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Thermal expansion of Li_2O–ZnO–Al_2O_3–SiO_2 glasses and corresponding glass–ceramics

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The thermal expansion behaviour of some glasses and glass–ceramics within the system Li_2ZnSiO_4–$LiAlSi_2O_6$ is described. The effect of TiO_2 and ZrO_2 additions is also evaluated. The expansion coefficient (α) of the glasses increases with an increase of the Li_2ZnSiO_4 component in the glass composition. TiO_2 and ZrO_2 were found to decrease the thermal expansion of the glasses investigated. The dilatometric transition and softening points of the glasses showed the reverse behaviour. The thermal expansion of the glass–ceramics exhibited a wide range, depending upon the type and relative proportions of the crystalline phases present. The α values of the glasses ranged between 73.6 and $97.4 \times 10^{-7}\,°C^{-1}$ in the temperature range 20–450 °C and those for the crystalline products ranged from 36.1 and 102.6×10^{-7} in the temperature range 20–450 °C.

1. Introduction

Glass–ceramics are formed by the conversion of glasses through an appropriate (usually two-stage) heat treatment into fine-grained polycrystalline materials. In contrast to oriented surface crystallization, which is commonly observed during the devitrification of glass, nucleation and growth of randomly oriented fine-grained crystals occur throughout the bulk of the glass during heat treatment. Bulk nucleation, in most glass–ceramic systems, is accomplished with the aid of special additives. The addition of nucleation catalysts such as TiO_2 or ZrO_2 is required to transform glasses in the Li_2O–ZnO–Al_2O_3–SiO_2 system into glass–ceramic materials [1–4].

Thermal expansion is one of the most important properties of glass–ceramics, as it directly or indirectly affects their commercially important properties and is often extremely influential in restricting the usefulness of a particular base composition. Glass–ceramic compositions with low thermal expansion coefficients are valued for their excellent thermal shock resistance, and much effort has been expended in their characterization. Less effort has been directed toward the full characterization of the high or moderately high expansion glass–ceramics which are finding applications in the areas of glass–metal or ceramic–metal sealing and porcelain enamelling [2–5].

In an earlier paper [6, 7], the crystallization of some spodumene ($LiAlSi_2O_6$)–lithium zinc orthosilicate (Li_2ZnSiO_4) glasses was investigated. The study demonstrated that the parent glass composition, nucleant used, and crystallization conditions determine the crystalline phase constitution and microstructures of the resultant materials, leading in some cases to transparent glass–ceramics.

The purpose of the present work is to report the details of the thermal expansion characteristics of glasses within the above-mentioned system and their corresponding glass–ceramics, and to relate the expansion coefficients obtained to the parameters of heat treatment and consequently to the type and amount of crystal phases present.

2. Experimental procedure

All glasses (Table I) were prepared from high-grade quartz powder and analytical reagents Li_2CO_3, ZnO, Al_2O_3, TiO_2 and ZrO_2. The batches were thoroughly mixed and were melted in platinum crucibles in an electrically heated furnace at 1400–1450 °C for 3 h with occasional stirring. The homogeneous melts were cast into rods of 1 cm^2 cross-section and 10 cm length, which were then properly annealed in a muffle furnace.

Measurements of thermal expansion were made on a Netzsch dilatometer of type 402 EP, using a fused silica bar as a standard. The heating rate was set at $5\,°C\,min^{-1}$. 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 are plotted graphically as ΔL versus temperature, where ΔL is the change in the original length L. The expansion coefficient (α) was then calculated from the equation

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

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TABLE I Compositions of the glasses studied

Glass No.	Calculated phase constituents (mol %)		Constituent oxides (wt %)				Yield
	Li_2ZnSiO_4	$LiAlSi_2O_6$	Li_2O	ZnO	Al_2O_3	SiO_2	
G2	20	80	9.79	8.89	22.27	59.05	Clear glass
G4	40	60	11.61	18.06	16.98	53.35	Clear glass
G5	50	50	12.54	22.77	14.26	50.43	Brilliant clear glass
G6	60	40	13.49	27.55	11.50	47.46	Devitrified

