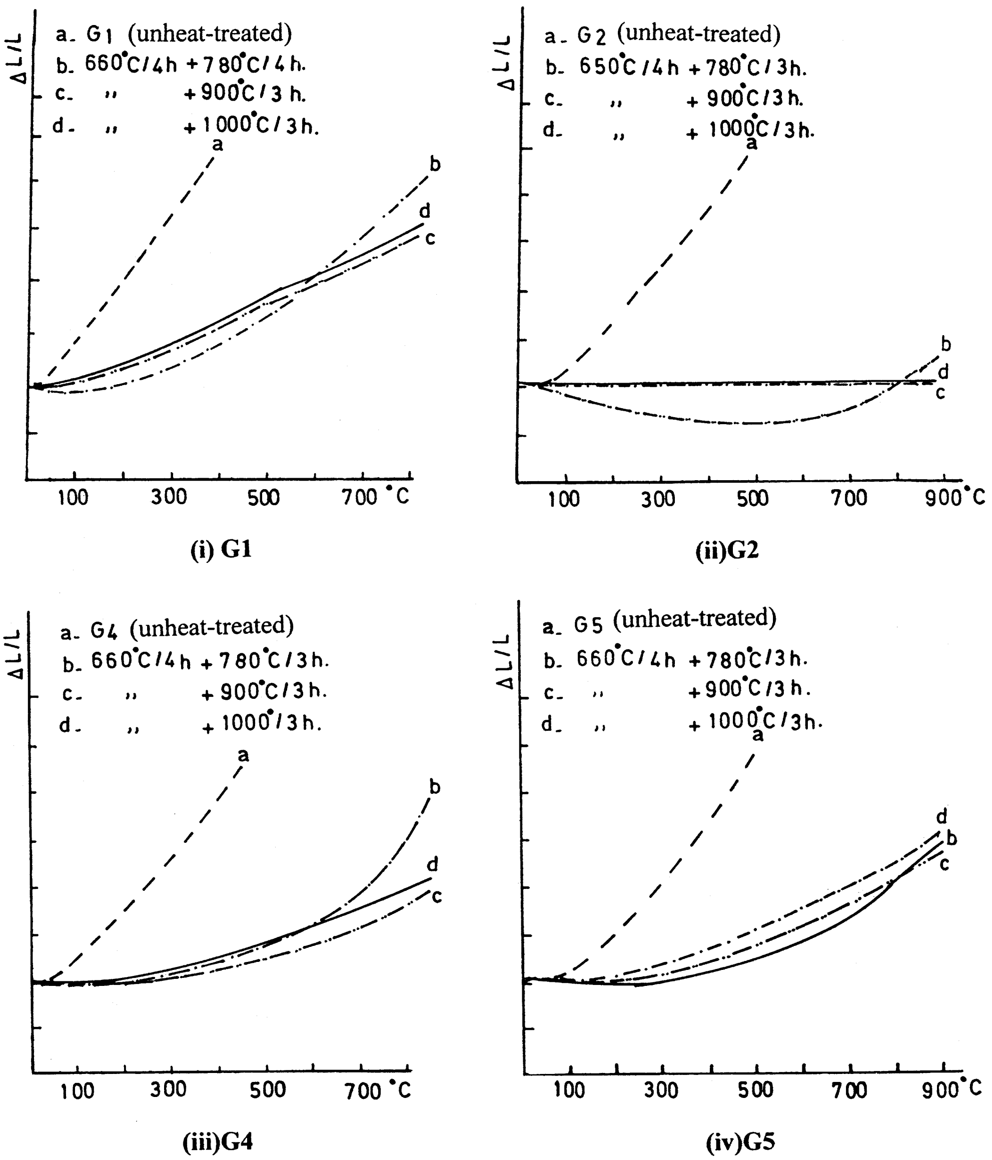
Thus, β-spodumene ss developed by recrystallization of the primarily formed metastable β-eucryptite ss rather than by direct crystallization from the glass [12]. It was reported that [10] the density of spodumene glass (2.370) is closer to that of β-eucryptite (2.352) than to the density of β-spodumene (2.406). This is also in favor of the first crystallization of β-eucryptite rather than β-spodumene in the investigated glasses. At temperatures higher than 900°C, the β-eucryptite ss transformed into β-spodumene ss. On prolonged heating (15 h at 1000°C) the latter showed, a characteristic net-like structure and sometimes a fish-scale appearance.

The β-eucryptite ss has previously been reported to be metastable along the join, Li_2O. Al_2O_3–SiO_2, and barely persisted as temperatures high as 1000°C, except for compositions approaching eucryptite stoichiometry ($Li_2O.Al_2O_3.2SiO_2$) [13,14].

