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Expansion characteristics of some Li_2O–BaO–Al_2O_3–SiO_2 glasses and glass-ceramics

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Abstract

The thermal expansion characteristics of some glasses and glass-ceramics within the system $LiAlSi_2O_6$–$BaAl_2Si_2O_8$ are described. The expansion coefficient of glass decreases with the increase of $BaAl_2Si_2O_8$ content, while both the transformation (T_g) and softening (T_s) temperatures increased. The thermal expansion coefficients of glass-ceramics exhibited a wide range depending upon the type and relative proportions of the crystalline phases present.

The α-values of the studied glass ranged from 58.34 to 75.03 $\times$ 10^{-7}/°C in the 20–300 °C temperature range and those of the crystalline products ranged from 3 to 80 $\times$ 10^{-7}/°C in the same temperature range. The break in the expansion curves of the crystalline samples at about 300 °C defined the reversible transformation temperature of the orthorhombic ⇆ hexagonal-celsian.

Keywords: C. Thermal expansion; β-eucryptite ss; β-spodumene ss; Hexacelsian; Monoclinic celsian; Orthorhombic celsian; Crystallization; Heat-treatment

1. Introduction

Thermal expansion is one of the most important properties of glasses and glass-ceramics as it directly or indirectly affects all the commercially important properties of the material and is often restricting the usefulness of particular glass compositions. A thorough understanding of this property is important as it would permit the development of new glass-ceramics having desired properties and would lead to a better understanding of the structure of glass itself.

Thermal expansion coefficient of a glass-ceramic can be markedly different from that of the parent glass. The process of controlled crystallization introduced phases having coefficients of thermal expansion of a higher or lower value depending on the frequency and type of crystal phase(s) formed and the amount of residual glass. The linear thermal expansion characteristics of a material are particularly influenced by the properties of each phase present in the material. Thus, to obtain a low expansion glass-ceramic, a low expanding crystalline phase such as monoclinic celsian (22 $\times$ 10^{-7}/°C) β-eucryptite (−86 $\times$ 10^{-7}/°C) and β-spodumene (3 to 9 $\times$ 10^{-7}/°C) must be present as a major phase(s) while for a moderately high expansion glass-ceramic may contain major proportions of crystals such as hexacelsian (80 $\times$ 10^{-7}/°C).

Polymorphism and stability relationships in the various compositions celsian ($BaAl_2Si_2O_8$) and spodumene ($LiAlSi_2O_6$) have attracted extensive research in the last years. These materials, apart from having a wide academic interest, are valuable to various materials science fields mainly due to the high heat resistance, low thermal expansion coefficient and remarkable dielectric properties which some of them posses [1–6].

There are two main high-temperature crystalline polymorphs of celsian: monoclinic and hexagonal (hexacelsian). Monoclinic celsian is stable below 1590 °C and hexacelsian is stable from 1590 °C to the melting point of 1760 °C [2]. β-eucryptite solid solution(s) (ss) and β-spodumene ss are among the most promising low-expansion glass-

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ceramic-forming phases and therefore attracted considerable attention [7–10].

Aluminosilicate glass-ceramics are of great commercial interest because they combine exceptional thermal-dimensional stability with good chemical durability. Strong resistance to thermal shock is based on the very low to moderate thermal expansion coefficients found in many aluminosilicate framework structures, e.g. β-quartz solid solution, β-spodumene solid solution, and cordierite ($Mg_2Al_4Si_5O_{18}$). The base system Li_2O–Al_2O_3–SiO_2 has produced glass-ceramics of the lowest thermal expansion coefficient based on either β-quartz or β-spodumene (keatite) solid solution crystal phases.

The present work describes the thermal expansion characteristics of glass and glass-ceramics prepared from the above system. It also aims to relate the expansion coefficients obtained to the parameters of heat-treatment and, consequently, to the type and amount of the crystalline assemblage formed.

2. Experimental procedure

Nine glass compositions within the spodumene ($LiAlSi_2O_6$)-celsian ($BaAl_2Si_2O_8$) system were selected for the present work. These compositions are based on the spodumene ($LiAlSi_2O_6$) composition with successive additions of celsian up to 80 wt.% at 10% intervals of the celsian component. The compositions studied were designated G0–G8. The batches corresponding to these compositions were prepared by calculating the appropriate proportions of local Saudi kaolinitic 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. Table 1 gives the details of glass compositions in oxide percentages and percentages of raw materials.