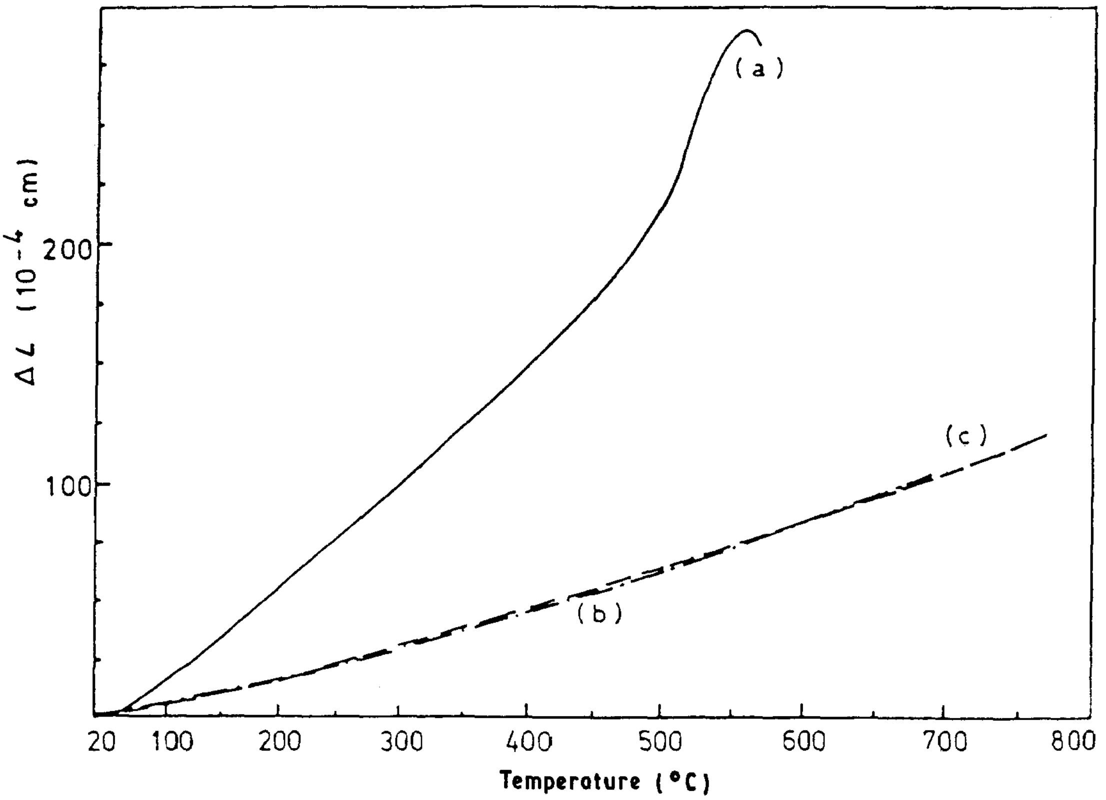

Figure 1 Effect of heat treatment on thermal expansion of glass G4. (a) Original glass; (b) 535 °C, 1 h + 685 °C, 1 h; (c) as (b) + 950 °C, 1 h. $L = 4.990$ cm.

where ΔT is the temperature interval over which glass was heated and 5.4×10^{-7} is the correction factor of the quartz tube.

Details of melting, heat treatment, X-ray diffraction analysis and microscopic examinations are described elsewhere [6, 7].

3. Results and discussion

3.1. Thermal expansion characteristics of nucleant-free glasses and glass–ceramics

The dilatometric curves of the parent glasses and their corresponding glass–ceramics are shown in Figs 1 and 2. Table II lists the heat-treatment parameters, type and concentration of nucleant added, the developed crystalline phases, and the thermal expansion coefficients over different ranges of temperature as well as the dilatometric transition (T_g) and softening (T_s) temperatures.

The curves (a) of the parent glasses exhibit normal behaviour. In general, they express higher thermal expansion coefficients than the corresponding fully crystallized glass–ceramics. The coefficients of expansion of these glasses are dependent on the original base glass composition. As the calculated percentage of the Li_2ZnSiO_4 component was increased in the glass composition from G2 to G5 (and consequently the alkali content, see Table I), the expansion coefficient revealed higher values (Table II). Thus glass G5, with the highest content of this component, showed the highest expansion coefficient. In contrast, both the dilatometric transition and softening temperatures were decreased on increasing the Li_2ZnSiO_4 component in the base glass.

It must first be mentioned that the thermal expansion is a complex property connected with the magnitude and distribution of forces acting in the system, and it reflects any change in the distribution of forces with increasing thermal vibrations [8]. It is due, basically, to the presence of anharmonic vibrations of atoms about their equilibrium position in the solid lattice. Biscoe *et al.* [9] gave a good explanation of the