3.2. *Effect of heat-treatment on thermal expansion*

The thermal expansion curves (Fig. 4) of the untreated glasses (curves a) are quite different from the corresponding crystalline products (curves b, c and d) where the former, show relatively steeper slopes, thus expressing higher thermal expansion coefficients (Table 2). The expansion curves of the low-temperature heat-treated glasses (curves b) are anomalous to those of the higher-temperature heat-treatments (curves c and d). The latter's are almost similar in character and magnitude.

After the low temperature heat-treatment, the materials consist mainly of β-eucryptite ss with minor β-Zn_2SiO_4



(i) G1

(ii)G2

(iii)G4

(iv)G5

Fig. 4. Thermal expansion curves of glasses G1, G2, G4 and G5 (i, ii, iii and iv) before and after heat-treatment at different temperatures.

(G2 and G4) and/or minor diopside (G5 and G1). As the temperature of heat-treatment increases to 900°C other phases of relatively higher thermal expansion coefficients, develop along with the major β-eucryptite ss (Table 2). It is worthy to mention that the glass–ceramic material produced from G2 gave, surprisingly low, thermal expansion coefficients of almost zero values over the whole 20–900°C temperature range. This result was confirmed twice and found reproducible.

It is well known that β-eucryptite is highly anisotropic in its thermal expansion. It possesses a high negative directional expansion coefficient (-17.6×10^{-6}/°C) along the c-crystallographic axis and a positive one of (8.2×10^{-6}/°C) in the perpendicular direction in the 20–700°C temperature range [15,16]. Similarly the stuffed derivative phases of the high-quartz structures, containing Li, Mg and Zn, exhibit negative or slightly positive expansions [14,6,7]. The incorporation of Zn lowers the expansion, whereas, Mg increases it. Accordingly to these authors, Mg^{2+} and Al^{3+} in the pseudooctaheral stuffing position cause an increase in thermal expansion, while Li and Zn cause a slight decrease in this parameter. Willemite has a low coefficient of expansion of 15×10^{-7}/°C [5]. No data for the thermal expansion of β-Zn_2SiO_4 phase are available. Dopside has high positive values of thermal expansion of $50–150\times10^{-7}$/°C (20–600°C) [17].

It is known that in the case of solid solutions, the coefficients of expansion would have intermediate values between those of the end members. Accordingly, and because most of the phases developed in our glass–ceramics, namely β-eucryptite, β-spodumene, β-Zn_2SiO_4, willemite and diopside, can form solid solutions, the thermal expansion data (Table 2) could be interpreted in terms of the expansion characteristics, nature and frequency of the crystalline phases present. The effect of a particular phase is, of course, dependent on its concentration as well as on its individual thermal expansion characteristics. The considerable difference between the thermal expansions of G1 and G2 (which have the same spodumene content and a reverse willemite: diopside ratio), i.e. low positive values of G1 and negative expansion values of G2 (upon low-temperature heat-treatment) cannot be attributed solely to the minor amounts of either diopside or β-Zn_2SiO_4 phases which result along with the major β-eucryptite ss phase. This expansion difference, therefore, based on the nature of solid solution described above, may most probably be due to the incorporation of some Mg and/or Zn ions in the interstitial positions of the resultant β-eucryptite ss. The expansion behaviour of G5 is similar to G1 but with lower values. This is probably due to the relatively higher willemite (with low thermal expansion) and lower diopside (with high thermal expansion) contents of G5 than G1.

4. Summary

The studied glasses, within the spodumene–willemite–diopside system with compositions in wt.% 47–58 SiO_2, 11–17 Al_2O_3, 8–30 ZnO, 2–8 MgO, 3–11 CaO and 11–17 Li_2O, generally exhibit good meltability, workability and crystallizability upon heat-treatment.

The crystallization sequence in the glass begins with the formation of metastable β-eucryptite ss followed by, or concurrent with, the crystallization of β-Zn_2SiO_4 and then diopside (in amounts much less than its nominal values). By increase of the temperature up to ~640°C a rapid transformation of $\beta \rightarrow \alpha$ Zn_2SiO_4 takes place and at 900°C the β-eucryptite ss begins to transform into stable β-spodumene ss. The results show that β-Zn_2SiO_4 ss has a much narrower thermal stability field than β-eucryptite ss.

The bulk glasses crystallized through internal rather than surface nucleation and yielded satisfactory crystalline products.

The resultant crystalline products have hardness and density values ranging from 593 to 836 kg /mm^2 and 2.641 to 2.989 g/cm^3, respectively. The liner thermal expansion coefficients are generally around 17×10^{-7}/°C in the 20–500°C temperature range. One of the crystallized glasses (G2)gave α values around zero in the temperature range from ambient to 900°C.

It is expected that the system under consideration would, by further study, be more promising as to produce commercial glass-ceramics with such important technical properties.

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