After being thoroughly mixed, the weighted powdered batch materials were melted in Pt crucibles in a Globar furnace at temperatures ranging from 1450 to 1550 °C for 2–3 h depending upon composition, the melts become more viscous with increasing celsian and compositions. The 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.

Measurements of linear thermal expansion coefficients of the glasses and glass-ceramics were carried out using a thermo-dilatometeric analyzer of (Harrop, USA) Model TD-722, using a fused silica bar as a standard. Specimen rods of about 3–5 cm length were prepared and heated at a rate of 5 °C/min and the elongation on the chart was printed on A4 paper. The thermal expansion of the annealed glass specimens was measured from room temperature up to temperatures slightly exceeding their dilatometric softening points. These glass rods were then subjected to thermal treatment and their expansion again measured from room temperature up to the maximum heat-treatment temperatures. The results obtained were represented graphically as ΔL versus temperature, where ΔL is the change in microns in the original length (L) of the specimen. The expansion coefficient (α) was calculated from the equation:

$$\alpha = \frac{\Delta L}{L\Delta T} + 5.4 \times 10^{-7}/^{\circ}\mathrm{C}$$

where ΔT is the temperature difference over which the specimen was heated, and 5.4×10^{-7} is the correction factor of the quartz tube. The transition temperature (T_g) and the softening temperature (T_s) of the glass were determined from the expansion curves of the annealed glasses.

Details of melting, heat-treatments, DTA, X-ray diffraction analysis and microscopic examinations are described in the previous paper [3,4].

3. Results

3.1. Glasses

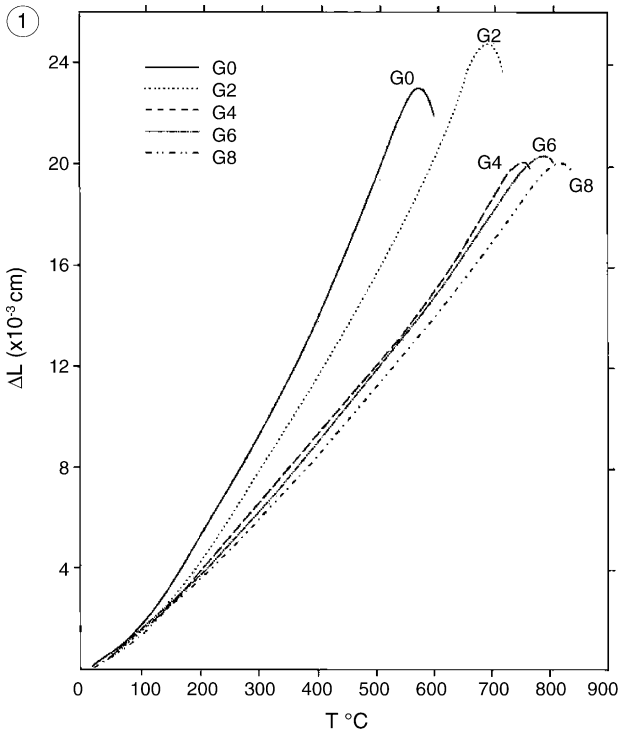
Figs. 1 and 2 show the thermal expansion curves of the investigated glasses G0–G8.

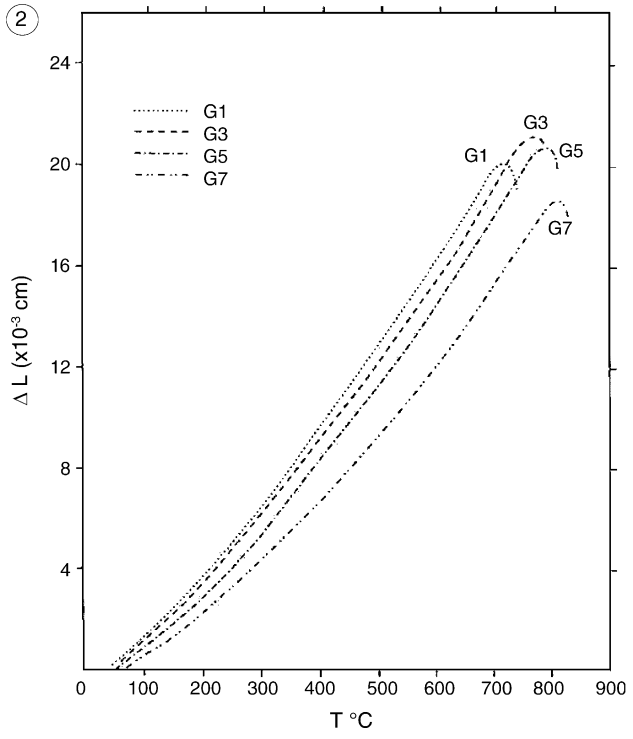
The thermal expansion curves of the investigated glasses are generally similar to those characteristic of most silicate glasses. The linear thermal expansion coefficient (α) of the