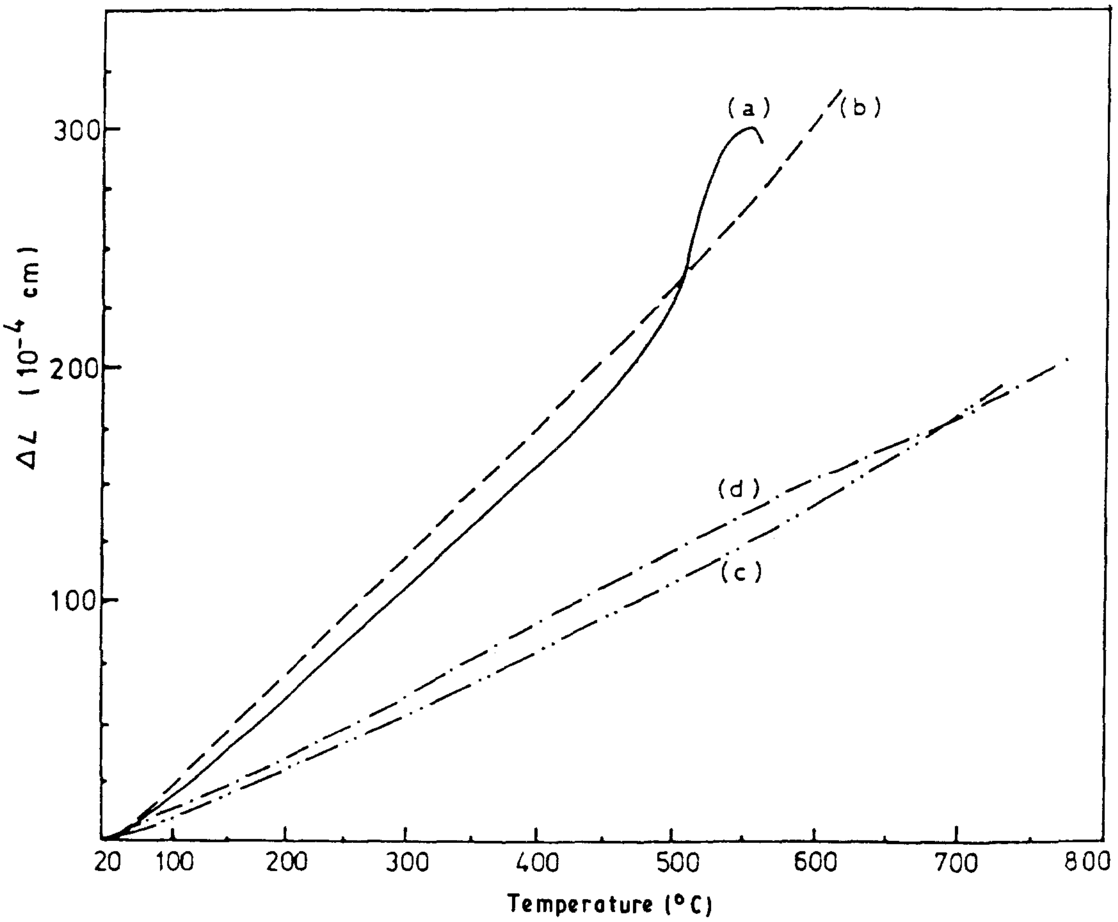

Figure 2 Effect of heat treatment on thermal expansion of glass G5. (a) Original glass; (b) 520 °C, 1 h + 610 °C, 1 h; (c) as (b) + 715 °C, 1 h; (d) as (c) + 950 °C, 1 h. $L = 4.995$ cm.

small thermal expansion of silica glass. As a result of the periodic arrangement in crystals, every crystallographically identical distance and valency angle varies in the same degree with a given temperature rise; being of identical direction, the addition of these variations causes a considerable increase in the thermal expansion. In silica glass the lattice is non-periodic and the vectorial addition of every single displacement becomes statistically nearly zero, due to the fact that the displacements sometimes occur in a negative and sometimes in a positive direction. In silicate glasses [10] the thermal expansion is mainly the result of the effect of the alkali and alkaline earth ions, since these ions are not bound by higher forces to the anions and their thermal vibration expands the cavities of the lattice isotropically. Following Takahashi's view about the thermal expansion and the structure of glass [11], the Si–O bond is far more covalent and stronger than any other M–O bonds contained in such silicate glasses, which are mainly ionic, so that the expansion coefficients are larger as the electrostatic bond strength between cations and oxygen ions decreases. The expansion becomes larger in the order MO_2, $MO_{1.5}$, MO and $MO_{0.5}$ and that for the alkalis is the highest.

In the present work the thermal expansion coefficients as well as the transition and softening points of the studied base glasses were found to be a function of the Li_2ZnSiO_4 content, or more specifically the Li_2O content, in the base glass. With increasing lithium oxide content the expansion coefficient increased and both T_g and T_s decreased. These facts may be explained on the above-mentioned basis, that successive increase of the modifying Li_2O will introduce more weaker Li–O bonds which result in a much less rigid or more loosely compacted nature of the glass structure, leading to high expansion values and lower transition and softening temperatures.

Upon crystallization, marked changes in the thermal expansion occur depending on the type and amount of the developing crystalline phases. The thermal expansion data (Table II) can be interpreted in terms of the expansion characteristics of the phases present.

It will be noted that the coefficient of thermal expansion varies considerably with the temperature range in which it is measured, and hence a comparison of the literature data is sometimes really difficult. The thermal expansion of the lithium aluminosilicate phases has been extensively studied. B-quartz and its stuffed derivative B-eucryptite and B-spodumene and their solid solutions with each other or with silica, all have negative or low positive thermal expansion coefficients [12–15]. However, B-spodumene and its solid solutions show higher expansion coefficients than B-eucryptite and its solid solutions. The Li,Zn-containing high-quartz phases also exhibit negative or slightly positive thermal expansion coefficients [16].

No data for the thermal expansion of Li_2ZnSiO_4 phases are available except those estimated by West

TABLE II Thermal expansion coefficients of Li_2ZnSiO_4–$LiAlSi_2O_6$ glasses and their corresponding glass–ceramics