Table 1
Chemical compositions and corresponding batch percentages of the investigated glasses

Glass no.	Nominal phase[a] composition (wt.%)	Calculated oxide constituents				Batch ingredient (wt.%)			
		SiO_2	Al_2O_3	Li_2O	BaO	Silica sand	Kaolinitic clay	Li_2CO_3	$BaCO_3$
G0	0% Cel + 100% spod	64.57	27.40	8.03	0.00	58.01	24.36	17.63	0.00
G1	10% Cel + 90% spod	61.42	27.38	7.23	4.08	22.50	59.45	13.94	4.11
G2	20% Cel + 80% spod	58.08	27.35	6.42	8.17	19.94	59.44	12.40	8.22
G3	30% Cel + 70% spod	54.81	27.33	5.62	12.25	17.47	59.36	10.85	12.32
G4	40% Cel + 60% spod	51.55	27.30	4.82	16.34	14.98	59.29	9.30	16.43
G5	50% Cel + 50% spod	48.29	27.27	4.02	20.42	12.49	59.24	7.75	20.52
G6	60% Cel + 40% spod	45.03	27.26	3.21	24.50	9.99	59.19	6.20	24.62
G7	70% Cel + 30% spod	41.78	27.23	2.41	28.59	7.48	59.13	4.65	28.74
G8	80% Cel + 20% spod	38.52	27.21	1.61	32.67	5.04	59.04	3.10	32.82

[a] Cel = celsian, spod = spodumene.





Figs. 1–2. Linear thermal expansion curves of the investigated glasses.

investigated glasses was calculated over 20–300 °C and 300–500 °C temperature ranges are given in Table 2 with the dilatometric transition (T_g) and softening (T_s) temperatures. The relation between the expansion coefficient or T_g and T_s versus variation in the base composition, i.e. the successive increase of the calculated celsian content in the glasses G0–G8 are plotted in Fig. 3.

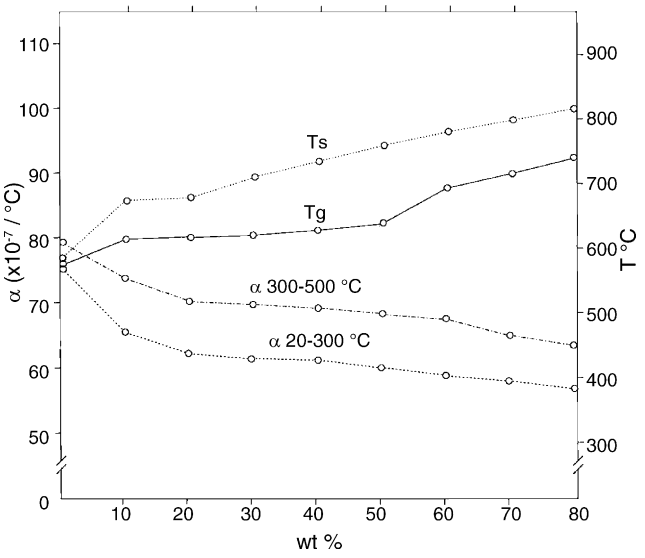


Fig. 3. Change of (α), T_g and T_s values as a function of celsian content of the investigated glasses.

The expansion curves (Figs. 1 and 2 and Table 2) showed the familiar expansion pattern characterizing normal glasses. The linear expansion coefficient in the 20–300 °C temperature range, lies in the range between 75.03 and 58.34×10^{-7}/°C, while both transformation (T_g) and softening (T_s) temperatures are in the range 500–728 °C and 553–813 °C, respectively. Generally, glasses with the lower expansion coefficient have higher transition and softening temperatures and vice-versa. However, it can be seen from Fig. 3 that the expansion remarkably diminishes on adding the first 10 wt.% celsian addition (G1) relative to the original spodumene glass G0 after which the coefficient expansion steadily decreases with the increase of the calculated celsian in the glasses.

The dilatometric T_g and T_s temperatures of the studied glasses showed a reverse behavior when compared with the expansion coefficient behavior, i.e. they increase with the increase of celsian content.

3.2. Glass-ceramics

Figs. 4–6 show the expansion versus temperature of the crystallized base glasses G3, G4, G6 and G8 after being heat-treated at the endothermic peak temperature 690 °C for 1 h and then at 950 °C for 1 h or at 1050 °C for 40 h. The calculated mean thermal expansion coefficient over different temperature up to 700 °C, thermal treatment condition, and the crystalline mineral phases developed are given in Table 3. The expansion-temperature curves of the crystallized materials (Fig. 4), resulting after 690 °C for 1 h + 950 °C for 1 h treatment of G3, G4, G6 and G8 are similar and exhibiting a discontinuity (break) around 300 °C. After this break, the curves show less steeper slopes expressing lower rates for increasing of elongation with temperature and thus lower thermal expansion

Table 2
Thermal properties of the investigated glasses

Glass no.	Li_2O/BaO	Linear expansion coefficients (α) $\times 10^{-7}$/°C		Transition (T_g)	Softening (T_s)
		20–300 °C	300–500 °C		
G0		75.03	79.24	500	553
G1	1.77	65.17	73.75	607	660
G2	0.79	62.42	70.68	611	680
G3	0.46	62.13	70.25	623	713
G4	0.30	61.34	69.44	630	727
G5	0.20	60.25	69.27	640	773
G6	0.13	59.83	69.07	693	780
G7	0.08	59.21	68.69	712	800
G8	0.05	58.34	68.23	728	813

coefficients. This break, appearing on the curves at about 300 °C, became more explicit in the celsian-rich G4, G6 and G8 compositions (Fig. 4) which can be attributed to the reversible transformations of the metastable orthorhombic ↔ hexacelsian phases which depend on the cooling rate of the sample as revealed early by X-ray analysis. When the glass was subjected to prolonged durations at higher temperatures for 40 h at 1050 °C, the break becomes less pronounced (Figs. 5 and 6) because of the irreversible transformation of the metastable orthorhombic celsian and hexagonal celsian phases (causing such discontinuity) into the stable monoclinic celsian phase.

However, the expansion values of the crystalline specimens of glasses G3–G8 are affected by the course of thermal-treatment applied. Ortho- and/or hexacelsian with β-eucryptite ss are formed when relatively low crystallization temperature (950 °C) is used. On the other hand, it is formed with β-spodumene when higher crystallization temperature (1050 °C) was used (Table 3). The relative proportions of these phases are expected to vary with the composition of the investigated glasses. As the celsian content of the glass was increased and, consequently, the spodumene was decreased, the crystallizing high expanding, celsian phases increased and spodumene phases decreased in the same order, the expansions values were increased.

Table 3 showed that the expansion characteristics of specimens of G3, G4 and G8 treated at 950 °C for 1 h were higher than those treated at higher temperature (1050 °C) for long durations (40 h). For example, the mean thermal expansion coefficients of the crystalline glasses of G4

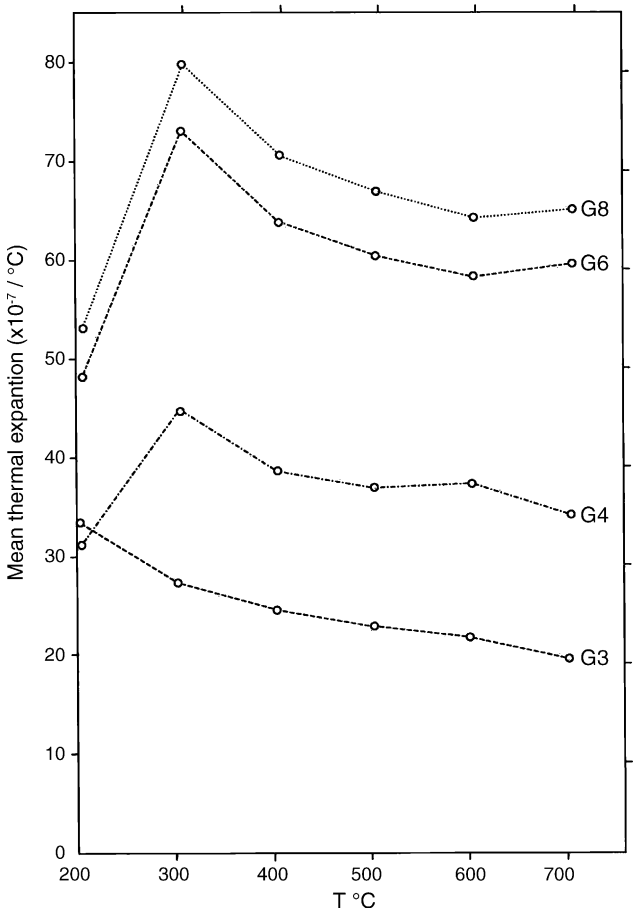


Fig. 4. Expansion vs. temperature curves for crystallized glasses G3, G4, G6 and G8 heat-treated at 690 °C for 1 h and then at 950 °C, 1 h.