Glass composition	Thermal treatments (°C, h)	T_g (°C)	T_s (°C)	Expansion coefficient α (10^{-7} °C^{-1})			Identified phases[b]
				20–300 °C	20–450 °C	20–700 °C	
G2[a]	–	533	608	73.1	73.6	–	Amorphous
G4	–	497	554	86.1	93.5	–	Amorphous
	(a) 535 °C, 1 h + 685 °C, 1 h	–	–	31.5	38.6	–	B-euc. + $B_{II'}$-Li_2ZnSiO_4
	(b) (a) + 950 °C, 1 h	–	–	33.7	40.0	46.3	B-spod. + γ_0-Li_2ZnSiO_4
G5	–	493	550	88.5	97.4	–	Amorphous
	(a) 520 °C, 1 h + 610 °C, 1 h	–	–	89.6	102.6	–	Proto-B-Li_2ZnSiO_4
	(b) (a) + 715 °C, 1 h	–	–	43.1	49.3	57.8	B-euc. + $B_{II'}$-Li_2ZnSiO_4
	(c) (b) + 950 °C, 1 h	–	–	48.3	55.0	58.0	B-euc. + B-spod. + γ_0-Li_2ZnSiO_4
G4 + 5% TiO_2	–	515	565	84.9	91.7	–	Amorphous
	(a) 580 °C, 1 h + 710 °C, 1 h	–	–	32.6	40.2	47.2	B-euc. + $B_{II'}$-Li_2ZnSiO_4
	(b) (a) + 785 °C, 1 h	–	–	30.7	37.0	44.8	B-euc. + $B_{II'}$-Li_2ZnSiO_4
	(c) (b) + 940 °C, 1 h	–	–	37.9	43.3	48.5	B-spod. + γ_0-Li_2ZnSiO_4
G4 + 7% TiO_2	–	520	578	82.4	88.2	–	Amorphous
	(a) 555 °C, 1 h + 605 °C, 1 h	–	–	83.4	94.9	–	Proto-B-Li_2ZnSiO_4
	(b) (a) + 630 °C, 1 h	–	–	88.2	99.8	–	Proto-B-Li_2ZnSiO_4
	(c) (b) + 680 °C, 1 h	–	–	37.4	42.7	–	B-euc. + $B_{II'}$-Li_2ZnSiO_4
	(d) (c) + 720 °C, 1 h	–	–	33.6	39.4	47.2	B-euc. + B-spod. + $B_{II'}$-Li_2ZnSiO_4
	(e) (d) + 910 °C, 1 h	–	–	39.2	45.9	49.4	B-spod. + γ_0-Li_2ZnSiO_4
	(f) (e) + 1020 °C, 1 h	–	–	38.9	44.6	49.2	B-spod. + γ_0-Li_2ZnSiO_4 + rutile
G4 + 1.5% ZrO_2	–	504	560	79.0	91.8	–	Amorphous
	(a) 540 °C, 1 h + 710 °C, 1 h	–	–	38.6	45.3	51.8	B-euc. + γ_0-Li_2ZnSiO_4
	(b) (a) + 900 °C, 1 h	–	–	42.2	48.8	53.1	B-spod. + γ_0-Li_2ZnSiO_4
G4 + 3% ZrO_2	–	516	570	77.6	91.2	–	Amorphous
	(a) 550 °C, 1 h + 740 °C, 1 h	–	–	28.8	36.1	39.9	B-euc. + γ_0-Li_2ZnSiO_4
	(b) (a) + 800 °C, 1 h + 980 °C, 1 h	–	–	38.5	45.2	50.4	B-spod. + γ_0-Li_2ZnSiO_4

[a] Glass G2 could not give undeformed heat-treated specimens suitable for thermal expansion measurements.

[b] B-euc. = B-eucryptite ss; B-spod. = B-spodumene.

and Glasser [17] from high-angle X-ray photographs. These authors mentioned that the crystallographic directional coefficients of thermal expansion of Li_2ZnSiO_4 increase very markedly with increasing temperature. They give coefficients of 80, 90 and 90 $\times 10^{-7}$ °C^{-1} for the *a*, *b* and *c* axes, respectively, in the 20–400 °C temperature range; 140, 110 and 170 $\times 10^{-7}$ °C^{-1} in the 75–700 °C range; and 160, 110 and 180 $\times 10^{-7}$ °C^{-1} in the range 25–1030 °C.

In the present investigation, the thermal expansion coefficient of G4 composition first falls sharply from 93.5×10^{-7} °C^{-1} for untreated glass to 38.6 $\times 10^{-7}$ °C^{-1} (in the 20–450 °C temperature range) after heat treatment at 685 °C for 1 h. This figure represents the mean value resulting from the B-eucryptite ss (with negative thermal expansions) and the $B_{II'}$-Li_2ZnSiO_4 (with high positive thermal expansion coefficients) structures present in the resulting glass–ceramic. Actually the presence of these phases was confirmed by X-ray diffraction analysis, the former being the predominating phase. As the treatment temperature was increased to 950 °C, the B-eucryptite ss and $B_{II'}$-Li_2ZnSiO_4 phases were transformed into their respective B-spodumene and γ_0-Li_2ZnSiO_4, resulting in a slight increase in the thermal expansion coefficient ($\alpha = 40.0 \times 10^{-7}$ °C^{-1}). West and Glasser [17] reported that the different modifications of lithium zinc orthosilicate showed comparable values of calculated thermal expansion coefficients. Thus, the formation of B-spodumene may be responsible for this slight variation in thermal expansion.

For the G5 composition, the expansion coefficient of the glass–ceramic resulting after heat treatment at 520 °C for 1 h followed by treatment at 610 °C was found to be of a higher value than the thermal expansion coefficient of the original untreated glass in the same temperature range. This is due to the formation of proto-B-Li_2ZnSiO_4 as the sole crystalline phase developed in this semi-crystalline sample after such low temperature treatment. The proto-B-phase is known to have a high thermal expansion coefficient [17] and so imparts this property to the material. The decrease of the thermal expansion of the residual glass phase due to its depletion in alkali ions seems to be slight and little affects this value. At 715 °C, B-eucryptite ss was formed and at the same time the proto-B-Li_2ZnSiO_4 phase was completely transformed into $B_{II'}$-Li_2ZnSiO_4. The appearance of B-eucryptite ss in the phase assemblage resulted in a considerable decrease in the overall thermal expansion of the material (Table II). The slight increase of the expansion coefficient exhibited by the material after heat treatment at 950 °C could also be attributed, as for G4, to the transformation of the lower-expanding B-eucryptite ss into B-spodumene of a relatively higher coefficient of thermal expansion.

The expansion coefficients of G4 glass–ceramics were generally lower than those of glass–ceramics obtained from glass of composition G5 (Table II). This is mostly due to the difference in concentration of the crystalline phases present. Glass–ceramics obtained from glass G4 contain higher concentrations of the lithium aluminosilicates (low expansion) and lower contents of Li_2ZnSiO_4 (high expansion) than those obtained from G5. This phase frequency was confirmed by X-ray diffraction analysis [6, 7]. Consequently, glass–ceramics containing the same crystalline phase but in different proportions may have noticeably different thermal expansion coefficients.

Thus, a considerably wide range of thermal expansion coefficients could be covered by the development of the above-mentioned different crystal types in appropriate proportions, and the production of a glass–ceramic having a definite value of thermal expansion coefficients can be obtained by the controlled crystallization of such glasses. A glass–ceramic of moderately low expansion (of the order of 30 $\times 10^{-7}\,°C^{-1}$) may thus contain B-eucryptite ss and/or B-spodumene as major phases, while glass–ceramics with moderate to high expansion may contain major proportions of the different polymorphic modifications of the Li_2ZnSiO_4 phase, namely, proto B-, $B_{II'}$- and γ_0-Li_2ZnSiO_4 with the first variety exhibiting the highest value of thermal expansion coefficient.

3.2. Thermal expansion of nucleant-containing glasses and glass–ceramics

The introduction of different amounts of the nucleation catalysts TiO_2 and ZrO_2 in the glasses studied remarkably affects their thermal properties. The thermal expansion of G4 glasses containing 5 and 7 g TiO_2/100 g glass as well as 1.5 and 3.0 g ZrO_2/100 g glass are given in Table II together with their T_g and T_s. It can be seen that the thermal expansion coefficient of the glass is dependent upon the amount of nucleant added. At the nucleant concentrations used, the thermal expansion coefficient of the glass decreases with an increase in the concentration of nucleant (TiO_2 or ZrO_2). On the other hand, the dilatometric transition (T_g) and softening (T_s) points of these glasses showed a reverse character, i.e. they increase with an increase of nucleant concentration.

It is well known that Ti^{4+} can be accommodated in the glass structure either as network-former or as network-modifier [18]. The Ti^{4+} occupancy of Si^{4+} sites in the glass structure introduces a Ti–O bond that is weaker than the Si–O bond [19]. This relatively weaker Ti–O bond is more readily ruptured by the alkali ions forming non-bridging oxygens than the Si–O bond. This leads to an increase of bridging oxygens per silicon atom, i.e. the number of $\equiv$Si–O–Si$\equiv$bonds increases in the presence of Ti^{4+}. This in turn will result into a firmer glass structure with lower thermal expansion values and high T_s and T_g points. The same explanation can be also applied for ZrO_2 additions.

The effects of different nucleation catalysts, namely TiO_2 and ZrO_2 on the thermal expansion of glass–ceramics from G4 are clearly shown in Figs 3–6 and Table II. It should be mentioned that heat treatment of these nucleated glasses was based on the results of differential thermal analysis. The samples were first heated for 1 h at the endothermic peak