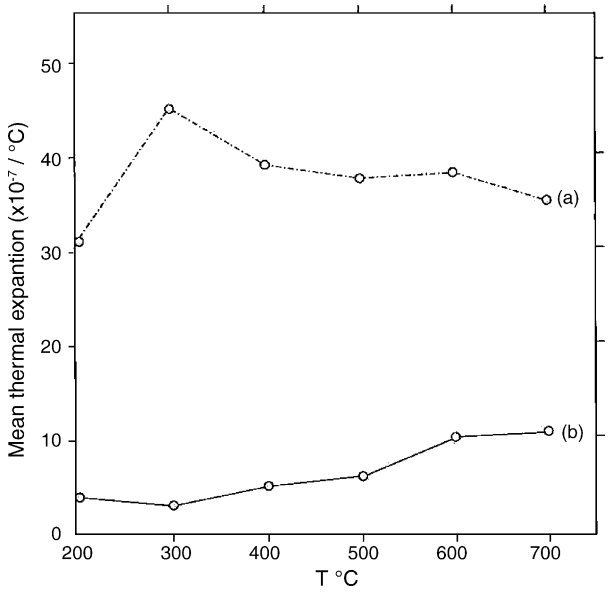


Fig. 5. Comparison of the mean thermal expansions of the crystalline glass G4 heat-treated at: (a) 950 °C for 1 h and (b) 1050 °C for 40 h.

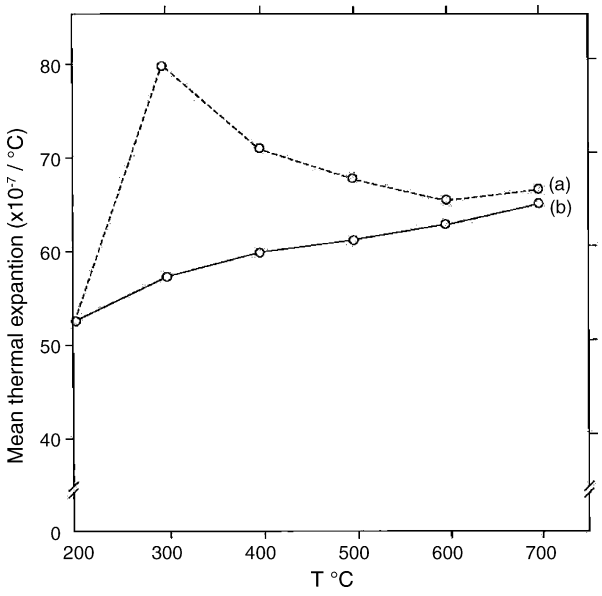


Fig. 6. Comparison of the mean thermal expansions of the crystalline glass G8 heat-treated at: (a) 950 °C for 1 h and (b) 1050 °C for 40 h.

were decreased from 45×10^{-7} to 3×10^{-7}/°C in the temperature range (20–300 °C). The decrease of expansion coefficient with the increase of heat-treatment parameter is due to the transformation of the high-expanding metastable ortho- and hexa-phase (71×10^{-7} and 80×10^{-7}/°C, respectively) into the low-expanding monoclinic celsian (22.9×10^{-7}/°C).

From the above dilatometric results, the monoclinic celsian is more favorable than either hexagonal or orthorhombic celsian and its formation in glass-ceramic materials diminishes the stresses due to volume change resulting from irreversible ortho ↔ hexa transformation and imparts lower expansion coefficient to the materials.

4. Discussion

4.1. Thermal expansion of glassy materials

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 [11]. The small cations, with higher field strengths seem to produce more strongly bound structures than the larger cations, and consequently smaller cation based glasses are generally characterized by lower expansion coefficient [12].