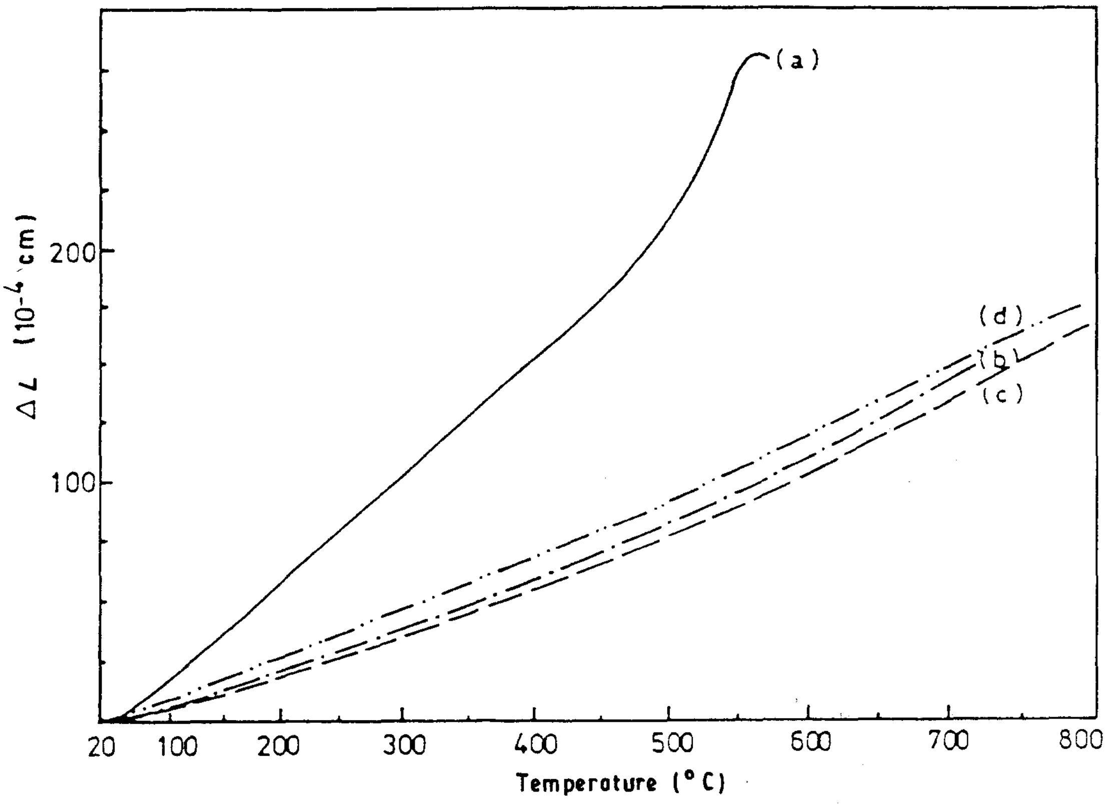

Figure 3 Effect of heat treatment on thermal expansion of glass G4 nucleated by 5% TiO_2. (a) Original glass; (b) 580 °C, 1 h + 700 °C, 1 h; (c) as (b) + 780 °C, 1 h; (d) as (c) + 940 °C, 1 h. $L = 4.940$ cm.

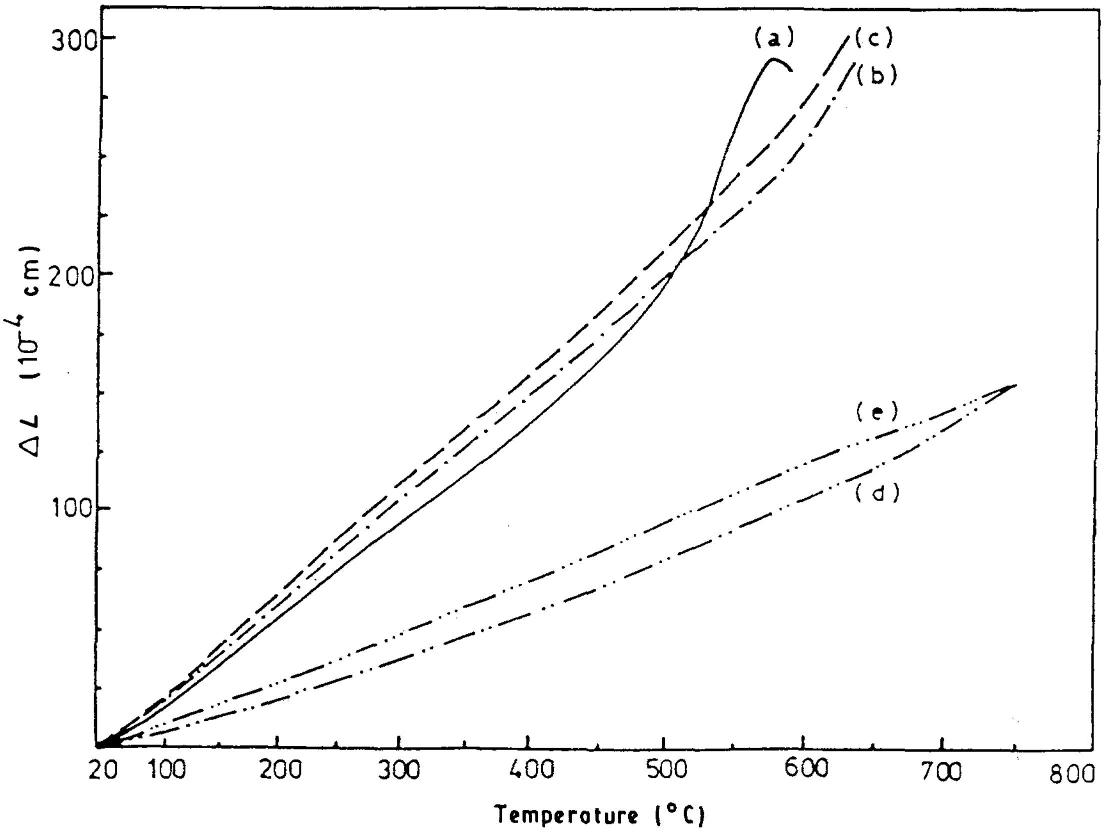

Figure 4 Effect of heat treatment on thermal expansion of glass G4 nucleated by 7% TiO_2. (a) Original glass; (b) 555 °C, 1 h + 605 °C, 1 h; (c) as (b) + 630 °C, 1 h; (d) as (c) + 720 °C, 1 h; (e) as (d) + 910 °C, 1 h. $L = 4.810$ cm.

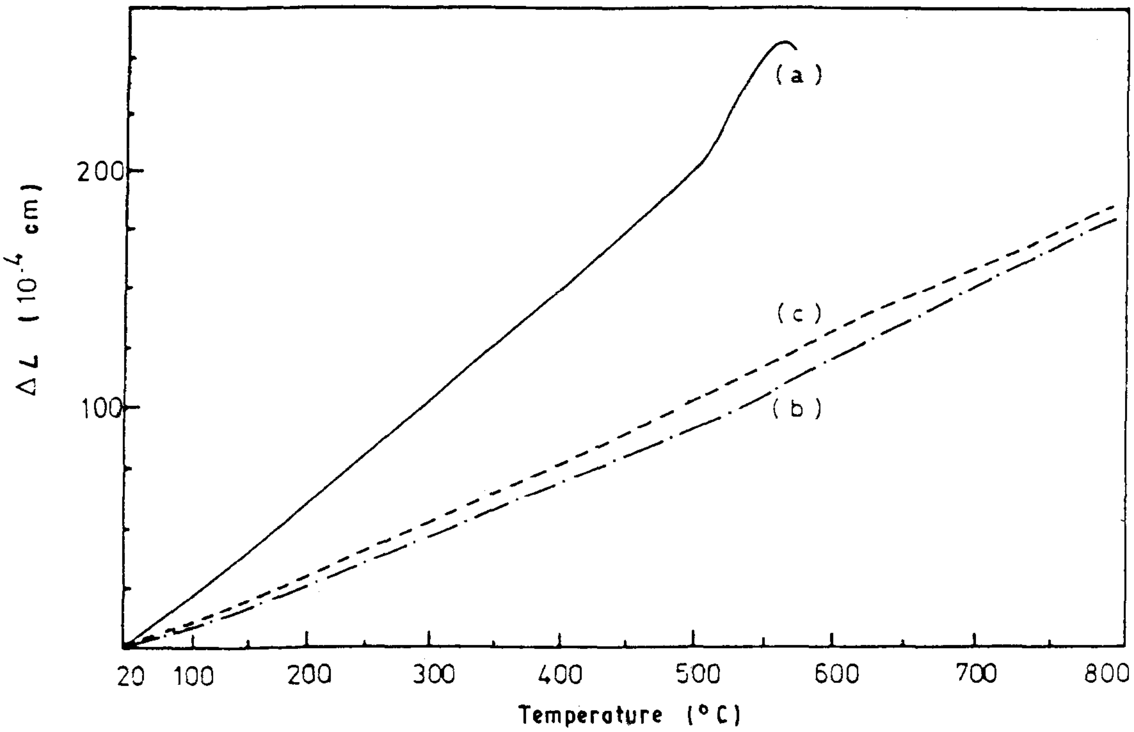

Figure 5 Effect of heat treatment on thermal expansion of glass G4 nucleated by 1.5% ZrO_2. (a) Original glass; (b) 540 °C, 1 h + 710 °C, 1 h; (c) as (b) + 900 °C, 1 h. $L = 4.850$ cm.

temperature, followed by another hour at each of the exothermic crystallization peak temperatures.

It is clear that the thermal expansion values of the crystallized glasses are particularly influenced by the type and amount of the crystalline phases present (Table II). All the nucleating agents concerned had a significant effect on the resulting crystalline phases, as mentioned earlier [6, 7]. It therefore follows that the thermal expansion coefficient will be sensitive to the type and concentration of the nucleating agents since

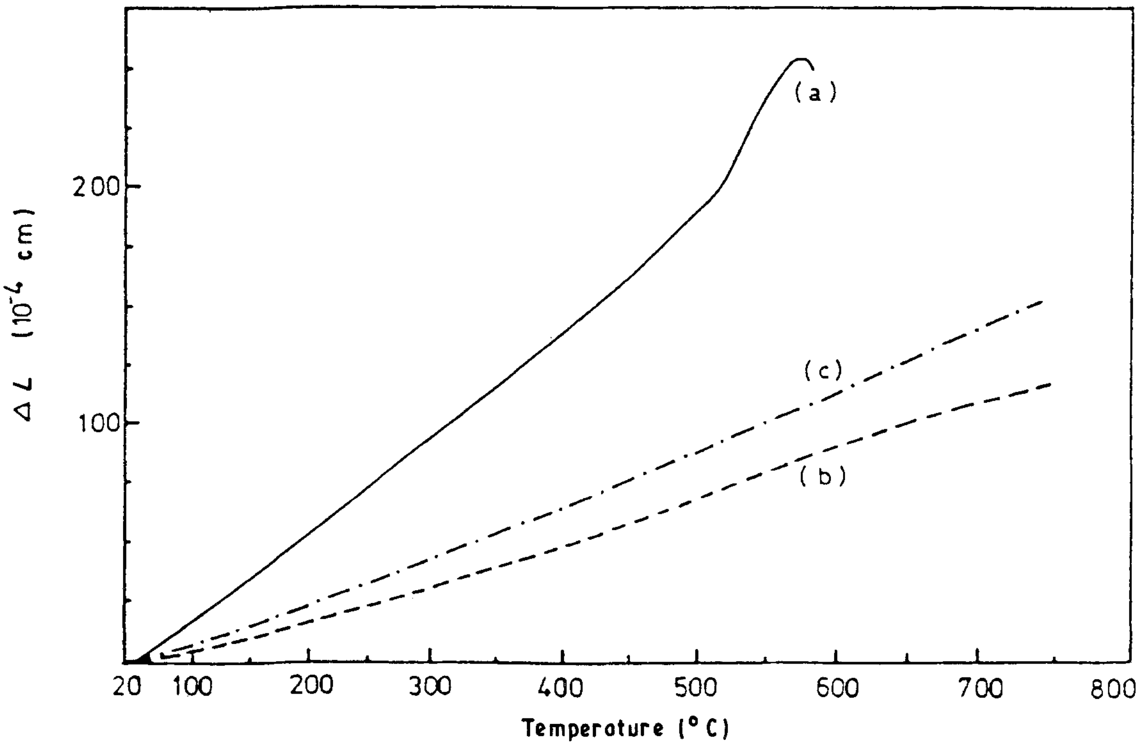

Figure 6 Effect of heat treatment on thermal expansion of glass G4 nucleated by 3% ZrO_2. (a) Original glass; (b) 550 °C, 1 h + 740 °C, 1 h; (c) as (b) + 980 °C, 1 h.

these will produce different crystalline phase assemblages.