It is evident from the results obtained (Table 2) that the thermal expansion of the studied glasses is almost a function of the Li_2O/BaO ratio present in the glasses. In glasses with high Li_2O/BaO ratio the α-values are high, while both dilatometric transformation (T_g) and softening (T_s) temperatures of the glasses are of low values. This may be explained on the basis that in such glasses the Li–O bonds of weaker character than Ba–O are present in high proportions. Consequently, high α-values and lower values for the transformation and softening temperatures are expected. This might be due to the less rigid or loosely compact nature of the structure [13].

4.2. Thermal expansion of glass-ceramic materials

It is reported that [7] 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 coefficient and may cover a wide range of α-values.

The baria-aluminosilicates, in the form of monoclinic celsian, have low expansion as compared with hexacelsian or orthorhombic celsian [14]. The expansion coefficient of monoclinic celsian is 22.9×10^{-7}/°C (20–1000 °C) and for orthorhombic celsian is 71×10^{-7}/°C (20–300 °C) as compared with that of hexacelsian which is 80×10^{-7}/°C (in the range 300–1000 °C).

Lithia-aluminosilicates, like β-spodumene ss, have low expansion as compared with fused silica [15]. The expansion coefficient (25–500 °C) of pure β-spodumene, in which the ratio of Li_2O–Al_2O_3–SiO_2 is equal to 1:1:4 was 9×10^{-7} and 5×10^{-7} for 1:1:6 solid solution, while it was 3×10^{-7} for 1:1:8 solid solution.

Table 3
Mean thermal expansion of some heat-treated glasses

Glass no.	Heat-treatment °C (h)	Mean expansion coefficient (10^{-7}/°C)						Phases developed
		20–200 °C	20–300 °C	20–400 °C	20–500 °C	20–600 °C	20–700 °C	
G3	690 °C, 1 h + 950 °C, 1 h	33	28	25	24	23	21	B-Euc.ss + hexacel
	690 °C, 1 h + 1050 °C, 40 h	9	11	13	13	14	14	β-Spod.ss + monocel
G4	690 °C, 1 h + 950 °C, 1 h	31	45	39	38	38	35	β-Euc.ss + hexacel
	690 °C, 1 h + 1050 °C, 40 h	4	3	5	6	10	11	β-Spod.ss + monocel
G6	690 °C, 1 h + 950 °C, 1 h	48	73	64	61	59	61	Hexacel + β-euc.ss
G8	690 °C, 1 h + 950 °C, 1 h	53	80	71	67	65	66	Hexacel + β-euc.ss
	690 °C, 1 h + 1050 °C, 40 h	54	57	60	61	63	64	Monocel + β-spod.ss

It is evident, therefore, that polycrystalline materials such as glass-ceramics which contain various crystalline phases in different proportions, may have different thermal expansion coefficients from their parent glasses.

In the present work it can be seen that (Table 3) as the Li_2O/BaO ratio in the original glass was increased, the α-values of the corresponding crystalline ceramic specimens were generally decreased. This may be attributed to the increase of the crystallization of the low expanding lithium aluminosilicates (β-eucryptite and β-spodumene) instead of the relatively higher barium aluminoslicate (hexacelsian and monoclinic celsian) as indicated by the X-ray studies. The Li_2O/BaO ratio in glass 3 as compared with that of glass 8, this explain the low α-values given by glass G3 in comparison with that obtained from glass G8.

The development of the monoclinic celsian phase completely vanishes the undesirable sudden discontinuity in the expansion curves at around 300 °C of the ortho–hexa transformation and gave expansion curves without break (e.g. Figs. 5 and 6). Thus, the presence of monoclinic celsian is more favorable than the other $BaAl_2SiO_2O_8$ modification where it greatly diminishes the stresses due to volume change resulting from irreversible ortho ↔ hexa transformation and imparts lower expansion coefficient to the material.

5. Conclusions

The thermal expansion of some glasses and glass-ceramics within the system $LiAlSi_2O_6$–$BaAl_2Si_2O_8$ have been measured. The coefficients of expansion in the range 20–300 °C were found to vary from 75.03×10^{-7}/°C for a glass-rich spodumene content to 58.34×10^{-7}/°C for a glass-rich celsian content, while both the transformation (T_g) and softening (T_s) temperature are in the range 500–728 °C and 553–813 °C, respectively. But in glass-ceramics the α-values ranged from 3×10^{-7}/°C for a glass-ceramic rich spodumene to 80×10^{-7}/°C for a glass-ceramic rich celsian in the temperature range 20–300 °C. The linear thermal expansion of the glass-ceramics was particularly influenced by the type and nature of the crystalline phases present.

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