For G4 nucleated by 5% TiO_2, (Fig. 3), B-eucryptite ss and $B_{II'}$-Li_2ZnSiO_4 were formed at 710 °C resulting in mean value of expansion coefficient of the material amounting to $40.2 \times 10^{-7}\,°C^{-1}$ in the 20–450 °C range. On further heating at 785 °C, crystallization of B-eucryptite ss predominated and the α value of the resulting material was thus reduced to its lowest value ($37.0 \times 10^{-7}\,°C^{-1}$). At 940 °C the B-eucryptite ss was transformed into B-spodumene, which is of relatively higher expansion than B-eucryptite, and consequently the material exhibits a higher expansion coefficient ($43.3 \times 10^{-7}\,°C^{-1}$).

The efficiency of 7% TiO_2 in catalysing the crystallization of proto-B-Li_2ZnSiO_4 is extensively large, and this imparts to the crystalline material a higher expansion character than the corresponding original glass (Fig. 4). The expansion coefficient firstly increases (in G4 + 7% TiO_2) with an increase of heat-treatment temperature up to 630 °C (Fig. 4 curves b and c). This is due to the progressive increase in the amount of the crystallizing highly expanding proto-B-phase. After that, a noticeable reduction in the thermal expansion coefficient from 99.8 to $39.4 \times 10^{-7}\,°C^{-1}$ is observed for samples heat-treated at temperatures up to 720 °C (Fig. 4 curves b–d). This is due to the appearance of B-eucryptite ss among the crystallization products and to the increase of its amount. At higher heat-treatment temperatures (above 900 °C) a slight increase in expansion character could be observed (Fig. 4 curve e), due mainly to the transformation of B-eucryptite ss into B-spodumene.

ZrO_2 nucleation favours the formation of B-eucryptite ss even at higher temperatures. The formation of such a low-expansion phase imparts a low expansion value to the material. As the percentage of ZrO_2 increased the B-eucryptite ss phase was increased and consequently expansion decreased. Figs 5 and 6 and Table II clearly illustrate these features. The slight increase in the α values after heat treatment at temperatures higher than 900 °C may be due to the slight transformation of B-eucryptite ss into B-spodumene which is of relatively higher thermal coefficient values.

It follows therefore that through different heat-treatments and/or different concentrations of the nucleation catalysts, it is possible to obtain glass–ceramic materials with a wide range of thermal expansion coefficients from the same parent glass.

References

1. S. D. STOOKEY and R. D. MAURER, in "Progress in Ceramic Science", Vol. 2, edited by J. E. Burke (Pergamon, New York, 1962) p. 77.
2. P. W. McMILLAN, "Glass–Ceramics" (Academic, London, 1979).
3. M. TASHIRO, *Glass Indi* (July 1966) 366.
4. *Idem., ibid.* (August 1966) 428.
5. A. W. A. EL-SHENNAWI, PhD thesis, Cairo University (1977).
6. A. A. OMAR, A. W. A. EL-SHENNAWI and A. R. EL-GHANNAM, in Abstracts of 15th Conference on Silicate Industry & Silicate Sciences (Siliconf), Budapest, 1989.
7. *Idem., J. Mater. Sci.* **26** (1991) in press.
8. W. A. WEYEL and E. C. MARBOE, "The Constitution of Glasses", Vol. II (John Wiley, New York, 1963) p. 486.

9. J. A. BISCOE, C. S. ROBINSON and B. E. WARREN, *J. Amer. Ceram. Soc.* **22** (1939) 180.
10. I. NÁRAY-SZABÓ, "Structure and Physical Properties of Glass", in Proceedings of the VII Conference on the Silicate Industry (Siliconf, 1963) (Akadémiai Kiadó, Budapest, 1965) p. 25.
11. K. TAKAHASHI, *Bull. Fac. Eng. Yokohama Nat. Univ.* **1** (1952) 145.
12. F. A. HUMMEL, *J. Amer. Ceram. Soc.* **34** (1951) 235.
13. W. OSTERTAG, G. R. FISCHER and J. P. WILLIAMS, *ibid.* **51** (1968) 651.
14. F. H. GILLERY and E. A. BUSH, *ibid.* **42** (1959) 175.
15. D. A. DUKE and G. A. CHASE, *Appl. Opt.* **7** (1969) 813.
16. J. PETZOLDT, *Glastech. Ber.* **40** (1967) 385.
17. A. R. WEST and F. P. GLASSER, *J. Mater. Sci.* **5** (1970) 676.
18. M. M. MORSI and A. W. A. EL-SHENNAWI, *Egypt. J. Phys.* **15** (1984) 111.
19. R. C. TURNBULL and W. G. LAWRENCE, *J. Amer. Ceram. Soc.* **35** (1952) 48.

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